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Alternatives to perfluoroalkyl and polyfluoro-alkyl substances (PFAS) in textiles

LOUS

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Alternatives to perfluoroalkyl and polyfluoroalkyl substances (PFAS) in textiles

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Foreword

A survey of perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and other perfluoroalkyl and polyfluoroalkyl substances were undertaken in 2012 as part of the Danish Environmental Protection Agency's (EPA) surveys of the 40 substances/substance groups on the Agency's List of Undesirable Substances (LOUS). On the basis of the survey, the Danish EPA developed three strategy papers addressing (Danish EPA, 2013):

- risk management of PFOS and PFOS substances;
- risk management of PFOA and PFOA substances; and
- risk management of other perfluorinated substances.

Here, the substances are collectively referred to as PFAS.

The strategy papers note that there is a general lack of published data on the properties of the alternatives to the PFAS of most concern, partly because the data usually are protected by trade secrets, and partly because most of the scientific research has focused on a few polyfluorinated substances such as PFOS and PFOA, historically the substances of most concern.

In order to obtain further information on alternatives to the PFAS of most concern and to PFAS in general, the Danish EPA has launched two reviews:

- This study on non-fluorinated alternatives to PFAS-based impregnations agents for textiles, and
- a review of environmental and health properties of short-chain PFAS.

The objective of this study is:

- To identify non-fluorinated alternatives available for surface treatment and impregnation of textiles including waterproofing spray for private use. The alternatives may include other chemicals and technical non-chemical solutions;
- To provide environmental and health assessments for chemical alternatives.

Concurrently, under the Danish EPA's programme for surveys of chemical substances in consumer products, a survey of PFAS in textiles for children, including environmental and risk assessments of the releases of PFAS from the textiles, is being carried out.

The results of the projects contribute to the Danish EPA's considerations regarding the need for and feasibility of further regulation of the group of PFAS substances.

The project has been followed by a steering group consisting of:

- Louise Grave-Larsen, Danish Environmental Protection Agency
- Carsten Lassen and Marlies Warming, COWI
- Allan Astrup Jensen, NIPSECT.

Conclusion and summary

Objectives
The objectives of this study are to identify non-fluorinated alternatives available for surface treatment and impregnation of textiles and to provide environmental and health assessments for the chemical alternatives.

Performance criteria
Impregnation agents based on polyfluoroalkyl substances (PFAS) are widely used in textiles in order to achieve water, oil and dirt repellency of the fabric, while at the same time maintaining breathability. Besides repellency to water, oil and dirt, the PFAS-based impregnation agents provide repellency to alcohol and a high level of washing and dry cleaning durability.

Technical properties of marketed alternatives
Many manufacturers of impregnating agents have developed non-fluorinated alternatives to PFAS-based finishing agents in recent years in response to a demand for more "environmentally-friendly" finishing agents. Many different agents providing water repellency are marketed, but none of these agents provides efficient repellency against oil, alcohol and oil-based dirt. The alternatives may be used for both clothing and technical textiles, and agents appear to be available for all types of fibres and fibre blends.

Water repellent finishing agents based on paraffin and silicone chemistries have been available on the market for many years, and have been used for those applications where repellency against oil, alcohol and oil-based dirt have not been required.

Water repellent dendrimer-based impregnation agents are a relatively new group of repellents on the market. According to a new Danish survey of PFAS in children's clothing, many of the manufacturers of children's clothing have changed from PFAS technology to non-fluorinated dendrimer technology in recent years.

Alternatives based on polymer coatings (e.g. PVC or PUR) may provide repellency against water, oil and dirt, but the fabrics are not breathable, and have not been assessed further.

In summary, it can be concluded that no alternatives matching the PFAS-based repellents on all technical parameters are available. For some applications, where repellency against oil, alcohol and oil-based dirt is not required, the alternatives are considered to provide acceptable properties at costs at the same level as the costs of using the PFAS-based agents.

Paraffin repellents
Health assessment - The products in this group are liquid emulsions that, according to the producers, should not to be classified as hazardous to health. However, some of the known ingredients seem to be harmful. The main ingredient in most products is paraffin oil/wax, i.e. mixtures of long chain alkanes (linear aliphatic hydrocarbons), which is harmless in its pure form. The compositions of the products are mainly confidential, but some products also contain isocyanates, dipropylene glycol, metal salts or other unspecified substances, which may be harmful.

Environmental assessment - The products in this group are liquid emulsions that, according to the producers, should not to be classified as hazardous for the environment. Most components are

readily biodegradable, are not bioconcentrated or accumulated in organisms and food chains, and the toxicity to aquatic and terrestrial organisms is insignificant even at concentrations above the water solubility.

Silicone repellents

Health assessment - The silicones most used in textile impregnation agents are based on polydimethylsiloxanes (PDMS). These siloxanes are registered in REACH; they are inert and generally have no adverse effects. Various other siloxanes, especially the cyclic siloxanes known as D4, D5 and D6 and the linear siloxanes HMDSO, MDM, MD2M and MD3M, are intermediates for synthesis of silicone polymers used for textile impregnation. The siloxanes are volatile and most exposures will occur by inhalation. Specifically D4 is suspected of damaging fertility, and D5 is a potential carcinogen. The commercial emulsions often contain other substances such as isotridecylalcohol, which is registered under REACH and is more harmful than the siloxanes. Some commercial products contain substances that are powerful irritants.

Environmental assessment - Siloxanes are persistent and are widespread in the environment but are found mostly in urban areas and in the aquatic environment. High levels have been found in livers of fish caught close to outlets of sewage treatment plants. The siloxanes are removed from the aqueous phase by sedimentation, and have a long half-life in sediments. In soils, depending on the conditions, siloxanes are transformed into hydroxylated forms, which may still be persistent.

The bioconcentration factors and bioaccumulation factors for D4 are high, indicating D4 may have a high potential to accumulate in aquatic organisms. According to an ECHA expert group, D4 met the criteria for a PBT and a vPvB substance[1]. D5 also met the criteria for a vPvB substance due to its persistence in sediments and a high bioconcentration factor in fish. D6, MM, MDM, MD2M, and MD3M were not considered PBT or vPvB substances by the notifiers under REACH, but the substances have not yet been evaluated by ECHA. PDMS has not been evaluated for lack of data.

The commercial products also contained substances other than siloxanes; some known, some unknown. Isotridecyl alcohol is less persistent but more toxic to aquatic organisms. A quaternary ammonium compound used was classified as harmful for the environment.

Dendrimer-based repellents

Health assessment - There are no data on health properties of the active substances and other components, but the producers of commercial products have included a few health data in the MSDSs and made some proposals for classification of the product. According to the producer's information, these products should not be labelled or classified as harmful. The product compositions were not specified sufficiently for an assessment, but some of the products contain unknown siloxanes (likely among those discussed above), cationic polymers, isocyanates or powerful irritating organic acids. In general, the health assessment information for this group of chemicals is insufficient for an assessment of the possible health effects of the impregnation agents.

Environmental assessment - The product compositions of these repellents were not specified sufficiently for an environmental assessment, but some of the products contain unknown siloxanes, cationic polymers, isocyanates or powerful irritating organic acids. According to the producer's information, these products should not be labelled or classified as harmful for the environment, but on the basis of the available information, it is not possible to evaluate these statements.

Polyurethane repellents

Health assessment - Only one commercial product is identified. Its composition is not detailed, either qualitatively or quantitatively. According to the producer's information, the product should

[1] PBT: persistent, bioaccumulative and toxic. vPvB: very persistent and very bioaccumulative

not be labelled or classified as harmful to health. Nevertheless, several health hazard precaution phrases are mentioned in the MSDS. Generally, the content of organic isocyanates makes products potentially hazardous to skin and mucous membranes. Therefore, it is not possible to assess the possible health effects of the agents in detail.

Environmental assessment - The composition of the commercial product is not detailed, either qualitatively or quantitatively. According to the producer's information, the products should not be labelled or classified as harmful for the environment. However, it is not possible to verify these claims because of lack of relevant data.

Other repellents

Health assessment - For one commercial product, described as a non-ionic polymer, ester and hydrocarbon compound, it is indicated by the manufacturer that the product include "no reportable quantities of hazardous ingredients". However, no documentation for this was provided, and some risk phrases were mentioned for the product indicating skin- and eye irritating properties and harmfulness if swallowed. Therefore, it was not possible to verify the producers' claim that it is non-hazardous product.

For a cationic pyridine derivative and a nanomaterial based repellent, the health data were insufficient for an assessment.

Environmental assessment - For one commercial product, described as a non-ionic polymer, ester and hydrocarbon compound, it is indicated by the manufacturer that the product include "no reportable quantities of hazardous ingredients. However, no documentation for that claim regarding effects on the environment was given.

For a cationic pyridine derivative repellent, the environmental data were insufficient for an assessment.

Summary regarding persistence

One of the main concerns regarding the PFAS-based impregnating agents is the formation and release of persistent PFAS or precursors for persistent PFAS. Some uncertainty exists as to the potential release of persistent siloxanes during the lifecycle of silicone-based repellents. For the other alternatives, the available data do not indicate the potential for any significant releases of persistent substances.

Main data gaps

For most of the alternative impregnation agents reviewed, there is insufficient qualitative and quantitative public information about the ingredients. Most products do not have information available because they are protected by trade secrets. Only a few specific ingredients are declared, and for these, only limited data on health and environmental properties are available. For some siloxanes used as intermediates in production of silicon polymers, much information on health and environmental properties of the substances exists, but it is unclear to what degree these siloxanes are ingredients or impurities in the commercial products.

For all of the alternatives, hardly any information on trace levels of raw materials, intermediates and degradation products in the final textile products is available. Furthermore, no data on the possible formation of hazardous degradation products by waste disposal of the textiles are available. However, based on the available knowledge about chemical structures, persistence, bioaccumulation and toxicities of the assessed alternatives, the conclusion is that most of the alternatives (apart from those that are silicone-based) possibly do not contain or generate persistent substances at significant levels and are therefore preferable to the persistent PFAS-based impregnation agents from an environmental perspective.

Konklusion og sammenfatning

Formål
Formålet med denne undersøgelse er at identificere ikke-fluorerede alternativer til overfladebehandling og imprægnering af tekstiler og udarbejde miljø- og sundhedsmæssige vurderinger for de kemiske alternativer.

Funktionskrav
Imprægneringshandlingsmidler baseret på polyfluoralkyl stoffer (PFAS) er almindeligt anvendt i tekstiler for at give disse vand-, olie- og smudsafvisende egenskaber, mens stoffets åndbarhed samtidig bevares. Udover at gøre tekstilerne afvisende over for vand, olie og snavs, gør de PFAS-baserede imprægneringmidler tekstilerne afvisende over for alkohol og midlerne har samtidig en god bestandighed ved vask og kemisk rensning.

Tekniske egenskaber af markedsførte alternativer
Mange producenter af imprægneringsmidler har i de senere år udviklet ikke-fluorerede alternativer til PFAS-baserede efterbehandlingsmidler som følge af en efterspørgsel efter mere "miljøvenlige" imprægneringsmidler. Der markedsføres mange forskellige midler, som kan gøre tekstilstoffer vandafvisende, men ingen af disse midler er effektive med hensyn til at gøre tekstilerne afvisende over for olie, alkohol og oliebaseret snavs. Alternativerne kan anvendes til både beklædning og tekniske tekstiler, og der synes at være midler tilgængelige for alle typer af fibre og fiberblandinger.

Vandafvisende efterbehandlingsmidler baseret på paraffin- og silikonekemi har været tilgængelige på markedet i mange år, og er blevet brugt til de anvendelser, hvor afvisende egenskaber i forhold til olie, alkohol og oliebaseret snavs ikke har været påkrævet.

Vandafvisende, dendrimer-baserede imprægneringsmidler er en relativt ny gruppe af imprægneringsmidler på markedet. Ifølge en ny dansk kortlægning af PFAS i børnetøj, har mange af producenterne af børnetøj i de seneste år skiftet fra PFAS teknologi til ikke-fluoreret dendrimerteknologi.

Alternativer baseret på polymerbelægninger (f.eks. PVC eller PUR) kan gøre tekstiler afvisende over for vand, olie og snavs, men tekstilstofferne er ikke åndbare, og er ikke vurderet yderligere.

Sammenfattende kan det konkluderes, at der ikke findes alternativer, som matcher PFAS-baserede imprægneringsmidler på alle tekniske parametre. Til nogle anvendelser, hvor afvisende egenskaber i forhold til olie og oliebaseret snavs ikke er påkrævet, anses alternativerne for at give acceptable egenskaber. Omkostningerne ved brug af de alternative midler er på niveau med omkostningerne ved anvendelse af de PFAS-baserede midler.

Paraffin-baserede imprægneringsmidler
Sundhedsvurdering - Produkterne i denne gruppe er flydende emulsioner, der ifølge producenterne, ikke skal klassificeres som sundhedsfarlige. Men nogle af de kendte bestanddele synes at være skadelige. Den vigtigste bestanddel i de fleste produkter er paraffinolie/voks, dvs. blandinger af langkædede alkaner (lineære alifatiske kulbrinter), der er harmløse i sin rene form. Produkternes sammensætningerer primært fortrolige, men det vides at nogle produkter også indeholder isocyanater, dipropylenglycol, metalsalte eller andre uspecificerede stoffer, som kan være skadelige.

Miljøvurdering - Produkterne i denne gruppe skal ifølge producenterne, ikke klassificeres som farlige for miljøet. De fleste er let bionedbrydelige, biokoncentreres ikke og ophobes ikke i organismer eller fødekæder, og toksiciteten over for vand- og jordorganismer er ubetydelig, selv ved koncentrationer over vandopløseligheden.

Silikone-baserede imprægneringsmidler

Sundhedsvurdering - De silikoner, som mest anvendes i imprægneringsmidler til tekstiler, er baseret på polydimethylsiloxaner (PDMS). Disse siloxaner er registreret i REACH, de er inerte og har generelt som polymere ingen skadelige effekter. Forskellige andre siloxaner, især de cykliske siloxaner kendt som D4, D5 og D6 og de lineære siloxaner HMDSO, MDM, MD2M og MD3M, er mellemprodukter ved syntese af de silikone-polymere, der anvendes til tekstilimprægnering. Siloxanerne er flygtige, og de største eksponeringer vil forekomme ved indånding. Specifikt D4 er mistænkt for at skade forplantningsevnen, og D5 har potentielt kræftfremkaldende egenskaber. De kommercielle emulsioner indeholder ofte andre stoffer, såsom isotridecylalcohol, som er registreret i REACH, og er mere skadelig end siloxanerne. Nogle kommercielle produkter indeholder stoffer, som er stærkt irriterende.

Miljøvurdering - Siloxaner er persistente og er udbredt i miljøet, men findes primært i byområder og i vandmiljøet. Høje niveauer er fundet i lever af fisk, fanget tæt på udløb fra renseanlæg. Siloxanerne fjernes fra vandfasen ved sedimentation, og har en lang halveringstid i sedimenter. I jord bliver siloxaner, afhængigt af forholdene, omdannet til hydroxylerede metabolitter, som dog stadig kan være problematiske.

Biokoncentrerings- og bioakkumuleringsfaktorerne for D4 er høje, hvilket indikerer, at D4 kan have et stort potentiale for ophobning i vandlevende organismer. Ifølge en ECHA ekspertgruppe, opfylder D4 kriterierne for at være et PBT og vPvB stof[2]. D5 levede også op kriterierne for at være et vPvB-stof på grund af sin persistens i sedimenter og en høj biokoncentrationsfaktor i fisk. D6, MM, MDM, MD2M, og MD3M blev ikke betragtet som PBT eller vPvB stoffer af registranter under REACH, men stofferne er endnu ikke blevet evalueret af det Europæiske Kemikalieagentur, ECHA. PDMS er på grund af manglende data ikke blevet evalueret.

De kommercielle produkter indeholdt også andre stoffer end siloxaner - nogle kendte, andre ukendte. Isotridecyl alkohol er mindre persistent, men mere giftigt for vandlevende organismer. En kvaternær ammoniumforbindelse, som er anvendt, blev klassificeret som skadelig for miljøet.

Dendrimer-baserede imprægneringsmidler

Sundhedsvurdering - Der er ingen data om sundhedsmæssige egenskaber af de aktive stoffer og andre komponenter, men producenterne af kommercielle produkter har medtaget et par sundhedsdata i sikkerhedsdatabladene og givet nogle forslag til klassificering af produktet. Ifølge producentens oplysninger skal disse produkter ikke mærkes eller klassificeres som skadelige. Produkternes sammensætninger blev ikke angivet i tilstrækkelig grad til en vurdering, men nogle af produkterne indeholder ukendte siloxaner (sandsynligvis blandt de som er diskuteret ovenfor), kationiske polymere, isocyanater eller stærkt irriterende organiske syrer. Generelt er der utilstrækkelige sundhedsmæssige informationer for denne gruppe af kemikalier til, at der kan udarbejdes en sundhedsvurdering af imprægneringsmidlerne.

Miljøvurdering - Produktsammensætningen af disse imprægneringsmidler blev ikke angivet tilstrækkeligt detaljeret til, at der kan foretages en miljøvurdering, men nogle af produkterne indeholder ukendte siloxaner, kationiske polymerer, isocyanater eller kraftigt irriterende organiske syrer. Ifølge producentens oplysninger, skal disse produkter ikke mærkes eller klassificeres som

[2] PBT: persistent, bioakkumulerende og toksisk. vPvB: meget persistent og meget bioakkumulerende.

skadelige for miljøet, men på grundlag af de foreliggende oplysninger, er det ikke muligt at vurdere dette.

Polyurethan-baserede imprægneringsmidler
Sundhedsvurdering - Der er kun fundet to kommercielle produkter. Deres sammensætninger er ikke beskrevet, hverken kvalitativt eller kvantitativt. Ifølge producentens oplysninger, skal disse produkter ikke mærkes eller klassificeres som sundhedsskadelige. Ikke desto mindre er der flere faresætninger for sundhedsfare nævnt i sikkerhedsdatabladet for et af produkterne. Generelt kan indholdet af organiske isocyanater gøre disse produkter potentielt farlige på hud og slimhinder. Det er derfor ikke muligt at vurdere de mulige sundhedsmæssige affekter af imprægneringsmidlerne i detaljer.

Miljøvurdering - Sammensætningen af de kommercielle produkter er ikke beskrevet, hverken kvalitativt eller kvantitativt. Ifølge producentens oplysninger, skal disse produkter ikke mærkes eller klassificeres som skadelige for miljøet. Det er imidlertid ikke muligt at verificere disse udsagn, da der mangler relevante data.

Andre imprægneringsmidler
Sundhedsvurdering - For et kommercielt produkt, der er beskrevet som en ikke-ionisk polymer, organisk ester og carbonhydrid, er det angivet af producenten at produktet ikke indeholder ”indberetningspligtige mængder af farlige stoffer". Der er dog ikke givet dokumentation for denne påstand vedrørende sundhedsmæssige effekter, og der er for produktet angivet nogle risikosætninger, som indikerer, at produktet er hud- og øjenirriterende og skadeligt ved indtagelse. Det var derfor ikke muligt at verificere producenternes angivelse af, at produktet er ufarligt.

For et kationisk pyridinderivat og et nano-baseret imprægneringsmiddel var de sundhedsmæssige data utilstrækkelige for en vurdering.

Miljøvurdering - For et kommercielt produkt, der er beskrevet som en ikke-ionisk polymer, ester og carbonhydrid, blev det angivet af produktet ikke indeholdt: "indberetningspligtige mængder af farlige stoffer". Der har ikke været nogen dokumentation for dette til rådighed.

For et kationisk pyridinderivat imprægneringsmiddel var de tilgængelige miljødata utilstrækkelige for en vurdering.

Sammenfatning vedrørende persistens
En af de største bekymringer vedrørende PFAS-baserede imprægneringsmidler er dannelse og udslip af persistente PFAS eller forstadier (precursers) til persistente PFAS. Der er nogen usikkerhed med hensyn til de potentielle udslip af persistente siloxaner i livsforløbet af silikone-baserede imprægneringsmidler. For de andre alternativer, indikerer de foreliggende data ikke noget potentiale for væsentlige udslip af persistente stoffer.

Vigtigste datamangler
For de fleste af de alternative imprægneringsmidler, som er gennemgået, er der ikke tilstrækkelig kvalitativ og kvantitativ, offentligt tilgængeligt information om bestanddelene. De fleste produkters sammensætning er forretningshemmeligheder. Kun nogle få specifikke bestanddele er angivet, og for disse er der kun begrænsede data om sundheds- og miljømæssige egenskaber tilgængelige. For nogle siloxaner, der anvendes som mellemprodukter i produktionen af silikone-polymere, findes der megen information om stofferne sundheds- og miljøegenskaber, men det er uklart, i hvilken grad disse siloxaner er til stede som tilsigtede bestanddele eller urenheder i de kommercielle produkter.

For alle alternativerne, er der næsten ingen oplysninger om rester på sporniveau af udgangsstoffer, mellemprodukter og nedbrydningsprodukter i de endelige tekstilprodukter. Desuden er der ingen data til rådighed om den mulige dannelse af farlige nedbrydningsprodukter ved bortskaffelse af tekstilerne som affald. Baseret på den tilgængelige viden om kemiske strukturer, persistens, bioakkumulering og toksicitet af de vurderede alternativer, kan det konkluderes, at de fleste af alternativerne (bortset fra de silikone-baserede) formentligt ikke indeholder eller genererer persistente stoffer i signifikante mængder, og som derfor ud fra et miljømæssigt perspektiv vil være at foretrække frem for de persistente PFAS-baserede imprægneringsmidler.

1. Introduction

1.1 Background

Finishing agents based on polyfluoroalkyl substances (PFAS) are widely used in textiles in order to achieve water, oil and dirt repellency of the material, while at the same time maintaining breathability. The use of PFAS in textile production accounts for about 50% of global use of PFAS.

PFAS-based agents for impregnation of textiles are polymers which consist of a non-fluorinated backbone with polyfluoroalkyl side chains, also designated side-chain-fluorinated polymers (Buck et al., 2011). The main polymers can be distinguished from one another by the linkage (acrylate and/or methacrylate, urethane, and oxetane) between the polymer backbone and the length of the polyfluoroalkyl side chains.

Until recently, the side-chains have mainly been based on 8:2 fluorotelomer alcohols, i.e. they consist of a chain of eight perfluorinated carbon atoms and two carbon atoms without fluorine (C_8 chemistries). PFAS extracted from textiles have varying chain lengths as demonstrated in many studies (e.g. Herzke et al., 2009; Knepper et al., 2014), and similarly, the side-chain-fluorinated polymers probably have fluoroalkyl side-chains of varying length. PFAS extracted from textiles with agents based on C_8 chemistry have been demonstrated to include significant amounts of substances with longer chain lengths. Due to increased attention to the harmful effects of C_8 substances on human health and the environment, the application of polymers with polyfluoroalkylated side chains based on short-chain fluorine chemistry (C_4-C_6 chemistry) has been growing in recent years. Several of the ongoing projects on substitution of the PFAS-based impregnation agents concern the feasibility of using agents based on short-chain fluorine chemistry.

The side chains of the PFAS-based polymers typically include a perfluorinated part. If released by degradation of the impregnating agents, the substances may subsequently be degraded to persistent perfluorinated compounds in the environment. The short-chain PFAS are as persistent in the environment as long-chain homologues, but do not bioaccumulate to the same extent as the long-chain substances, as they are excreted more rapidly from the organisms studied (as reviewed by Lassen et al., 2013).

Our knowledge of most PFAS is limited in terms of usage and possible environmental and health impacts. Therefore, more knowledge is required about PFAS, but also about other textile impregnation agents based on chemistries other than PFAS. In this project, the term “alternatives to PFAS” in textiles refers to textile impregnation agents being free of fluorine chemistry.

1.2 Contact to manufacturers and users of the products

During searching for alternative products and communication with the industry, the following manufacturers of fluorine-free water repellents have been contacted:

- Rudolph Group
- Organoclick
- Nicca
- Archroma
- Schoeller

- Crypton/Nanotex
- Huntsman
- 3M
- Freudenberg.

The companies were contacted by telephone and/or -e-mail and asked for product information on:

1) Application ranges of the alternative agents,
2) Technical advantages and disadvantages as compared to fluorocarbon-based agents,
3) Price of agents as compared to fluorocarbon-based agents,
4) Chemical composition of alternatives and the generated surface film, and
5) Data on the environmental and health properties of alternative agents and their constituents.

Some of the companies provided technical and material data sheets, whereas other companies considered such documents as confidential. Of the 11 companies contacted, nine have responded and provided information with varying levels of detail.

Some of the companies openly shared their product information. Most were less willing to share details on the chemical composition of their products. This clearly reflects that the market for non-fluorinated alternatives for textile impregnation is relatively young and under development, causing product developers to carefully protect their innovations. In some cases, a company might even refrain from patenting their solution because, globally, patents are not necessarily respected.

Apart from the suppliers of alternatives, the following organizations/companies have been contacted in order to identify the relevant manufacturers of alternatives as well as to gather more general information about the topic with a focus on Danish activities:

- Kvadrat (manufacturer of design textiles)
- IKEA (furniture manufacturer and retailer)
- Egetæpper (manufacturer of carpets)
- Ecco (manufacturer of shoes)
- Euratex (European trade association)
- TEGEWA (German trade association)
- Dansk Fashion and Textile (Danish trade association)
- SWEREA Group (Swedish Research Institute).

Limited information has been obtained from these market actors, as the companies consider information on suppliers to be confidential information.

1.3 Research activities and assessments of alternatives

In order to develop, test and assess alternatives to PFAS-based textile finishing technology, several research activities have been undertaken or are ongoing.

"Zero Discharge of Hazardous Chemicals (ZDHC)" - A research report on “Durable Water and Soil Repellent Chemistry in the Textile industry” has been published within the framework of the Roadmap to Zero Discharge of Hazardous Chemicals (ZDHC) concerted action. ZDHZ was formed in 2011, consisting of a group of major apparel and footwear brands and retailers helping lead the industry towards zero discharge of hazardous chemicals by 2020. The ZDHC brands have collaborated with the Outdoor Industry Association (OIA), the European Outdoor Group (EOG), Bundesverband der Deutschen Sportartikel-Industrie e.V. (BSI) (German Sporting Goods Association), and representatives from the chemical industry to understand opportunities, challenges and limitations for eliminating durable water repellent (DWR) technologies associated with long-chain

PFAS. The project included non-fluorinated DRW chemistries as well as short-chain fluorine chemistries.

SUPFES – In Sweden, an ongoing project called “Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources” (SUPFES), coordinated by Swerea IVF, aims to help industry find alternatives that can replace fluorinated chemicals in textiles. Within the project, a number of scientific and industrial partners collaborate to assess the risks of different PFAS-free finishing agents and ensure that the new alternatives really provide the desired functionality. Contact has been established with the project. The project started in the middle of 2013, and the project secretariat has informed the authors that initial project outputs are expected in 2015.

”Development of environmentally friendly impregnation agents for textiles” – The Danish Technological Institute is currently conducting a project to develop environmentally friendly impregnating agents for the textile industry, supported by the Danish EPA. The project runs for two years and builds on existing knowledge and known alternative products. The alternatives are examined to determine whether they can be improved or form a basis for the development of new repellent agents. So far, no agents beyond the marketed alternatives described in this survey have been developed or tested.

TEX-SHIELD project - The TEX-SHIELD project "Environmental friendly and durable oil and water repellent finish on technical textile" is a new project supported by funding from the European Union’s seventh Framework Programme and started in January 2013. The overall project aim is to provide the European textile industry with an alternative material to C_8 PFAS chemistries whilst refining comparable performance. The project also includes finishing agents based on short-chained PFAS. The project has so far not published outputs, but some draft documents are available via the internet (TEX-SHIELD, 2013).

"Smart Textiles" - Within the Smart Textiles framework (cooperation between University of Borås, SP Technical Research Institute of Sweden, Swerea IVF and the Inkubator in Borås), a collaborative project between Smart Textiles and the manufacturer of finishing agent OrganoClick has been undertaken. In the project, a fluorocarbon-free, biodegradable and durable treatment has been tested in cooperation with major outdoor apparel brands such as Haglöfs, Norröna and Bergans (Smart Textiles, 2014). Contact has been established with the project coordinators. The agents from OrganoClick are further described in section 0 along with information obtained on environmental and health properties.

"Smart Finishing Agents" – The Danish Technological Institute, in cooperation with the Knowledge Centre for Intelligent Textiles, released the report "Smart finishing agents” as a result of the project "More functionality in everyday clothes". The aim of the report was to help apparel manufacturers who want to implement more functionality in their products. The project did not specifically focus on the identification of non-PFAS technologies. The finishing agents identified that can provide stain-resistant and stain removal properties all involved PFAS technologies.

UNEP assessment of alternatives to PFOS - Within the framework of the Stockholm Convention, alternatives to perfluorooctane sulfonate (PFOS) and its derivatives are currently reviewed by the Persistent Organic Pollutants (POPs) Review Committee. The review includes, among other applications, the use of PFOS and its derivatives in textiles. Although the PFAS-based repellents for textiles are not based on PFOS, the review includes information on some of the chemical groups considered alternatives for PFAS-based repellents. The chapters on human health and environmental assessments of alternatives make reference to the most recent draft version of the review (UNEP, 2013). A final version of the review is under preparation, but was not published when the editing of this report closed.

2. Overview of fluorine-free alternatives

2.1 Performance criteria and action of the PFAS-based repellents

Durable water and oil repellents are topical finishes applied to fabrics to provide protection against water, oil and soil. These finishes also extend the life of products and keep them looking newer longer (ZDHC, 2012).

The required performance level of the repellent finishes is dependent on their intended uses, the apparel products and other important factors such as their durability to laundering and dry-cleaning, resistance to abrasion and fabric breathability (ZDHC, 2012).

As described by ZDHC (2012), durable water repellent (DWR) finishes are mostly applied to fabrics after dyeing and/or printing, but before the fabrics are made into garments. The PFAS-based repellents are polymers with pendant fluoroalkyl chains attached to the polymer backbone. The side-chain fluorinated polymers are applied as a thin film on the fabric surface, usually in combination with other finishing auxiliaries, by a pad-dry-cure process (as reviewed by Knepper et al., 2014). In this process, the dry fabric is passed through a bath of the aqueous dispersion, and then squeezed under high pressure between pads to remove excess material, followed by drying and curing in an oven at temperatures up to 180°C. The term drying is used for the evaporation of the solvent, whereas curing is a synonym for the polymerization of the individual monomers. Curing is mandatory for cross-linking techniques (as reviewed by Knepper et al., 2014).

An optimized water and oil repellent finish is designed for a specific fabric based on its fibre type and fabric construction. The finish forms an array of microscopic polymer domains on the fabric surface (not a film or coating) with the fluorinated chains perpendicular to the fabric surface and close enough to one another to act like a continuous surface, thus preventing water and oils from reaching the fabric (ZDHC, 2012).

The requirements as to breathability exclude various polymer coatings used to waterproof textiles as possible alternatives. The polymer coatings based on e.g. PVC, PU or acrylic are used to waterproof some types of rainwear, tarpaulins, bags, etc. and may also provide some resistance to oil and dirt.

2.2 Overview of chemistry of alternatives on the market

According to a research report on "Durable Water and Soil Repellent Chemistry in the Textile industry" (ZDHC, 2012), it is possible to differentiate between five non-fluorinated water-repellent chemistries. The specific products typically contain smaller modifications to the general chemistries, e.g. through the presence of certain functional groups.

The five non-fluorinated chemistries mentioned in detail in the report are:

- Paraffin repellent chemistries;
- Stearic acid-melamine repellent chemistries;

- Silicone repellent chemistries;
- Dendrimer based repellent chemistries;
- Nano-material based repellent chemistries.

The report briefly mentions that the information on commercially available non-fluorinated chemistries made available by chemical manufacturers includes the acrylic- and urethane-based (PUR-based) chemistries, but the report does not describe these chemistries in detail.

The report reached the conclusion that there are a number of products on the market based on non-fluorinated chemistries, which provide durable water repellency, whereas non-fluorinated chemistries for oil and dirt repellency are limited (ZDHC, 2012).

A recent review of non-PFAS alternatives for water repellency and stain release from the apparel manufacturer Marks & Spencer (2014) provides a non-exhaustive list of products with an indication of repellent types and the fibres that can be treated (Table 1). The table indicates a broader range of products than indicated above.

The review (Marks & Spencer, 2014) also lists a few PFAS-free products offering stain release (see Table 1). For Arristan HPC, product details were not available on how stain repellency was achieved from the report or the suppliers' website. Technical data sheets of the Phobotex products disclose that the property applies only to water-based stains and not to oil-based stains.

TABLE 1
WATER REPELLENCY (INCLUDING WATER-BORNE STAINS) – EXAMPLES OF SUGGESTED PRODUCTS (MARKS & SPENCER, 2014)

Supplier	Product	Type	Fibres
Huntsman	Phobotex RHP Phobotex RSH Phobotex RHW Phobotex JVA	Fat modified resin	All
	Phobotex WS/BC	Silicone	Synthetics/blends
	Phobotex SSR* Phobotex HSR*	Hydrophilic copolymer	Synthetic and blends
Archroma	Arkophob FFR	Wax	All
CHT/Bezema	Zero F1	Paraffin dispersion	All
	Arristan HPC*	Hydrophilic copolymer	Synthetics
Devan	H2O Repel	Not known	Cotton, Polyester
LJ Specialities	Itoguard NFC	Fatty acid/paraffin	Cellulosic, Synthetics
	Itoguard NFC 90	Botanical extracts	Cellulosic, Synthetics
Rudolf	Ruco-dry ECO	Dendrimer	All
Sarex	Careguard FF	Not known	All
Schoeller	ecorepel	Paraffin	All
Texchem	Texfin HTF	Modified wax dispersion	All

Supplier	Product	Type	Fibres
Tanatex	Baygard WRC	'3D' Molecules	Cotton, blends
	Baygard WRS	'3D' Molecules	Synthetics, blends

* Products also offering stain release. Stain release is only available for synthetic fibres (Marks & Spencer, 2014).

2.3 Overall comparison between PFAS-technology and alternative technologies as provided by manufacturers

Several of the manufacturers produce repellents based both on PFAS and alternative technologies and provide an overall view of the differences in performance between the different technologies. The following tables provide comparisons as described by the manufacturers themselves.

According to Rudolf Group, which manufactures PFAS-based impregnating agents based on C_6 and C_8 chemistry as well as alternatives based on dendrimer technology (see section 5), the dendrimer-based agents have some drawbacks as they do not provide oil repellency (Table 2). The dendrimers technically have some advantages in providing soft textiles and excellent low-temperature curing. Prices are indicated as "very competitive".

TABLE 2
COMPARISON OF PERFORMANCE OF IMPREGNATING AGENTS SUPPLIED BY RUDOLF GROUP AS DESCRIBED BY THE COMPANY (RUDOLF GROUP, 2010)

Performance	C_8-chemistry	C_6-chemistry	Bionic-Finish ECO Dendrimer technology
Water repellency	Very good	Very good	Very good
Oil repellency	Good	Alike	No oil repellency
Washing durability	Very high	High	High
Dry cleaning	Good	Moderate	None
Low-temperature curing	Poor	Good	Excellent
Handle	Moderate	Slightly softer	Soft
Price	"Normal"	Higher	Very competitive

SIMILARLY ARCHROMA, WHICH PRODUCES AN ALTERNATIVE IMPREGNATING AGENT BASED ON ENCAPSULATION WAX TECHNOLOGY (SEE SECTION 3) AND VARIOUS PFAS-BASED AGENTS, INDICATES THAT THE NON-FLUORINATED ALTERNATIVES HAVE THE DRAWBACKS OF NOT PROVIDING OIL AND ALCOHOL REPELLENCY, AS WELL AS OIL AND WATER-BASED STAIN RELEASE (TABLE 3). ALL TYPES OF AGENTS PROVIDE WATER REPELLENCY.

TABLE 3
COMPARISON OF PERFORMANCE OF IMPREGNATING AGENTS AS DESCRIBED BY THE ARCHROMA (BASED ON ARCHROMA, 2014)

Performance	Water repellency	Oil repellency	Alcohol repellency	Stain release *	Abrasion resistance	Self cleaning
Fluorinated						
F-(Meth)Acrylates	+	+	+	+	+/-	-
F-Urethanes	+	+	+	+	+	-

Performance	Water repellency	Oil repellency	Alcohol repellency	Stain release *	Abrasion resistance	Self cleaning
F-Silicones	+	+	+	+	-	-
F-Particle	+	+	+	-	+	+
Non-fluorinated						
(Meth)Acrylates/ Urethanes	+	-	-	+/-	+/-	-
Silicones	+	-	-	-	-	-
Waxes	+	-	-	-	-	-
Dendrimers	+	-	-	-	+/-	-
Particle	+	-	-	-	+	+

* Oil and water-based stains.

These comparisons are in accordance with the general view that non-fluorinated alternatives do not provide oil and alcohol repellency, but otherwise largely are comparable with the fluorinated impregnation agents.

3. Paraffin repellent chemistries

3.1 Chemistry

Water repellent chemistry based on paraffin is one of the earliest technologies used. Paraffins/alkanes are long-chain hydrocarbons with the general molecular formula C_nH_{2n+2}.

The repellent products are typically emulsions of paraffins containing metal salts of fatty acids, usually stearic acid. The metals used most are aluminium, zinc and zirconium.

The metal ion, e.g. Zr^{2+}, provides fixation onto the fibre, and ensures that the water repellent groups have the right orientation on the fibre surfaces (Figure 1). The paraffin emulsions are generally compatible with other types of textile finishes, but show also increased flammability (ZDHC, 2012). Water repellency arises also from the ability of the metal ions to support the formation of macromolecules, which arrange as a fatty layer around the fibre (Lang, 2014, personal comm.).

Paraffinic repellents do not repel oil and are generally not (very) durable to laundering and dry cleaning. Additionally, fabrics treated with paraffin-based finishes are less permeable to air and vapour, resulting in a poorer wear comfort unless further refinement of the finishing occurs. Wash resistance, breathability, and soft handling can be improved by adding cross-linking agents such as isocyanates for fixation on the fibre. This technology is used in some commercial products.

Products consisting of solely paraffin and/or wax (bee wax) are also available as consumer impregnation products for outdoor clothing (e.g. Fjällraven Greenland Wax[3]).

Paraffinic emulsion repellents can be applied by both padding and bath exhaustion finishing processes (ZDHC, 2012; both processes are wet processes).

[3] http://www.fjallraven.com/guides/material-guides/greenland-wax

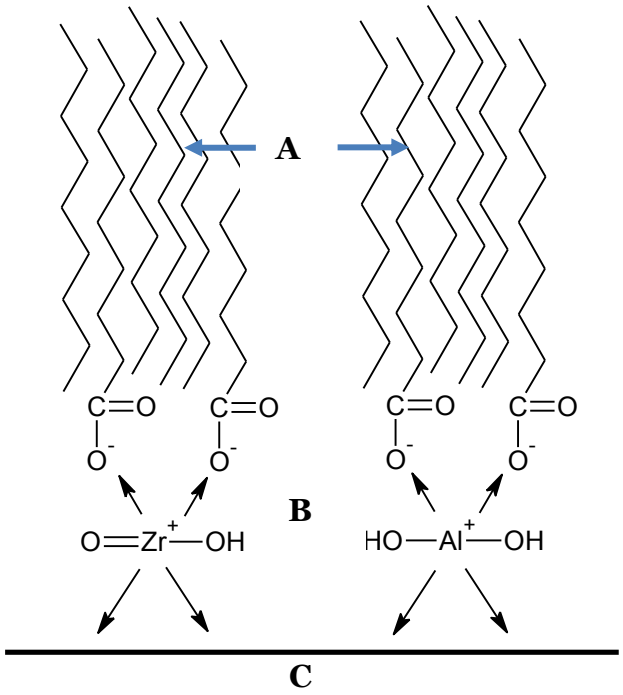
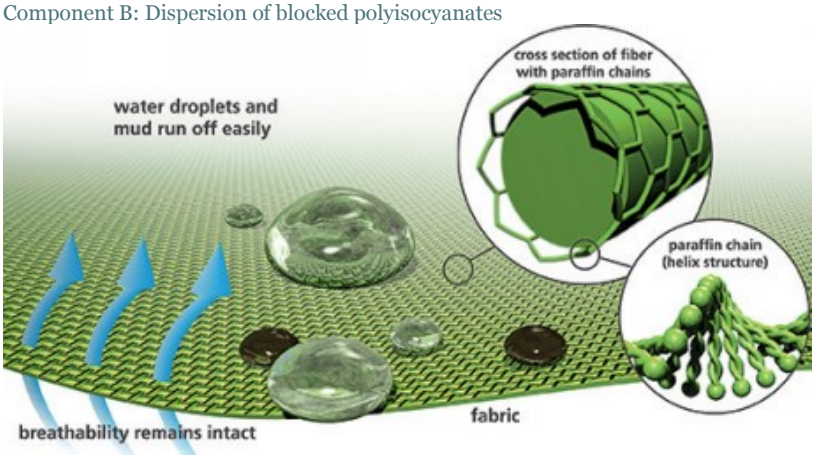


FIGURE 1.
EXAMPLES OF A FATTY ACID METAL SALT ON A FIBRE SURFACE. A: HYDROFOBIC INTERACTIONS, B: POLAR INTERACTIONS, C: FIBRE SURFACE (BASED ON SCHINDLER AND HAUSER, 2004)

3.2 Examples of marketed products

Examples of marketed, paraffin-based products for which data have been received are shown below. Other marketed products for which detailed data have not been obtained include Texfin® HTF from Texchem®, zeroF from the German company CHT/Bezema and Itoguard NFC from LJ Specialities. The details on classification, environmental and health properties given in the tables below apply to the product (or, if specified, the components of the product) and not to single ingredients of the product/component.

Schoeller Textil AG	
Product name	ecorepel®
Chemical properties	Two component system: Component A: Dispersion of paraffins and fatty acid modified melamine resin. This component corresponds to separately marketed product: Schoeller protec-FF. Component B: Dispersion of blocked polyisocyanates  *Source: Schoeller Technologies AG*

Schoeller Textil AG	
Functional properties	• Water repelling. The ecorepel® finish can be optimized to ensure passage of the Raintest AATCC Test Method 35-2006. • Watery dirt such as sludge and mud are much less able to adhere to the fabric • Complies with the bluesign® standard and passes Oeko®-Tex Standard 100. • No effect on breathability (in accordance with ISO 11092). • Abrasion resistant: No effect on the feel despite a high level of resistance to abrasion and chaffing (AATCC 22-1996/ISO 4920)
Application areas	Clothing and non-clothing, effective on many types of fibres and many blends (cotton, polyester, wool).
Application process	Padding, Coating, Foam, Spray, Garment
Wash resistance	Good washing resistance (min. 30 washing cycles at 40° C). Function can be easily reactivated in the dryer (no more ironing necessary); alternatively, line drying is also possible
Price	Cheaper than PFAS-based products
Information on release/emissions of the substance during use and/or wash	No data.
Classification of the product	No hazard classification according to EU directives
Human health properties	Component A: Acute oral toxicity : LD_{50} > 2.000 mg/kg (rat) Component B: Acute oral toxicity : LD_{50} > 2.000 mg/kg (rat) Mutagenicity: negative (Ames test) Not skin sensitizing (OECD 406)
Environmental fate properties	Components are easily biodegradable in accordance with OECD 302 B (80–100 %, precipitation effect 49 %). Component A: BOD_5 3 mg/g COD 861 mg/g TOC 20% Nitrogen content of 0.66% Component B: BOD_5 37 mg/g COD 610 mg/g TOC 22% Nitrogen content of 2.8%
Environmental effects properties	Component A: Crustacean toxicity (*Daphnia magna*): LC_{50} > 100 mg/l, 48 h Sewage sludge bacteria toxicity: EC_{50} > 2000 mg/l, 3 h (OECD 202, part 1) Component B: Fish toxicity (zebra fish): LC_0 10.000 mg/l, LC_{50} > 10.000 mg/l, 48 h (OECD 203)

Archroma Management GmbH	
Product name	Arkophob FFR liq
Chemical properties	Encapsulation wax technology. Hydrocarbon polymer dispersion. Mixture of linear and branched hydrocarbons, which are applied with a crosslinking component to the textile fibre, generating a surface film comparable with a fatty film. Weakly cationic.
Functional properties	• Durable water repellent, comparable to PFAS-based products • No oil-repellency • Good abrasion resistance (abrasion resistance of the fibre improved) • Bluesign approved and can pass the Oekotex standard • No yellowing • Soft handling
Application areas	Clothing and non-clothing textiles, suitable for most textiles. Mostly for outdoor wear.
Application process	by Pad-Dry-Cure process, or exhaust process (e.g. on yarn)
Wash resistance	Displays wash resistance after 20 wash cycles, but slightly less wash resistant compared to PFAS-based products (C_6).
Price	Comparable to PFAS-based products (the product is cheaper compared to a fluorocarbon, but the lower efficiency requires a higher dosage).
Information on release/emissions of the substance during use and/or wash	No data.
Classification	The product is not classified as dangerous according to EC Directives/the relevant national laws.
Human health properties	Acute oral toxicity : LD_{50} > 2.000 mg/kg (OECD Test Guideline 420) Irritant effect on skin : No skin irritation (OECD Test Guideline 404) Irritant effect on eyes : No eye irritation (OECD Test Guideline 405)
Environmental fate properties	Biodegradability : > 90 % (28 d, DOC decrease) (OECD Test Guideline 302B) COD: 650 mg/g - Based on the components. Bioaccumulation of the product: not tested. Mobility in soil: no data available Behaviour in environmental compartments: no data available Results of PBT and vPvB assessment: no data available
Environmental effects properties	Fish toxicity : LC_{50} > 100 mg/l (OECD Test Guideline 203) Bacteria toxicity : IC_{50} > 100 mg/l (OECD Test Guideline 209) No tests on *Daphnia* or algae.

Huntsmann, Phobotex product range				
Product name	Phobotex APK	Phobotex JVA	Phobotex RCO	Phobotex ZAN
Chemical properties	Paraffin dispersion containing aluminium salt. Cationic.	Dispersion of paraffin oils and a fat modified melamine resin. Nonionic/cationic.	Dispersion of paraffin wax and acrylic copolymer. Nonionic/cationic. Contains also: 7-13% oxydipropanol CAS: 25265-71-8 1-3% Polyoxyethylene stearyl ammonium chloride CAS: 68187-69-9	Paraffin dispersion containing zirconium salt. Cationic. Contains also 3-7% Zirconium acetate, CAS 4229-34-9
Functional properties	Water repellent	Water repellent Compatible with PFAS-based polymers for additional oil- and alcohol repellency	Water repellent	Water repellent high resistance to sublimation
Application areas	Water repellent finish of cellulose, wool, synthetic/cotton and synthetic qualities. Waterproof finish of cotton and synthetic/cotton camping articles and cotton tarpaulins.	Women's and men's outerwear, leisure wear, work wear, technical textiles		E. g. tent materials, tarpaulins, rainwear, linings and umbrellas
Application process	Padding, drying temperature: 110 – 130 °C	Padding, but exhaustion method is possible, too.		Padding, but exhaustion method is possible, too.
Wash resistance	Non-durable	Good durability to laundering		Non-durable
Price	No information	No information	No information	No information
Information on release/emissions of the substance during use and/or wash	No data.	No data.	No data.	No data.
Classification of the product	The product is not classified as dangerous according to Directive 1999/45/EC and its amendments.	The product is not classified as dangerous according to Directive 1999/45/EC and its amendments.	The product is not classified as dangerous according to Directive 1999/45/EC and its amendments.	The product is not classified as dangerous according to Directive 1999/45/EC and its amendments.
Human health properties*	LD_{50} Oral Rat >2000 mg/kg, Eyes Non-irritant (Rabbit), Skin Non-irritant (Rabbit). (based on a product with comparable composition)	LD_{50} Oral Rat >2000 mg/kg, Skin Mouse Not sensitizing	No data.	LD_{50} Oral Rat >2000 mg/kg Eyes Non-irritant (Rabbit), Skin Non-irritant (Rabbit).
Environmental fate properties*	Biodegradability: Inherent (OECD 302B modified, 80 to 100% Inherent 28days (DOC)) BOD_5 15 mg/g COD 420 mg/g TOC 19 % PBT: Not applicable	Biodegradability: Inherent (OECD 302B modified, 80 to 100% Inherent – 1 days (DOC)) Conclusion: Eliminated by adsorption onto effluent treatment sludge BOD_5 3 mg/g COD 861 mg/g TOC 20 %	No data.	Biodegradability: Inherent (OECD 302B modified, 80 to 100% Inherent 28 days (DOC)) BOD_5 21 mg/g COD 890 mg/g TOC 24 % PBT: Not applicable

Huntsmann, Phobotex product range				
Product name	Phobotex APK	Phobotex JVA	Phobotex RCO	Phobotex ZAN
		PBT: Not applicable		
Environmental effects properties*	Acute LC_{50} >300 mg/l (Bacteria, 3 hours), Acute LC_0 1000 mg/l (Rainbow trout, 48 hours, OECD 203), Acute LC_{50} > 1000 mg/l (Rainbow trout, 48 hours, OECD 203)	Acute EC_{50} >2000 mg/l (Bacteria, 3 hours), Acute LC_{50} >100 mg/l (*Daphnia*, 48 hours, OECD 202 Part 1)	No data.	Acute IC_{50} >300 mg/l (Bacteria, 3 hours), Acute LC_0 1000 mg/l (Rainbow trout, 48 hours, OECD 203), Acute LC_{50} > 1000 mg/l (Rainbow trout, 48 hours, OECD 203)

* Further toxicity data for single compounds are available in some cases. Here only data for the whole product are included.

3.3 Health assessment

3.3.1 Health data on specific impregnation agents

The ecorepel® product is based on long paraffin chains that wrap themselves, spiral-like, around the individual fibres, filaments or yarns in a very fine film. A sophisticated docking system binds them to the fibres. The honeycomb-like paraffin structures consist of hydrocarbon chains that are arranged over the whole area and reduce the surface tension. Water droplets and even mud with significantly higher surface tension simply run off. No hazard classification of the product according to EU directives. It is a two-component product.
Component A is a dispersion of paraffin- and fatty acid-modified melamine resin. The acute oral toxicity in rats is LD_{50} > 2.000 mg/kg.
Component B is a dispersion of blocked polyisocyanates. The acute oral toxicity is LD_{50} > 2.000 mg/kg (rat). The mutagenicity is negative (Ames test). It is not skin sensitizing (OECD 406).

Schoeller protec-FF is a dispersion of a fat modified melamine resin and paraffin oils similar to component A in Ecorepel. The substances are not further specified. The product is not classified as dangerous according to Directive 1999/45/EC and its amendments. The oral rat LD_{50} is > 2 g/kg, meaning no acute toxicity in rats, as well as no skin- or eye irritation.

Arkophob FFR liq is a polymeric dispersion (liquid wax) of unknown composition; it is water repellent only. The producer claims that the product should not be classified or labelled as dangerous according to EC Directives/the relevant national laws. As a polymer, this may be true, but the first-aid measures mentioned in the MSDS do not indicate a totally harmless chemical. The product has an acute oral toxicity: LD_{50} > 2.000 mg/kg (OECD Test Guideline 420). No irritation of skin and eyes were observed.

PHOBOTEX®APK is a liquid paraffin wax dispersion containing aluminium salt; this normally is applied by padding. In the SDS, it is stated that the product is not hazardous and not classified as dangerous according to Directive 1999/45/EC and its amendments. The oral rat LD_{50} is > 2 g/kg; therefore, there is no acute toxicity in rats. No skin- or eye irritation is observed. It is, however, mentioned that: “This product contains substances for which Chemical Safety Assessments are still required”. On this basis, it is difficult to accept that the product presents no hazards.

PHOBOTEX®JVA Hydrophobic Agent is a dispersion of a fat modified melamine resin and paraffin oils. The product is not classified as dangerous according to Directive 1999/45/EC and its amendments. The oral rat LD_{50} is > 2 g/kg; therefore, there is no acute toxicity in rats. No skin or eye irritation is observed. In general, there is insufficient information for a health evaluation of this product.

PHOBOTEX®RCO is a dispersion of paraffin wax and an acrylic copolymer. The product is not classified as dangerous according to Directive 1999/45/EC and its amendments. However, according to the SDS it contains materials which may cause damage to the kidneys and central nervous system (CNS).

The product contains 7-13 % of dipropylene glycol/oxydipropanol with CAS no 25265-71-8/EC No. 246-770-3.It should be considered that glycol ethers generally have easy skin absorption/penetration. Most notifications in REACH about classification and labelling, according to CLP criteria, conclude that no classification of oxydipropanol was necessary. However, some notifiers proposed classifications as skin and eye irritants for H315 and H 319. Oxydipropanol has a registration dossier in REACH both on its own and in mixtures (ECHA, 2014a). The oral rat LD_{50} for oxydipropanol is 5 g/kg; therefore there would be no acute toxicity in rats. The $^{4h}LC_{50}$ was > 2.34 mg/L air. No skin- or eye irritation or sensitization in humans. In a repeated exposure study, rats were exposed to the glycol orally via drinking water for 105 weeks. The no observable adverse effect level (NOAEL) for liver effects was 470-530 mg/kg bw/d, high dosages. It must be emphasised that glycol ethers often are more toxic to humans than to experimental animals. Mutagenicity- and carcinogenicity tests were also negative.

The product also contains 1-3 % of CAS no. 68187-69-9: Polyoxyethylene stearylammonium chloride, a chemical which is self-classified as skin and eye irritating. It belongs to the important group of ethoxylated quaternary ammonium compounds.

PHOBOTEX®RCO: Dispersion of paraffin wax and acrylic copolymer, also containing 7-13% oxydipropanol, CAS: 25265-71-8 and 1-3% polyoxyethylene stearyl ammonium chloride. The CAS number is 68187-69-9. There is no data available on toxicity.

PHOBOTEX®ZAN Hydrophobic Agent is a paraffin dispersion containing zirconium acetate. It functions by cross-linking between textile substrates and films of water-repellent wax. Zirconium substitutes aluminium and increases the durability of the textile impregnation. In addition zirconium has a function as a flame retardant in the textiles.

It is mentioned in the SDS that the product itself is not classified as dangerous according to Directive 1999/45/EC and its amendments. The oral rat LD_{50} *of the product* is > 2 g/kg; thus no acute toxicity occurs in rats, and surprisingly no skin- or eye irritation or sensitization is observed.

The product contains 7-13 % of zirconium (IV) acetate (CAS no. 4229-34-9/EC no. 224-179-1), which is classified by the EU as a skin and eye irritant. CLP:

- Skin Irrit. 2 (H315)
- Eye Irrit. 2 (H319)

There is an ECHA registration of zirconium acetate (ECHA, 2014b).

- A DNEL of 23 mg/m^3 has been developed for workers exposed long-term by inhalation.
- A DNEL of 3.33 mg/kg bw/day has been developed for workers exposed long-term via the dermal route.
- A DNEL of 5.8 mg/m^3 has been developed for general population exposed long-term by inhalation.
- A DNEL of 1.67 mg/kg bw/day has been developed for the general population exposed long-term via dermal or oral route.
- Oral rat LD_{50} = 4.1 g/kg bw.
- Skin rat LD_{50} > 2 g/kg bw.
- Intraperitoneal rat LD_{50} = 122 mg Zr/kg bw.
- Corrosive or severely irritant to the eye.
- Medium hazard for the eyes in the general population

- Zirconium acetate solution (22%) was considered to have the potential to cause corrosion *in vivo*.
- In rat studies the NOAEL for systemic-, reproductive- and developmental toxicity in rats was considered to be ≥1000 mg/kg bw/day for males and females.
- It is not mutagenic in Ames-Test or other short-term tests performed.

PHOBOTEX®RHW Hydrophobic Agent is an aqueous formulation of a modified resin used as a water repellent. No further details are available about the chemical content. It is mentioned in the SDS that the product is not classified as dangerous according to Directive 1999/45/EC and its amendments.

The oral rat LD_{50} is > 2 g/kg; therefore there is no acute toxicity in rats. No skin- or eye irritation and sensitization are observed.

In the SDS it is also mentioned that the product "contains material, which may cause damage to the following organs: lungs, liver, and gastro-intestinal tract." In addition, exposure to decomposition products may cause a health hazard. Serious effects may be delayed following exposure. Thus the product may still be a health hazard to exposed people.

PHOBOTEX®RSH Hydrophobic Agent is an aqueous formulation of a modified resin used as a water repellent. No details are available about the chemical content. It is mentioned in the SDS that the product is not classified as dangerous according to Directive 1999/45/EC and its amendments. The oral rat LD_{50} is > 2 g/kg; therefore there is no acute toxicity in rats. No skin- or eye irritation and sensitization is observed.
In the SDS it is also mentioned that the product "contains material which may cause damage to the following organs: lungs, liver, and gastro-intestinal tract." In addition, exposure to decomposition products may cause a health hazard. Serious effects may be delayed following exposure. Thus the product may be a health hazard to exposed people.

PHOBOTEX®RHP is a fluorine-free water repellent for textiles. It is an aqueous solution/-formulation of a modified resin of unknown composition. In the SDS it is stated that the product is not hazardous and not classified as dangerous according to Directive 1999/45/EC and its amendments. The oral rat LD_{50} is > 2 g/kg; therefore there is no acute toxicity in rats. No skin- or eye irritation is observed.

However, it is also mentioned:

1. "Contains material which may cause damage to the following organs: lungs, liver, and gastrointestinal tract."
2. "Inhalation exposure to decomposition products may cause a health hazard. Serious effects may be delayed following exposure."
3. "This product contains substances for which Chemical Safety Assessments are still required".

The second point may indicate a risk for lung edema, a potentially fatal disease. Therefore, the potential health effects of using this product may be considerable.

PHOBOTEX®HSR Hydrophilic Stain Release Agent is a dispersion of a hydrophilic non-ionic polymer normally applied by padding. No SDS and no toxicity information have been obtained.

3.3.2 Risk of dangerous substances in the treated textiles

Classification - The products in this group do not have a harmonised classification as dangerous according to the CLP Regulation (Regulation (EC) No 1272/2008).

However, some of the known ingredients appear to be harmful, but most of the ingredients are not declared. Based on available information, there are no CMR-substances or endocrine disruptors in these paraffin-type products.

3.3.3 Risk of formation of dangerous substances by degradation of cured repellents

No information, but not likely.

3.4 Environmental assessment

Paraffin oils are mixtures of long chain alkanes (linear aliphatic hydrocarbons). Paraffin-based water repellents for textiles have been used for a long time. They are used as liquid emulsions typically with resins or salts of fatty acids.

3.4.1 Environmental data on specific impregnation agents

The ecorepel® brand from Schoeller is a two-component product. Component A is a dispersion of paraffin oils and fatty acid modified melamine resin. Component B is a dispersion of blocked polyisocyanates. The latter may contain traces of reactive isocyanates, hydrolysed easily in the environment. Both components were easily biodegradable in the OECD 302B test. Component A has been tested in an aquatic toxicity test with the Crustacean *Daphnia magna* and had a low acute toxicity ($^{48h}LC_{50}$ > 100 mg/L). In another test (OECD 202) with sewage sludge bacteria, the $^{3h}EC_{50}$ for component A was very high (>2000 mg/L) indicating very low toxicity. Component B was tested in a fish acute toxicity test (OECD 203) with zebra fish. The result was a very low acute toxicity ($^{48h}LC_{50}$ > 10.000 mg/L).

Schoeller protec-FF® from Schoeller is a dispersion of paraffin oils and a fat modified melamine resin, similar to component A in Ecorepel. The composition is not specified further. The product is easily biodegradable in the OECD 302B test. The product has been tested in an aquatic toxicity test with the crustacean *Daphnia magna* and had a low acute toxicity ($^{48h}LC_{50}$ > 100 mg/L). In another test (OECD 202) with sewage sludge bacteria, the $^{3h}EC_{50}$ for the product was very high (>2000 mg/L) indicating very low effect/toxicity. According to the SDS the product is self-classified according to Directive 1999/45/EC as potentially harmful to the water environment.

Arkophob®FFR liq from ARCHROMA is a polymeric dispersion (liquid wax) of unknown composition but probably paraffin-based; it is water repellent only. According to the SDS the product is not to be classified as dangerous according to EC Directives/the relevant national laws. It is easily biodegradable in the OECD 302B test. but bioaccumulation was not studied. Two ecotoxicity tests have been undertaken. The LC_{50} in a fish toxicity test (OECD 203) was >100 mg/L, and the IC_{50} in a bacteria toxicity test (OECD209) was > 100 mg/L; therefore, the ecotoxicity of this product is low.

PHOBOTEX®APK is a liquid paraffin wax dispersion containing an unspecified concentration of an aluminium salt. According to the SDS this product is not classified according to EU legislation. It was easily biodegradable in a modified OECD 302B test. The product has been tested in acute ecotoxicity tests with bacteria and fish. The acute $^{3h}IC_{50}$ for bacteria (type non-specified in the SDS) was >300 mg/L, and the $^{48h}LC_{50}$ for rainbow trout (*Oncorhynchus mykiss*) was > 1000 mg/L; therefore, in both instances the toxicity was low.

PHOBOTEX®JVA Hydrophobic Agent from Huntsman is a dispersion of paraffin oils and a fat modified melamine resin. It is likely similar to the Schoeller-Protec-FF product discussed above.

According to the SDS, this product is not classified as dangerous according to Directive 1999/45/EC and its amendments. It is easily biodegradable in a modified OECD 302B test. The product has been tested in acute ecotoxicity tests with non-specified bacteria with a $^{3h}IC_{50}$ > 2000 mg/L, and in an acute immobilisation test (OECD 202) with *Daphnia magna*, giving an $^{48h}EC_{50}$ > 100 mg/L; therefore, in both instances the toxicity was low.

PHOBOTEX®RCO is a dispersion of paraffin wax and an unknown acrylic copolymer. According to the SDS the product is not classified as dangerous according to Directive 1999/45/EC and its amendments.
The products contains 7-13 % of dipropylene glycol/oxydipropanol with CAS no. 25265-71-8/EC No. 246-770-3, which is not classified according to the CLP Directive but has a registration dossier in REACH (ECHA, 2014a). According to the registration dossier, oxydipropanol had a calculated atmospheric half-life of about 4 hrs, and it was easily biodegradable in a fresh water test but less biodegradable in sea water (OECD 306). In a test for bioaccumulation in fish (the common carp: *Cyprinus carpio*) (OECD 305C) the bioconcentration factor (BCF) was 0.3-4.6. The octanol-water partition coefficient log K_{oc} = -0.462. A EUSES model calculation determined the Henry's Law constant H at 12°C as 0.000907 Pa m^3/mol. A McKay distribution modelling exercise showed the relative percent distribution in media as 0.11% in air, 46.1 % in water, 53.7 % in soil and 0.08 % in sediment.

Oxydipropanol has been studied in several ecotoxicity tests:

- In a freshwater fish acute toxicity test with the goldfish (*Carassius auratus*) the $^{24h}LC_{50}$ was > 5000 mg/L
- in an acute immobilisation test (OECD 202) with *Daphnia magna* the $^{48h}EC_{50}$ was > 100 mg/L
- In an algae growth inhibition test (OECD 201) the $^{72h}EC_{50}$ was > 100 mg/L
- The substance initiates growth inhibition of the bacteria *Pseudomonas putida* at a concentration of 1000 mg/L
- The acute toxicity to an endangered frog species, *Rana porosa brevipoda,* inhabiting rice fields of western Japan, was determined as a $^{48h}LC_{50}$ = 5300 mg/L
- The acute toxicity in another frog species, *Xenopus laevis,* was $^{48h}LC_{50}$ = 3181 mg/L
- An avian acute oral toxicity test (EPA OPPTS 850.2100) the $^{14d}LD_{50}$ > 2000 mg/kg bw.

The conclusions of assessments of the hazard for oxydipropanol were:

- Freshwater organisms predicted no effect concentration (PNEC) = 0.1 mg/L with assessment factor 1000
- Marine water organisms PNEC = 0.01 mg/L with assessment factor 10000
- Intermittent releases PNEC = 1 mg/L with assessment factor 100
- Sewage treatment plant (STP) PNEC = 1000 mg/L with assessment factor 1
- Fresh water sediment PNEC = 0.238 mg/kg sediment dw
- Marine water sediment PNEC = 0.0238 mg/kg sediment dw
- Terrestrial organisms PNEC = 0.0253 mg/kg soil dw
- Predator secondary poisoning oral PNEC = 313 mg/kg food with assessment factor 3000.

The PHOBOTEX®RCO product also contains 1-3 % of CAS no. 68187-69-9: Polyoxyethylene stearylammonium chloride, a polymer which is classified in the CLP system as "Aquatic Chronic 3, with risk phrase: H412". The product has not been tested for biodegradation or in ecotoxicity tests.

PHOBOTEX® ZAN Hydrophobic Agent is a paraffin dispersion containing 7-13 % of zirconium (IV) acetate (CAS no. 4229-34-9/EC no. 224-179-1. According to the SDS, the product is not classified as dangerous as per Directive 1999/45/EC and its amendments. The product was easily biodegradable in a modified OECD 302B test. The product has been tested in acute ecotoxicity tests with bacteria and fish. The acute $^{3h}IC_{50}$ for bacteria (type not-specified in the SDS) was >300 mg/L,

and the $^{48h}LC_{50}$ for rainbow trout (*Oncorhynchus mykiss*) was > 1000 mg/L; thus in both instances toxicity was low. The identical test results indicate a close relationship to the previously discussed PHOBOTEX®APK containing an aluminium salt instead of a zirconium salt. There is an ECHA registration of the water soluble zirconium acetate (ECHA, 2014b).

In a 28 day screening test with a closed bottle (OECD 301D); the organic part of zirconium acetate was ready biodegradable in water. Being a natural element, the zirconium metal itself cannot degrade. Transfer of zirconium-ions from soil to tomato- and pea plants was studied in two soils during a 7-day exposure period, but the uptake was very low; thus, the potential for accumulation in plants is low. The acute toxicity of zirconium acetate to rainbow trout (*Oncorhynchus mykiss*) was studied in an aquarium test, and a $^{7d}LC_{50}$ was determined to be 58.7 mg/L. In a Respiration Inhibition Test with Activated Sludge (OECD 209), the 3 hours the no observable effect concentration (NOEC) was 742 mg zirconium acetate/L fresh water. Some other studies should be discarded, because they used water-free zirconium acetate, which is not water soluble. The conclusion was that there was no potential for bioaccumulation or ecotoxicological effects by zirconium acetate.

PHOBOTEX®RHW Hydrophobic Agent is an aqueous solution of a modified resin used as a water repellent. No further details are provided about the chemical content. According to the SDS, the product is not classified as dangerous according to Directive 1999/45/EC and its amendments. It was easily biodegradable in a modified OECD 302B test. In an acute ecotoxicity test with luminescent bacteria (DIN 384 12), the $^{½h}EC_{50}$ was > 1000 mg/L. In an acute immobilisation test (OECD 202) with *Daphnia magna*, the result was a $^{48h}EC_{50}$ 1-10 mg/L; in the last instance, therefore, a significant toxicity was observed.

PHOBOTEX®RSH Hydrophobic Agent is an aqueous formulation of a modified resin used as a water repellent. No details are provided about the chemical content. The SDS mentions that the product is not classified as dangerous according to Directive 1999/45/EC and its amendments. It was easily biodegradable in a modified OECD 302B test. In an acute ecotoxicity test with luminescent bacteria (DIN 384 12), the $^{½h}EC_{50}$ was > 1000 mg/L. In an acute immobilisation test (OECD 202) with *Daphnia magna*, the result was a $^{48h}EC_{50}$ 10-100 mg/L; therefore, in the last test the result showed this substance to be 10 times less toxic to *Daphnia* than the previously discussed PHOBOTEX®RHW.

PHOBOTEX® RHP is a fluorine-free water repellent for textiles. It is an aqueous solution/-formulation of a modified resin of unknown composition. The SDS mentions that the product is not classified as dangerous according to Directive 1999/45/EC and its amendments. It was easily biodegradable in a modified OECD 302B test. In an acute ecotoxicity test with luminescent bacteria (DIN 384 12) the $^{½h}EC_{50}$ was > 1000 mg/L. In an acute immobilisation test (OECD 202) with *Daphnia magna* the result was a $^{48h}EC_{50}$ 10-100 mg/L; therefore, these identical test results indicate a close relationship to the previously discussed PHOBOTEX®RSH.

PHOBOTEX® HSR Hydrophilic Stain Release Agent is a white dispersion of a hydrophilic nonionic polymer. No details about the chemical content, and no SDS or other information about environmental fate properties and toxicity are available. Therefore the product cannot be evaluated.

3.4.2 Risk of releases of dangerous substances from treated textiles

The products in this group do not have a harmonised classification as dangerous according to the CLP Regulation (Regulation (EC) No 1272/2008).

However, some of the known ingredients appear to be harmful but most of the ingredients are not listed. Based on available information these products do not contain PBT substances which may be released during processing and washing. The products and the known ingredients seem to be easily biodegradable, having low to moderate acute toxicity to aquatic organisms.

3.5 Summary

A**vailability and technical properties -** Many products are available and agents of this type have been on the market for many years. Used for clothing and non-clothing textiles, they are effective on many types of fibres and many blends. The agents provide durable water repellency but not oil repellency. For those products where the price indication is available, costs are comparable to PFAS-based agents (they are cheaper compared to the PFAS-based agents, but their lower efficiency requires a higher dosage).

Health assessment - The products in this group are liquid emulsions that, according to the producers, should not be classified as hazardous to health. However, some of the known ingredients appear to be harmful. The main ingredient in most products is paraffin oil/wax, i.e. mixtures of long chain alkanes (linear aliphatic hydrocarbons), which in pure form are harmless to human health. The compositions of the products are mainly confidential, but some products also contain isocyanates, dipropylene glycol, metal salts or other unspecified substances, which may be harmful.

Environmental assessment - The products in this group are liquid emulsions that according to the producers should not be classified as hazardous for the environment. The main known ingredient in most products is paraffin oil/wax, i.e. mixtures of long chain alkanes (linear aliphatic hydrocarbons), which in pure form are readily biodegradable, not bioconcentrated or accumulated in organisms and food chains. The toxicity to aquatic and terrestrial organisms is low even at concentrations above water solubility.

Main data gaps - More information about the composition of the products and the environmental and health properties of the ingredients is needed. For two-component products, more information is needed about the reaction product.

More information about the composition of the products and the environmental properties of the product and ingredients is needed. For two-component products, more information is needed for the fate of the reaction product.

There are few studies available regarding the products and ingredients that are of acute toxicity to terrestrial organisms, their chronic ecotoxicity in general, and their potential for bioaccumulation.

4. Silicone repellent chemistries

4.1 Chemistry

Polydimethylsiloxanes are the most common silicone repellents. Due to their structure, they form hydrogen bonds with fibres and exhibit repellency effects on the outer surface of fibres (ZDHC, 2012). See figure 2.

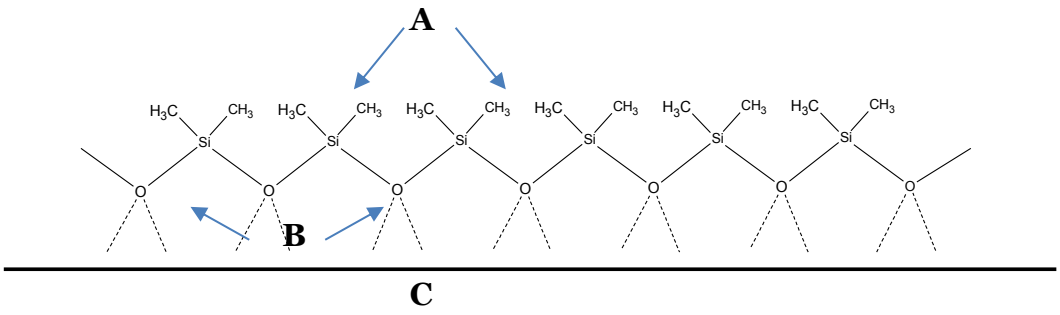


FIGURE 2
POLYDIMETHYLSILOXANE ON A FIBRE SURFACE. A – HYDROPHOBIC SURFACE, B – HYDROGEN BONDS TO POLAR SURFACE, C – FIBRE SURFACE (BASED ON SCHINDLER AND HAUSER, 2004)

Silicone repellents designed to be durable finishes generally consist of a polymer, silandiol, a polymer methyl silane, and a catalyst, e.g. tin octanoate. The silandiol and silane components react to form a three-dimensional cross-linked sheath around the fibres and the catalyst promotes alignment of the silicone film on the fibre surface (Figure 3). The methyl groups of the silicone polymer are positioned outwards and produce the water repellent effects. Hydrogen bonding between the polymer and textile surface, e.g. cellulose, provides fixation to the fibre (Schindler and Hauser, 2004; ZDHC, 2012).

Silicon repellents offer a high degree of water repellency at relatively low concentrations. Application of excess amounts, however, can reduce the water repelling effects. Silicon repellents have moderate durability for laundering and dry cleaning, because of possible hydrolysis of the siloxanes and rupture of the surface film, which can be caused by cellulose swelling. They provide no oil repellency. Waste waters, particularly from residual baths of the finish application processes, are mentioned to be toxic to fish (ZDHC, 2012).

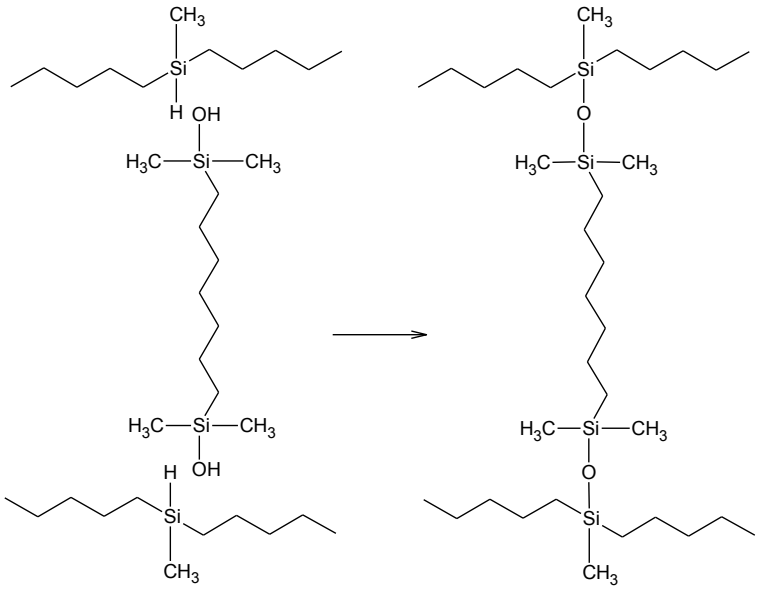
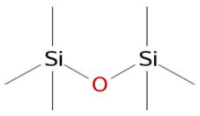
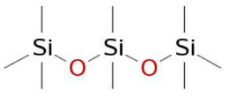
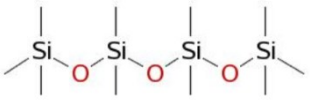
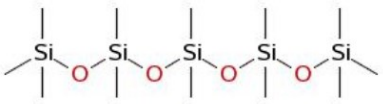
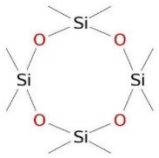
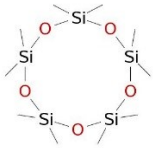
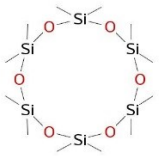


FIGURE 3

SILANOL-SILANE REACTION. A – CROSSLINKING BY REMOVAL OF H2, B – THE CROSSLINKED SI-O-SI POLYMER. TIN OCTOATE CATALYSES THE REACTION (BASED ON SCHINDLER AND HAUSER, 2004)

The following siloxanes, used as intermediates for polymer synthesis, and silicone polymers, used for textile impregnation (shown in Table 4) have been discussed in a background report on PFOS substitutes developed for the UNEP POPs Review Committee (UNEP, 2013).

TABLE 4
SILOXANES AND SILICONE POLYMERS (FROM UNEP, 2013)

Abbreviation	Name	Cas no.	Structure*
HMDSO	Hexamethyl disiloxane	107-46-0	 *
MDM	Octamethyl trisiloxane	107-51-7	 *
MD2M	Decamethyl tetrasiloxane	141-62-8	 *
MD3M	Dodecamethyl pentasiloxane	141-63-9	 *
D4	Octamethyl cyclotetrasiloxane	556-67-2	 **
D5	Decamethyl cyclopentasiloxane	541-02-6	 **
D6	Dodecamethyl cyclohexasiloxane	540-97-6	 **

* Chemical structures from http://esis.jrc.ec.europa.eu/.
** Chemical structures from registrations at ECHAs dissemination tool.

4.1.1 Other uses of silicon technology

Sometimes siloxane-based textile repellents are used along with the classic cationic textile surfactant 1-(stearamidomethyl) pyridinium chloride (below) – occasionally together with carbamide (urea) and melamine resins.

The dendrimer repellent chemistry described in section 5 includes the use of organopolysiloxane chemistry, but the chemistry of these repellents is essentially different from the silicones.

4.2 Examples of marketed products

Repellents based on silicone chemistry have been used for many years, and many products incorporating it are marketed.

Examples of marketed products and product details regarding classification, environmental and health properties are shown below. Other marketed products for which detailed data have not been obtained include Texfin®-HTF and Texfin®-SWR-A from Texchem, but many different brands are marketed.

Huntsman - part of Phobotex series			
Product name	**Phobotex Catalyst BC**	**Phobotex SSR**	**Phobotex WS Conc**
Chemical properties	Emulsion of polydimethylsiloxane and a self-crosslinking condensation product. Cationic Contains also 1-3% Alcohols, C_{11-14}-iso-, C_{13}-rich CAS: 68526-86-3	Dispersion containing hydrophilic polysiloxane and hydrophilic polyester. Nonionic.	Polysiloxane-based emulsion. Contains also 3-7% Cocoalkyl bis(2-hydroxyethyl) ethoxylated methyl ammonium chloride (no CAS, polymer)
Functional properties	Water repellent stability to weathering including UV light	Water repellent Antistatic finishing on synthetic fibres	Water repellent Increases fabric resilience
Application areas		Synthetic fibres and their blends	Pile, velvet fabrics and casual outerwear
Application process	Padding only	Padding	Padding only Should be applied together with Phobotex® Catalyst BC
Wash resistance	Good durability to laundering	Very high durability to washing, particularly on polyester and aramid fibres	Good durability to laundering
Price	No data.	No data.	No data.
Information on release/emissions of the substance during use and/or wash	No data.	No data.	No data.
Classification of the product	R52/53 - Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.	The product is not classified as dangerous according to Directive 1999/45/EC and its amendments.	Xi; R41 - Risk of serious damage to eyes R52/53 - Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
Human health properties*	LD_{50} Oral Rat >2000 mg/kg Eyes – Non-irritant. Rabbit Skin - Non-irritant. Rabbit	LD_{50} Oral Rat >2000 mg/kg Eyes Non-irritant (Species not known), Skin Non-irritant (Species not known).	LD_{50} Oral Rat >2000 mg/kg Eyes Irritant (Species not known), Skin Non-irritant (Rabbit).
Environmental fate properties*	Biodegradability: Not readily (OECD 303A modified, 25 to 50 % - 28 days (TOC)) BOD_5 15 mg/g COD 820 mg/g TOC 18 % PBT: Not applicable	Biodegradability: Eliminated by adsorption onto effluent treatment sludge (OECD 302B modified, 60 to 80%, 28days (DOC)) BOD_5 5 mg/g COD 317 mg/g TOC 10 % PBT: Not applicable	Biodegradability: Not readily (OECD 303A modified 50 to 100%, 28days (TOC)) BOD_5 60 mg/g COD 4780 mg/g TOC 14 % PBT: Not applicable

Huntsman - part of Phobotex series			
Product name	**Phobotex Catalyst BC**	**Phobotex SSR**	**Phobotex WS Conc**
Environmental effect properties*	Acute IC_{50} >300 mg/l (Bacteria, 3 h) Acute LC0 20 mg/l (Fish - Rainbow trout 48 hours, OECD 203) Acute LC_{50} 45 mg/l (Fish - Rainbow trout, 48 hours, OECD 203)	Acute EC_{50} >5000 mg/l (Bacteria Luminescent, DIN 38412 Lumistox test, 30 min) Acute IC_{50} >300 mg/l (Wastewater bacteria, 3 h) Acute LC_0 1000 mg/l (Rainbow trout, 48 h, OECD 203) Acute LC_{50} >1000 mg/l (Rainbow trout, 48 h, OECD 203)	Acute EC_{50} 100 mg/l (Daphnia, 48 h) Acute IC_{50} >300 mg/l (Bacteria, 3 h) Acute LC_0 20 mg/l (Rainbow trout, 48 h, OECD 203) Acute LC_{50} 45 mg/l (Rainbow trout, 48 h, OECD 203)

Bluestar Silicones - RHODORSIL TCS 7001	
Product name	RHODORSIL TCS 7001
Chemical properties	Alkyl polysiloxane solution in solvent phase (solvent: aliphatic hydrocarbon), contains 95% hydrocarbons, C_9-C_{10}, *n*-alkanes, isoalkanes, cyclics, <2% aromatics (EC No. 927-241-2) and <2 % naphtha (EC No. 265-150-3)
Functional properties	• Waterproofing to natural fabrics, synthetic fabrics, synthetic leathers. • Outstanding abrasion resistance in humid environments • Resistance to detergent washing
Application areas	Outdoor fabrics - natural and synthetic leathers. Aerosols for reproofing of fabrics and leathers (natural and synthetic).
Application process	Spray or impregnation waterproofing of fabrics and leathers. When using aerosols: it is recommended to use butane gas type propellant. In the case of fabric impregnation it is recommended to heat it for 3 minutes at a temperature of 150°C
Wash resistance	No data.
Price	Possibly less expensive than PFAS-based agents
Information on release/emissions of the substance during use and/or wash	No data.
Classification of the product	Classification according to Directive 67/548/EEC or 1999/45/EC as amended: R10 Xn; R65 R66 R67 R52/53 (corresponding to Aquatic Chronic 3;H412, Flam. Liq. 3;H226, STOT SE 3; H336, Skin Irrit. 3; H316, Asp. Tox. 1; H304)
Human health properties	No data.
Environmental fate properties	The product has the potential to bioaccumulate. Otherwise no data.
Environmental effects properties	No data.

4.3 Health assessment

4.3.1 Health data on specific impregnation agents

PHOBOTEX® CATALYST BC Hydrophobic Agent is an emulsion of a polydimethyl siloxane and a self-crosslinking cationic condensation product. It is volatile. The product is classified as harmful for aquatic organisms according to Directive 1999/45/EC and its amendments. The oral rat LD_{50} for the product was > 2 g/kg. Regarding toxicity see above.

The product contains 1-3% of CAS no. 68526-86-3/EU no. 271-235-6: Isotridecyl alcohol (mixed)/11-methyldodecan-1-ol, which is registered in REACH (ECHA, 2014l). The following DNELs are mentioned for this alcohol:

Long term	Inhalation	293.86 mg/m³	Workers Systemic
Long term	Dermal	416.67 mg/kg bw/d	Workers Systemic
Long term	Inhalation	89.96 mg/m³	Consumers Systemic
Long term	Dermal	250 mg/kg bw/d	Consumers Systemic
Long term	Oral	25 mg/kg bw/d	Consumers Systemic

The oral rat LD_{50} for isotridecyl alcohol was > 2 g/kg and the rat inhalation $^{6h}LC_{50}$ >12.2 mg/L; therefore there is no acute toxicity in rats. No skin- or eye irritation is observed. The alcohol was also negative in the three mutagenicity studies performed. In a study with rats dosed orally with the alcohol for 14 days, the NOAEL was 130 mg/kg bw/day. In a teratogenicity study with rats exposed for 10 days, the NOAEL was 100 mg/kg bw/day. These NOAEL values are of the same magnitude as the PFAS it substitutes, and this substance should be considered harmful.

PHOBOTEX® SSR Soft Stain Release Agent is a dispersion of hydrophilic polyester (polymer) with a functional polysiloxane. No further details from the SDS/TDS are available about the chemical content.

It is mentioned in the SDS that the product is not classified as dangerous according to Directive 1999/45/EC and its amendments. The oral rat LD_{50} is > 2 g/kg; therefore there is no acute toxicity of the product in rats. No skin- or eye irritation and sensitization is observed.

PHOBOTEX® WS CONC. Hydrophobic Agent is a non-ionic polysiloxane based emulsion. According to the SDS the product is classified as an irritant according to Directive 1999/45/EC and its amendments. The major human health hazard is: “Risk of serious damage to eyes”.
The oral rat LD_{50} *of the product* is > 2 g/kg; therefore there is no acute toxicity in rats.

The product contains 3-7% of the quaternary ammonium compound and emulsifier: Cocoalkylbis(2-hydroxyethyl) ethoxylated methylammonium chloride/ *N,N*-Diethoxylated-*N*-coco-*N*-methylammonium chloride (CAS no. 61791-10-4), which is pre-registered in ECHA (ECHA, 2014c). This *substance* has a rat oral LD_{50} = 580 mg/kg bw (ChemIDplus, 2014), and it is a powerful irritant for skin and especially eyes (CEFIC, 2006). Therefore, the SDS understates the hazard from the product.

For **OC-aquasil Tex W™, OC-aquasil Tex N™** no detailed information is available, other than that the product contains <10.5% an organic silicon compound and <5% of an organic acid. The product is not classified according to 1999/45/EC. It is stated that the product contained no substances that were classified as carcinogenic, mutagenic or toxic for reproduction.
However, the organosilicon compound is classified as skin irritating, group 2 (H315). The organic silicon compound (in concentrated form) had an oral rat LD_{50} > 5000 mg/kg. The organic acid is also classified as skin irritating, group 2 (H315). In addition, it is classified as eye irritating, group 2 (H319), and has specific target organ toxicity by single exposure in category 3 (STOT SE 3) (H335). In concentrated form it has LD_{50} (mouse) > 1500 mg/kg.

RHODORSIL/Bluesil TCS 7001 is an alkyl polysiloxane solution in a solvent phase. Classification has been done according to Directive 67/548/EEC or 1999/45/EC as amended: R10 Xn; R65 R66 R67 R52/53. No human health data are available.

4.3.2 Risk of dangerous substances in the treated textiles

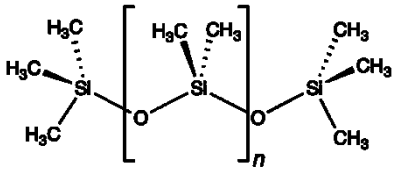
For most of the alternative products reviewed there is insufficient qualitative and quantitative public information available about the ingredients. Most products do not have information available because they are protected by trade secrets.. For some siloxanes used as intermediates in production of silicon polymers, much health and environmental information exists but it is unclear to what degree these siloxanes are ingredients or impurities in the commercial products or are present in the textiles.

Various siloxanes, especially the cyclic siloxanes known as D4, D5 and D6 and the linear siloxanes HMDSO, MDM, MD2M and MD3M, are used as intermediates for synthesis of silicone polymers, which in turn is used for *inter alia* textile impregnation (Gravier et al., 2003). As an example, according to one of the producers, D4 is used as a monomer ('building block') in the production of silicone polymers which may be oils, greases, rubbers and resins. Furthermore, it is used as an intermediate (starting material) in the production of other organosilicon substances (Momentive 2014).

4.3.3 Health assessment of siloxanes

Polydimethylsiloxanes (PDMS)

Some years ago linear polydimethylsiloxanes (PDMS ,CAS No. 63148-62-9) - a type of non-volatile (odourless), fluid (viscous) "silicones" - were evaluated in a comprehensive monograph published by the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC, 2011).



PDMS

Humans may be exposed to PDMS via oral ingestion and dermal contact. In laboratory animals, PDMS had a low potential for absorption via these routes. Swallowed PDMS is rapidly excreted unchanged in the faeces. Aerosolised PDMS may give rise to inhalation exposure, but there is no indication of any adverse effects. PDMS is not a skin irritant or a skin sensitizer, and it is only mildly to non-irritating to the eyes.

1. Acute and repeated dose toxicity studies conducted in laboratory animals on PDMS of different viscosities do not show any significant adverse effects. Long-term chronic/carcinogenicity and reproductive toxicity studies were also without adverse effects. PDMS is not mutagenic *in vitro*.
2. In humans, PDMS has no effect on the immune system. PDMS is used in urology, ophthalmology and dermatology (skin correction). Autoimmune disorders (e.g. scleroderma) cannot be linked to PDMS. Several human diseases (connective tissue, atypical connective tissue, rheumatic and autoimmune diseases, and breast cancer) have been reported after injection of PDMS (for cosmetic purposes) or placement of breast implants (made of high viscosity PDMS). These diseases are, however, not associated with PDMS.

Low-molecular-weight poly(dimethylsiloxanes)

Low-molecular-weight poly(dimethylsiloxanes) (MM, MDM, MD2M and MD3M) are used as intermediates in the synthesis of silicone polymers, but no data on the trace levels of low-molecular-weight poly(dimethylsiloxanes) in the final fabric are available.

Detailed health data for the low-molecular-weight poly(dimethylsiloxanes) from the REACH registration dossiers, available from ECHA's Dissemination Site Database (ECHA 2014, b), are shown in Appendix 1.

Low-molecular-weight poly(dimethylsiloxanes) have been studied by siloxane manufacturers, and they conclude that the poly(dimethylsiloxanes) studied all possess a very low potential for toxicity. Further information on HMDSO is included along with the description of the cycling siloxanes below.

Cyclic siloxanes
The cyclic siloxanes may be used as intermediates in the synthesis of silicone polymers, but no data on the trace levels of cyclic siloxanes in the final fabric is available.

Detailed health data for the cyclic siloxanes (D4, D5, D6) from the REACH registration dossiers, available from ECHA's Dissemination Site Database (ECHA 2014, b), are shown in Appendix 1.

In a study for the Danish EPA, the toxicological information which primarily existed for D4, D5 and HMDSO was reviewed (Lassen et al., 2005). The three siloxanes demonstrate a relatively low order of acute toxicity by oral, dermal and inhalation routes and do not require EU classification for this effect. They are not shown to be irritating to skin or eyes and are also not found to be sensitizing by skin contact. Data on respiratory sensitization have not been identified.

Sub-acute and sub-chronic toxicity studies show that the liver is the main target organ for D4, whereby hepatocellular enzymes are induced. This enzyme induction contributes to the elimination of the substance from the tissues. This enzyme induction contributes to the elimination of the substance from the tissues.

D5 has a similar liver enzyme induction profile as D4 but the primary target organ for D5 exposure by inhalation was the lung.

In sub-acute and sub-chronic inhalation studies with rats of HMDSO affects in particular the lungs and kidneys, which are the target organs.

None of the investigated siloxanes show any signs of genotoxic effects *in vitro* or *in vivo*. However, preliminary results indicate that D5 may induce uterine tumours in female rats, and this carcinogenic effect is considered the critical effect for D5 (US EPA, 2005).

Inhalation of D4 impaired fertility in rats, and that was considered the critical effect. D4 was also classified as a substance toxic to reproduction in category 3 with the risk phrase R62 ('Possible risk of impaired fertility').

The results of a study to screen for estrogenic activity indicated that D4 had both a very weak estrogenic and anti-estrogenic activity. Comparison of the estrogenic potency of D4 relative to ethinylestradiol (steroid hormone used in p-pills) indicated that D4 is 585,000 times less potent than ethinylestradiol in the rat and 3.7 million times less potent than ethinylestradiol in the Fisher-344 rat strain

A study carried out by the National Food Institute at the Technical University of Denmark investigated the toxic effects of siloxanes as a group in order to set a health-based quality criterion for ambient air. Toxic effects of D3, D4, D5, D6 and HMDSO were studied using a “read-across” modelling method based on structural similarity and its relation to toxicity. The linear siloxane HMDSO appeared to have lower potential for liver toxicity, but higher potential for lung toxicity, than the cyclic substances. Decreasing toxicity with increasing chain length was also observed. An ambient

quality criterion of 0.01 mg/m^3 was derived based on lung toxicity, including a safety factor of 250 (Greve et al., 2008).

The Scientific Committee on Consumer Products in the European Union has published an Opinion on D4 and D5 in which the safety of D4's use as a cosmetic ingredient was not questioned (SCCP, 2010).

In the United States, the Cosmetic Ingredient Review (CIR) panel has published an assessment of the safety of cyclic siloxanes: D3, D4, D5, D6 and D7. The panel concluded that D4, D5, D6 and D7 were safe for use in cosmetics, but D3 will be taken off the International Nomenclature of Cosmetic Ingredients (INCI) list, because it was not a commercial product (Johnson et al., 2011).

Other studies of siloxanes, however, indicate that they appear to be harmful when inhaled, and that exposure may induce serious damage to eyes. Prolonged and frequent skin contact with the product WorléeAdd® 340 may cause skin irritation. In short, knowledge of the toxicity of siloxanes is still incomplete.

Some siloxanes are metabolized and the metabolites (hydroxylation metabolites) are expected to be found in blood and urine. California State EPA notes the weak estrogenic activity of D4 combined with long half-life and uterine tumours resulting from D5 exposure. The California State EPA also noted that cyclosiloxanes appeared to have long half lives in people (California EPA, 2008).

4.3.4 Classification of siloxanes

The harmonised classification according to the CLP Regulation (Regulation (EC) No 1272/2008) and the classification as notified to the C&L inventory is indicated in the table below.

TABLE 5
HARMONISED CLASSIFICATION AND CLASSIFICATION INFORMATION NOTIFIED BY MANUFACTURERS AND IMPORTERS (C&L INVENTORY)

Substance	CAS No	Harmonised classification * C&L List (ECHA; 2014D)		
		Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
Polydimethylsiloxanes (PDMS)	63148-62-9	**Total** Not classified Aquatic chronic 4 Eye Irrit. 2 Aquatic chronic 2 Repr. 2 Flam. liq. 3 Skin corr. 1A Eye dam. 1 Asp. tox. 1 Acute tox. 1 Acute tox. 2	 H413 H319 H411 H361 H226 H314 H318 H304 H300 H300	**1405** 356 131 51 13 25 13 13 1 1 1
Octamethylcyclo-tetrasiloxane (D4)	556-67-2	Repr. 2 Aquatic chronic 4	H361f H413	Harmonised classification*

Substance	CAS No	Harmonised classification * C&L List (ECHA; 2014D)		
		Hazard Class and Category Code(s)	Hazard State-ment Codes	Number of notifiers
Decamethylcyclo-pentasiloxane (D5)	541-02-6	**Total** Not classified Aquatic chronic 4 Acute tox. 3 Skin irrit. 2 Eye irrit. 2 STOT SE 3	 H413 H331 H315 H319 H335	**1479** 1313 65 46 27 31 2
Dodecamethylcyclo-hexasiloxane (D6)	540-97-6	**Total** Not classified Eye Irrit. 2 Aquatic chronic 4	 H319 H413	**266** 230 19 16
Octamethyltrisiloxane (MDM)	107-51-7	**Total** Not Classified Flam. liq. 3 Aquatic chronic	 H226 H413	**224** 83 141 3
Hexamethyldisiloxane (HMDSO)	107-46-0	**Total** Not classified Flam. liq. 2 Aquatic acute 1 Aquatic chronic 1 Carc. 2 Aquatic chronic 2 Acute tox. 3 Acute tox. 4 Flam sol. 1 Water react. 1 Eye irrit. 2 Flam liq. 3 Asp. tox. 1 Skin irrit. 1	 H225 H400 H410 H351 H411 H301 H332 H228 H260 H319 H226 H304 H315	**924** 99 793 596 408 63 73 18 18 1 1 1 1 1 1

* According to Annex VI of Regulation (EC) NO 1272/2008 (CLP REGULATION).

4.4 Environmental assessment

4.4.1 Environmental data on specific impregnation products

PHOBOTEX®CATALYST BC Hydrophobic Agent from Huntsman is an emulsion of a PDMS and a self-crosslinking cationic condensation product. According to the SDS the product is classified as harmful for aquatic organisms and may cause long-term adverse effects in the aquatic environment (R52/R53) according to Directive 1999/45/EC and its amendments. In addition, the following safety phrase S61 applies: "Avoid release to the environment. Refer to special instructions/safety data sheet." The product has a low acute toxicity to bacteria with a $^{3h}IC_{50}$ >300 mg/L, but a higher toxicity to rainbow trout (*Oncorhynchus mykiss*) with a $^{48h}LC_{50}$ = 45 mg/L. The product was somewhat biodegradable (25-50 % in 28 days) in a test system (OECD 303A).

The product contains 1-3% of CAS no. 68526-86-3/EU no. 271-235-6: Isotridecyl alcohol (mixed)/11-methyldodecan-1-ol, which is classified harmful (N, R50; Aquatic Acute 1, H400) to the environment and registered in REACH (ECHA, 2014l).

Isotridecyl alcohol is easily biodegradable (>60%) in activated sludge over 28 days. It is also readily biodegradable in water (OECD 301F). The octanol-water partition coefficient is 5.4 (log K_{ow}) at 25°C. In a bioaccumulation test in rainbow trout (O*ncorhynchus mykiss*), according to OECD 305, the BCF was 30-60. Isotridecyl alcohol has a low potential to bioaccumulate in fish tissue. The BMF was even lower at 0.01. In an acute toxicity test with freshwater fish (OECD203), the $^{96h}LC_{50}$ was 0.42 mg/L to rainbow trout (O*ncorhynchus mykiss*). In an algae test with *Pseudokirchneriella subcapitata* the chronic ^{72h}NOEC was 1.5 mg/L and $^{72h}EC_{50}$ = 2.6-3.2 mg/L.

The conclusions of assessments of the hazard for isotridecyl alcohol were:

- Fresh water organism PNEC = 0.03 mg/l with assessment factor 1
- Marine water organism PNEC = 0.0003 mg/l with assessment factor 100
- Intermittent releases PNEC = 0.0022 mg/l with assessment factor 100
- STP PNEC = 105.3 mg/L with assessment factor 1
- Fresh water sediment PNEC = 115.6 mg/kg sediment dw with assessment factor 1
- Marine water sediment PNEC = 1.156mg/kg sediment dw with assessment factor 100
- Terrestrial organisms PNEC = 93.7 mg/kg soil dw with assessment factor 1
- Predator secondary poisoning oral PNEC = 22.22 mg/kg food with assessment factor 90.

PHOBOTEX®SSR Soft Stain Release Agent is a dispersion of hydrophilic polyester (polymer) with a functional polysiloxane. No further details from the SDS/TDS are available about the chemical content. It was easily biodegradable in the OECD 302B test. The product has been tested for acute toxicity in luminescent bacteria. The result was a $^{½h}EC_{50}$ > 5 g/L. In an acute fish toxicity test (OECD 203) with rainbow trout (*Oncorhynchus mykiss*) the $^{48h}LC_{50}$ was 1000 mg/L. Therefore, the acute toxicity of the product was low.

PHOBOTEX®WS CONC. **Hydrophobic Agent** is a non-ionic polysiloxane based emulsion. The product is classified as dangerous according to Directive 1999/45/EC and its amendments. It is harmful to aquatic organisms, and may cause long-term adverse effects in the aquatic environment. Besides the siloxane, the product contains 3-7% of the quaternary ammonium compound and emulsifier Cocoalkylbis(2-hydroxyethyl) ethoxylated methylammonium chloride/ *N,N*-Diethoxylated-*N*-coco-*N*-methylammonium chloride (CAS no. 61791-10-4), which is pre-registered in ECHA (ECHA, 2014c). According to the SDS, this chemical is classified as harmful for the environment (N, R51/53). The product was easily biodegradable (50-100%) in the OECD 303A test. The product has a low acute toxicity to bacteria with a $^{3h}IC_{50}$ >300 mg/L, but a higher toxicity to rainbow trout (*Oncorhynchus mykiss*) with a $^{48h}LC_{50}$ = 45 mg/L.

The Swedish OrganoTex® products (**OC-aquasil Tex W™, OC-aquasil Tex N™**) from Organo-Click mimicking nature (Lotus flower) contains <10.5% an unknown organic silicon compound and <5% of an organic acid. No information about their environmental properties is available.

RHODORSIL®TCS 7001 from Bluestar Silicones is an alkyl polysiloxane dispersion in a solvent phase (cyclohexane?) specifically developed for spray impregnation waterproofing. No environmental information is available. Classification has been done according to Directive 67/548/EEC with risk phrases: Harmful to aquatic organisms; may cause long-term adverse effects in the aquatic environment (R52/53).

4.4.2 Risk of releases of dangerous substances from treated textiles

The polymeric alternatives based on siloxanes for textile impregnation may contain and potentially release environmentally hazardous, very persistent and very bioaccumulative substances (vPvB) and substances evaluated to be persistent, bioaccumulative and toxic substances (PBT).

4.4.3 Overall environmental assessment of siloxanes

Detailed environmental assessment data for the cyclic and short-chain linear siloxanes are included in Appendix 2.

In a Nordic study, the occurrence of siloxanes (HMDSO, MDM, MD2M, MD3M, D3, D4, D5, and D6) in the Nordic environment (air, biota, sediment, sludge, soil, and water) was screened (Nordic Council of Ministers, 2005). Some factors relevant for the environmental assessment are taken from the Nordic report and shown in Table 6.

Siloxanes were found in all sample types except soil, and cyclic siloxanes occurred in all media in significantly higher concentrations than the linear siloxanes.

D5 was the dominating siloxane in all matrices except in air, where D4 dominated. Diffuse sources seem to be most important for the observed concentrations of siloxanes, and concentrations were generally elevated in urban areas and in areas close to STPs. Siloxanes were identified in fish livers, mainly from sites representing urban/diffuse sources, while only a few background samples showed detectable levels.

TABLE 6
THE OCTANOL-WATER PARTITION COEFFICIENT, BIOACCUMULATION FACTOR, HALF-LIFE IN AIR AND SOME ENVIRONMENTAL LEVELS FOR SOME SILOXANES FOUND IN THE AREA AROUND THE DANISH (COPENHAGEN) SEWAGE TREATMENT PLANT (STP) "LYNETTEN".

Substance	Log K_{ow}	BCF	Half-life in air, reaction with OH• (days)	Half-life in sediment (days)[a]	Waste water influent (µg/L)	Primary sludge (ng/g dw)	Waste water effluent (µg/L)	Fish from recipient area (ng/g ww)
D4	5.1[a]	12400; 1700[a]	16	38/340	0.28	740	<0.02	13.5
D5	5.2	5300;2000[a]	10	38/340	26	27000	0.063	52.3
D6					1.6	1100	<0.02	8.73
MM	4.2	900/340[a]	12	15/140	<0.01	<3	<0.02	<0.5
MDM	4.8	990[a]		38/340	0.0034	64	<0.02	<0.5
MD2M					0.041	450	<0.02	<0.5
MD3M	6				0.073	550	<0.02	<0.5

a) from Lassen et al. (2005).

Detailed ecotoxicity data from open literature was only obtained for D4 (see Table 7).

TABLE 7
ECOTOXICITY PARAMETERS FOR D4 (MODIFIED FROM NORDIC COUNCIL OF MINISTERS, 2005)

Organism	Endpoint	Adverse effect	Duration	Concentration (µg/L)
Opossum Shrimp (*Americamysis bahia*)	NOEC	Immobilisation	14 days	9.1
Midge (*Chironomus tentans*)	NOEC	Growth	14 days	> 15
Midge (*Chironomus tentans*)	NOEC	Mortality	14 days	>15
Sheepshead minnow (*Cyprinodon variegatus*)	NOEC	Mortality	14 days	6.3
Water flea (*Daphnia magna*)	NOEC	Immobilisation	48 hours	> 15
Water flea (*Daphnia magna*)	NOEC	Reproduction	21 days	1.7-15
Rainbow trout (*Oncorhynchus mykiss*)	LC_{50}	Mortality	14 days	8.5-13
Rainbow trout (*Oncorhynchus mykiss*)	LOEC	Mortality	14 days	6.9
Rainbow trout (*Oncorhynchus mykiss*)	NOEC	Mortality	14 days	≤ 4.4
Rainbow trout (*Oncorhynchus mykiss*)	NOEC	Multiple effects	93 days	4.4

Polydimethylsiloxanes (PDMS)
PDMS is an end-product, but it is pre-registered in REACH (ECHA, 2014c). It is notified in the C&L Inventory either as "not classified" or classified, among others, as Aquatic Chronic 2 and 4 (H411, H413) (ECHA, 2014d).

According to the producer Dow Corning, PDMS fluids pose no known hazard to the environment (Dow Corning, 1997). In the aquatic environment PDMS attaches to particulate matter and is removed from the water column by sedimentation. It is persistent and has no detectable Biological Oxygen Demand (BOD). In the soil PDMS may degrade abiotically in a few days to $(CH_3)_2Si(OH)_2$, a persistent metabolite. These organosilanols and low molecular weight linear PDMS and cyclic siloxanes may evaporate into the atmosphere. In the upper atmosphere they are oxidized by hydroxyl radicals to silica, water, and CO2 (Gravier et al. 2003).

4.5 Summary

Availability and technical properties - Many products are available and agents of this type have been on the market for many years. Various agents are available for different types of textiles. The agents provide durable water repellency but not oil repellency. For those products where the price indication is available, some are indicated as more expensive and other as less expensive than the PFAS-based agents.

Health assessment -. The most used silicones in textiles are polydimethylsiloxanes (PDMS). These siloxanes are registered in REACH, and they are relatively inert and generally have no adverse effects. They are volatile and most exposures will occur by inhalation. Various other siloxanes, especially the cyclic siloxanes known as D4, D5 and D6 and the linear siloxanes HMDSO, MDM, MD2M and MD3M, may be used as intermediates for synthesis of silicone polymers used for textile impregnation. Specifically, D4 is suspected of damaging fertility, and D5 is a potential carcinogen.

The commercial product emulsions often contain other substances such as isotridecylalcohol, which is registered in REACH and is more harmful than the siloxanes. Some of the commercial products contain substances that are powerful irritants.

Environmental assessment - Siloxanes are relatively persistent and are widespread in the environment but are found mostly in urban areas and in the aquatic environment, including fish livers, close to STPs. They are removed from the aqueous phase by sedimentation, and have a long half-life there. In soils, depending on the conditions, siloxanes are transformed into hydroxylated forms, which may still be persistent.

PDMS has not been evaluated for lack of data. The bioconcentration factors and bioaccumulation factors for D4 are high, indicating D4 may have a high potential to accumulate in aquatic organisms, and according to an ECHA expert group, D4 met the criteria for a PBT and vPvB substance. D5 also met the criteria for a vPvB substance in the environment due to its persistence in sediment and a high bioconcentration factor in fish. D6, MM, MDM, MD2M, and MD3M were not considered a PBT or vPvB substance by the notifiers but the substance has not yet been evaluated by ECHA.

The commercial products contained substances other than siloxanes; some known, some unknown. Isotridecyl alcohol is less persistent but more toxic to aquatic organisms. A quaternary ammonium compound used was classified as harmful for the environment.

Main data gaps - There are sufficient health data to evaluate the cyclic and linear siloxanes. However, data are lacking concerning the actual silicon polymers used on the textiles.

Data indicating to what extent the siloxanes may be released during production of the textiles, use of the textiles and waste disposal have not been identified.

The environmental data on polydimethylsiloxanes are insufficient and environmental data on other possible silicone polymers used in textile products are lacking.

5. Dendrimer-based repellent chemistries

5.1 Chemistry

Dendrimer-based repellent chemistry is a relatively new field of repellent chemistry. The term merely gives indications about the physical structure, not about the chemical composition of the repellent. Dendrimers are repetitively branched molecules leading to monodisperse, tree-like structures. A hypothetical example is given in Figure 4 and further illustrated by the description of specific products below. The synthesis of monodisperse polymers demands a high level of synthetic control, which can only be achieved through step-by-step reaction, in which the dendrimer is built up by one monomer layer at a time. The primary components of each dendrimer are the core, internal cavities, branching units and closely packed surface groups (ZDHC, 2012).

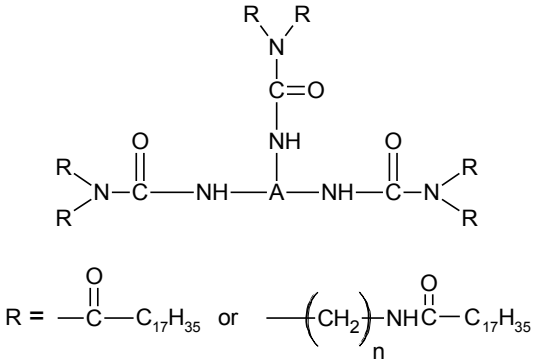


FIGURE 4
HYPOTHETICAL STRUCTURE OF A DENDRIMER SYNTHESIED FROM DISTERARYL-AMINES OR –AMIDES AND A TRIFUNCTIONAL ISOCYANATE (FROM SCHINDLER AND HAUSER, 2004).

Depending on the chemical composition, dendrimers can provide water and/or oil repellency. The company Rudolph Group, for example, offers different textile finish products based on dendrimer technology. The oil- and soil-repellent dendrimer finishes include a fluorocarbon resin in their structure, while the fluorocarbon-free dendrimers only provide water repellency. Compared to other PFAS-based repellents, the fluorine content of the oleophobic dendrimer finishes is reduced. The fluorocarbon-free dendrimers provide water repellency through closely packed surface groups, i.e. methyl groups.

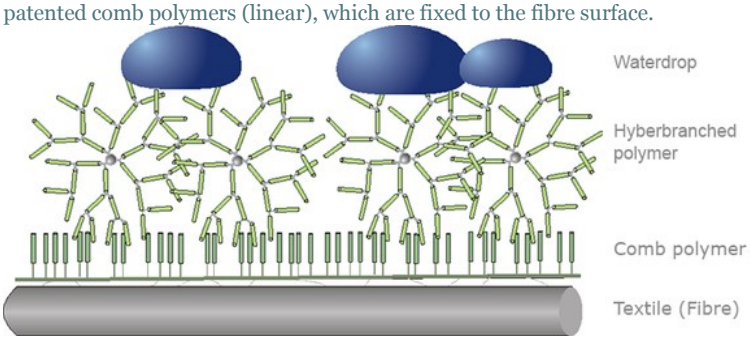
Commonly, these finishes are applied as two-component systems consisting of an emulsion containing the dendrimers and a solution containing a crosslinking substance providing the fixation to the fibre. Fluorocarbon-free dendrimers are based on hydrocarbon or polyurethane chemistry. Crosslinking is commonly achieved by chemical binding of the dendrimers with isocyanates to the fibre (Personal communication with the industry). Glycols are added as solvents and cationic surfactants in small amounts act as emulsifiers (UNEP, 2012 [Technical Paper]).

A number of products using this advanced technology are on the market. Regarding the innovation and research efforts, companies are investing in these products; it is typical that they do not disclose any chemical details on their products.

5.2 Examples of marketed products

The dendrimer-based repellents is a relatively new group of repellents on the market. According to a new Danish assessment of repellent finishing for children's clothes, many of the manufacturers have changed from PFAS-technology to non-fluorinated dendrimer-technology in recent years (Lassen et al., 2015).

Identified products from two manufacturers are listed below. The products Baygard WRC and Baygard WRS described as "3D" technology appear to apply a similar approach.

<table>
<tr><th colspan="2">Rudolf Group</th></tr>
<tr><td>Product name</td><td>®RUCO-DRY ECO (Brand BIONIC-FINISH® ECO)</td></tr>
<tr><td>Chemical properties</td><td>Polyurethane-dendrimer (hyperbranched polymers) with hydrophobic end groups connected to patented comb polymers (linear), which are fixed to the fibre surface.
 

Emulsion contains isocyanates as cross-linking agents, C_8-C_{18}-alkyl groups-containing organopolysiloxane, and emulsifiers.</td></tr>
<tr><td>Functional properties</td><td>• Water-repellent, no oil-repellency
• Better abrasion resistance than PFAS-based finishes
• Not resistant to dry cleaning (in contrast to PFAS-based agents)
• Soft handling (softer than fluorocarbon chemistry)
• High gliding properties of the finished textile
• Improves the sewability
• Suitable for all fibre types</td></tr>
<tr><td>Application areas</td><td>Clothing and non-clothing textiles made of cotton, polyester or blends.</td></tr>
<tr><td>Application process</td><td>No high curing temperatures necessary (recommended 150 °C for 2 min, 160 °C for 1 min or 170 °C for 30 s).</td></tr>
<tr><td>Wash resistance</td><td>High and comparable to C_6-fluorocarbon chemistry, but slightly worse than C_8-fluorocarbon chemistry.
Heat treatment above 65° C (tumbler "extra dry" or ironing) after each wash cycle to fully restore the effect level of the finish is recommended.
<table>
<tr><th></th><th></th><th>CO</th><th>PES</th><th>PA</th></tr>
<tr><td rowspan="3">Original</td><td>spray test AATCC 22</td><td>100</td><td>100</td><td>100</td></tr>
<tr><td>water repellency DIN 53888, Bundesmann rating</td><td>5</td><td>5</td><td>5</td></tr>
<tr><td>water absorption %</td><td>18.4</td><td>2.1</td><td>4.5</td></tr>
<tr><td>After 10 x home laundering at 40 °C, final ironing</td><td>spray test AATCC 22</td><td>100</td><td>100</td><td>100</td></tr>
<tr><td>After 20 x home laundering at 40 °C, final ironing</td><td>spray test AATCC 22</td><td>90</td><td>100</td><td>90</td></tr>
<tr><td>After 3 x home laundering at 40 °C, line drying (tumbling recommended)</td><td>spray test AATCC 22</td><td>90</td><td>90</td><td>90</td></tr>
</table></td></tr>
<tr><td>Price</td><td>"Competitive with fluorocarbon chemistry"</td></tr>
<tr><td>Information on release/emissions of the substance during use and/or wash</td><td>No data</td></tr>
<tr><td>Classification</td><td>The product is not required to be labelled according to Directive 1999/45/EC.</td></tr>
</table>

	Functionalized polymer (5-15%):Skin Irrit. 2, H315; Eye Irrit. 2, H319 Cationic surfactants (0.5-1%): Skin Corr. 1B, H314; Aquatic Acute 1, H400; Aquatic Chronic 2, H411; Acute Tox. 4, H302
Human health properties	Oral toxicity LD_{50} (rat) > 5000 mg/kg
Environmental fate properties	Easily eliminated from the effluent (> 80% by OECD 302 B) Environmentally friendly – no durable decomposition products Bioaccumulation: no data Soil mobility: no data COD: 590 mg/g BI5: 110 mg/g
Environmental effects properties	Water toxicity: EC_{50} (bacteria) > 100 mg/l, LC_{50} (fish) > 100 mg/l) Further ecotoxicity tests are not available. Results of PBT and vPvB assessment: Not relevant.

OrganoClick - OC-aquasil Tex W™, OC-aquasil Tex N™ (brand name OrganoTex®)	
Product name	OC-aquasil Tex W™, OC-aquasil Tex N™ (brand name OrganoTex®)
Chemical properties	The water repellent effect is based on hydrocarbon chains. The product contains an organic silicon compound (<10.5%) and organic acid (<5%). Composition of plant-based catalysts and organic polymers. The organic polymers have two different ends; one pointing outwards that is highly water repellent and one that is reactive that binds to the textile fibres. When the reactive end is unbound (before application to the textile) it is biodegradable. In the presence of the catalysts, the reactive end binds to the textile fibres and it is then rendered non-degradable and becomes highly durable instead.
Functional properties	• Water repelling • Increased softness (compared to some fluorocarbons) • Lower drying temperature (compared to some fluorocarbons) • Durable protection against water, snow and water-based soiling such as stains from red wine, coffee, ketchup, etc.
Application areas	Woven and knitted textiles (W), nonwoven (felt-like) material containing either cellulose-based or synthetic fibres (N)
Application process	Pad-dry-cure process. Coating, spraying or padding with subsequent drying.
Wash resistance	BEFORE HOME LAUNDRY / AFTER 20 HOME LAUNDRY CYCLES (ISO 6330) Spray test (ISO 4920): 5 of 5 / 4 of 5 Spray test (AATCC 22): 100 of 100 / 90 of 100
Price	More expensive (compared to some fluorocarbons)
Information on release/emissions of the substance during use and/or wash	No data.
Classification	This product is not classified as flammable, irritating or dangerous for the environment according to 1999/45/EC. Organic silicon compound: Skin irrit. 2 (H315) Organic acid: Skin irrit. 2, Eye irrit. 2, STOT SE 3 (H315, H319, H335)

OrganoClick - OC-aquasil Tex W™, OC-aquasil Tex N™ (brand name OrganoTex®)	
Human health properties	Information about the product is not available. Organic acid (in concentrated form) LD_{50} (mouse): > 1500 mg/kg Organic silicon compound (in concentrated form) LD_{50} (rat): > 5000 mg/kg Not classified as allergenic by inhalation or skin contact. The product does not contain any substances that are classified as carcinogenic, mutagenic or toxic for reproduction.
Environmental fate properties	The product is readily biodegradable according to OECD 301A/SS-EN ISO 7827:1996. Bioaccumulation-information about the product is not available. Organic acid (in conc. form): Log Kow: -1.26 Organic silicon compound (in conc. form): Is not regarded as being accumulative because it hydrolyses rapidly and will permanently bind to minerals, rendering it biologically unavailable. The product is soluble in water (soil mobility). The product is not considered to contain any substances that meet the criteria for classification as PBT or vPvB substances.
Environmental effects properties	Information about this preparation is not available. Organic silicon compound (in conc. form): LC_{50} (fish) > 1000 mg/L according to OECD 203, 96h LC_{50} (*Daphnia*) > 1000 mg/L according to OECD 202, 48h E_bC_{50}* (algae) > 30 mg/L according to OECD 201, 96h

* E_bC_{50} – effect concentration at which 50% reduction of biomass is observed

5.3 Health assessment

5.3.1 Health assessment on specific impregnation agents

RUCO-DRY ECO®: This dendrimer product is an emulsion containing isocyanates as cross-linking agents, C_8-C_{18}-alkyl groups containing organopolysiloxane, and emulsifiers. According to the SDS, the product is not required to be labelled according to Directive 1999/45/EC. The product's oral rat LD_{50} > 5 g/kg bw. It may irritate airways when used in spray cans. The product contains 5-15% of an unknown functionalized polymer, which is skin- and eye irritating group 2 (H315 + H319), and 0.5-1% of an unknown cationic surfactant, which is harmful by intake (acute toxic group 4, H302) and corrosive to skin (H314). The content of a siloxane makes this product a hybrid between the substances discussed in sections 3.3 and 3.2, where siloxanes are discussed.

BIONIC-FINISH® ECO is a hyperbranched/linear and cationic polymer, highly effective water-repellent agent for finishing fabrics of all fibre types, when combined with crosslinking boosters, such as RUCO-LINK RCX, RUCO-LINK DAL, RUCO-LINK BEW or RUCO-LINK EIT.
In the material from the producer there was no information on properties relevant for health.

OC-aquasil™ Tex W, according to the producer, is not classified as dangerous for the environment according to Directive 1999/45/EC. Information about the exact composition of the product is not available; however, it contains <10.5% of an unknown organic silicon compound, which is skin-irritating and has a low acute toxicity in rats (LD_{50} >5 g/kg bw). Hazard statement: H315: Causes skin irritation. The content of a siloxane makes this product a hybrid between the substances discussed in sections 3.3 and 3.2, where siloxanes are discussed. In addition, the product contains <5% of an unknown classified organic acid which irritates both skin and eyes and has a specific target organ toxicity after a single exposure (STOT SE 3). Its oral LD_{50} in mice is >1500 mg/kg bw. Hazard statements H315, H319: Causes serious eye irritation, and H335: May cause respiratory irritation.

The most important symptoms mentioned in the SDS were:

Inhalation:	May cause drowsiness, nausea, dizziness and light-headedness
Skin contact:	May cause skin irritation such as redness and pain
Eye contact:	May be irritating to the eyes causing pain, redness and tearing
Ingestion:	May cause nausea, pain, dizziness and breathing disorders.

This product and its ingredients seem to be more hazardous than the producer indicates, and without information about the exact chemicals and concentrations, it is impossible to clear this product as regards concern for health.

5.3.2 Risk of dangerous substances in the treated textile

No information but there may be residues of isocyanates and siloxanes.

5.3.3 Risk of formation of dangerous substances by degradation of cured repellents

No information but isocyanates and siloxanes may be formed and released by evaporation.

5.4 Environmental assessment

5.4.1 Environmental data on specific impregnation agents

RUCO-DRY®ECO from Rudolf Group is a dendrimer product formulated as an emulsion containing isocyanates as cross-linking agents, C_8-C_{18}-alkyl groups-containing organopolysiloxane, and emulsifiers. The product contains 5-15% of an unknown functionalized polymer, and 0.5-1% of an unknown cationic surfactant. The content of a siloxane makes this product a hybrid between the substances discussed sections 3.3 and 3.2. According to the SDS, the product is not required to be labelled according to Directive 1999/45/EC. The product was easily biodegradable (>80%) in the OECD 302B test. The product has not been tested for ecotoxicity but, by read across, the acute ecotoxicity for fish was estimated to LC_{50} >59 mg/L, and the EC_{50} for sewage sludge bacteria was >100 mg/L. The risk phrases H400: "Very toxic for aquatic organisms", and H411: "Toxic for aquatic organism; with long-term effects" is indicated in the MSDS.

BIONIC-FINISH®ECO from Rudolf Group is a hyperbranched/linear and cationic polymer, highly effective water-repellent agent, when combined with crosslinking boosters such as RUCO-LINK RCX, RUCO-LINK DAL, RUCO-LINK BEW or RUCO-LINK EIT. In the material from the producer there was no information on product composition or environmental properties.

OC-aquasil™ Tex W, according to the SDS from OrganoClick, is not classified as dangerous for the environment according to Directive 1999/45/EC. Information about the exact composition of the product is not available; however, it contains <10.5% of an unknown organic silicon compound, that makes this product a hybrid between the substances discussed sections 3.3 and 3.2. In addition, the product contains <5% of an unknown organic acid. The product is soluble in water and readily biodegradable according to OECD 301A. Neither the organic acid ($LogK_{ow}$ = -1.26) nor the silicon compound were assessed to be bioaccumulative. The silicon compound has been tested for ecotoxicity with the following results: $^{96h}LC_{50}$ (fish) > 1000 mg/L according to OECD 203, $^{48h}LC_{50}$ (*Daphnia*) > 1000 mg/L according to OECD 202, and $^{96h}EC_{50}$ (algae) > 30 mg/L according to OECD 201.

5.4.2 Risk of dangerous substances in the treated textile

No information but there may be residues of isocyanates and siloxanes.

5.4.3 Risk of formation of dangerous substances by degradation of cured repellents

No information but isocyanates and siloxanes may be formed and released by evaporation.

5.5 Summary

Availability and technical properties - The agents of this type are relatively new. Few types have been identified. Application areas cover various clothing and non-clothing textiles. The agents are currently widely used for children's clothing on the Danish market. The agents provide durable water repellency but not oil repellency. The prices range from comparable to the PFAS-based agents to more expensive.

Health assessment - There are no data available on health properties of these unknown active substances and other components, but the producers of commercial products have included a few health data in the MSDS's and made some proposals for classification of the product. According to the producer's information, these products should not be labelled or classified as harmful. The product compositions were not specified sufficiently, but some of the products contain unknown siloxanes likely discussed above, cationic polymers, isocyanates or powerful irritating organic acids. In general, relevant information for health assessment for this group of chemicals is insufficient. Therefore, it is not possible to assess the possible health effects of the agents.

Environmental assessment - The product compositions of these repellents were not specified sufficiently but some of the products contain unknown siloxanes, cationic polymers, isocyanates or powerful irritating organic acids. According to the producer's information, these products should not be labelled or classified as harmful for the environment, but it is not possible on the basis of the available information to evaluate these statements.

Main data gaps - In general, the relevant information for health and environmental assessment of this group of products with unknown ingredients is insufficient.

6. Polyurethane repellent chemistries

6.1 Chemistry

The polyurethane-based repellents represent a relatively new group of repellents. They are briefly mentioned in the report from ZDHC (2012), but not described in detail. They are not described by Schindler and Hauser (2004). Aside from the polyurethane polymer matrix, the repellent effect is caused by the covalent implementation of hydrophobic copolymers based on silicones and/or paraffins, and the product may alternatively have been grouped with the paraffin-based or silicone-based repellents.

The chemistry is described for one product in the next section with examples of marketed products. The manufactured fabric is breathable and the impregnation agent is therefore different from waterproof fabric coated with polyurethane used e.g. for raincoats.

6.2 Examples of marketed products

The polyurethane-based repellents represent a relatively new group of repellents on the market. One product has been identified and is listed below.

Freudenberg Group	
Product name	Purtex® WR water repellent
Chemical properties	Water-based, aliphatic polyurethane emulsion, two-component system Component A: Emulsion with polyurethane content of 70% Component B: Crosslinker containing blocked isocyanates The durable water repellent effect is caused by the covalent implementation of hydrophobic copolymers based on silicones and/or paraffins which also exert a positive influence on the softness of the finished textile.
Functional properties	• Durable water repellent, no oil-repellency • Good abrasion resistance (abrasion resistance of the fibre improved) • Heat treatment after wash to fully restore the effect level of the finish not necessary (Laundry air dry, LAD). • Soft handling (cotton becomes softer, polyester becomes more stiff) • Good ageing properties (light fastness) • Categorised as “extremely breathable” by external test institute
Application areas	Clothing and non-clothing textiles, suitable for most textiles
Application process	Usual wet finishing machine. Curing temperature 120-150°C. Component A can be diluted with water.
Wash resistance	Basically unchanged water repellency after 20 cycles of domestic laundering according to Bundesmann rain-shower test.

Price	Possibly comparable to PFAS-based products (depending on quality of the PFAS-based product, functional requirements and application)
Information on release/emissions of the substance during use and/or wash	Good hydrolysis resistance VOC and solvent free No isocyanate or VOC emissions as tested by headspace and extraction GC/MS
Classification	Product not classified according to EC regulation 1272/2008 (CLP).
Human health properties	Prepolymer: Oral toxicity LD_{50} (rat) > 5000 mg/kg (OECD 423) Mutagenicity: negative (Escherichia coli – OECD 471), negative (Salmonella typhimurium – OECD 471)
Environmental fate properties	No data on PBT or vPvB properties of the product. Prepolymer: Persistence in the environment possible. BCF < 500 (EpiWin calculated) Log Kow > 3 (EpiWin calculated) Log Koc > 3 (EpiWin calculated) No further data on PBT or vPvB properties.
Environmental effects properties	Prepolymer: NOEC (*Daphnia magna*) 100 mg/L (OECD 202) LOEC (*Daphnia magna*) >100 mg/L (OECD 202) EC_{50} (*Daphnia magna*) >100 mg/L (OECD 202) EC_{100} (*Daphnia magna*) >100 mg/L (OECD 202)

6.3 Health assessment

6.3.1 Health data on specific impregnation agents

There is no available health data on the ingredients in **Purtex® WR 6110**, a two-component water-based, aliphatic polyurethane emulsion system with a crosslinker containing blocked isocyanates.

The product and both components are considered not hazardous as per the EU Dangerous Substances Directives by the producer. Nevertheless, several health hazard precaution phrases are mentioned in the MSDS:

- P280: Wear protective gloves/protective clothing/eye protection/face protection.
- P311: Call a POISON CENTER or doctor/physician.
- P333/313: If skin irritation or rash occurs: Get medical advice/attention.

Furthermore, it is mentioned that inhalation of gases, vapours and aerosols and exposure to skin and eyes should be avoided. In addition, it is mentioned that heating may release harmful vapours. The toxicity tests applied on a prepolymer (unclear if it is component A or B) was an oral rat LD_{50} of > 5 g/kg bw; therefore, this component had no acute toxicity, and two tests for mutagenicity in bacteria were also negative but no details were given. Without the name and CAS no. of the isocyanates, the claims of the producer are impossible to verify.

However, organic isocyanates are generally highly irritating, allergic and toxic. For instance, methyl isocyanate is known as the Bhopal toxin. PUR may also contain residues/impurities of unreacted highly toxic isocyanates or aromatic amines.

6.3.2 Risk of dangerous substances in the treated textile

Residues of unreacted toxic isocyanates may be found.

6.3.3 Risk of formation of dangerous substances by degradation of cured repellents

It is stated that no evaporation of VOC and isocyanates takes place.

6.4 Environmental assessment

6.4.1 Environmental data on specific impregnation agents

Purtex®WR 6110 from Freudenberg is a two-component water-based, aliphatic polyurethane emulsion system with a crosslinker containing blocked isocyanates. No information about the substance composition is provided. The product and both the components are considered not environmentally hazardous as per the EU Dangerous Substances Directives (67-Directive and CLP) by the MSDS. The prepolymer has been tested according to OECD 202, and both the NOEC and LOEL in *Daphnia magna* was 100 mg/L. The BCF and log K_{ow} for the prepolymer has been calculated to be <500 and >3, respectively. There is no available environmental data on the other ingredient.

6.4.2 Risk of releases of dangerous substances from treated textiles

It is stated in the SDS that no evaporation of VOC and isocyanates take place.

6.5 Summary

Availability and technical properties - The agents of this type are relatively new. Only one type has been identified. This type of agent is suitable for most textiles. The agent provides durable water repellency but not oil repellency. Price information for one product indicated that the price is likely comparable to PFAS-based products.

Health assessment - Only one commercial product is identified. Its composition is not detailed, either qualitatively or quantitatively. According to the producer's information, the product should not be labelled or classified as harmful to health. Nevertheless, several health hazard precaution phrases are mentioned in the MSDS. Generally, the content of organic isocyanates makes the product potentially hazardous to skin and mucous membranes. Therefore, it is not possible to assess the possible health effects of the agents in detail.

Environmental assessment - The composition of the product is not detailed, either qualitatively or quantitatively. According to the producer's information, the product should not be labelled or classified as harmful to the environment. However, due to lack of relevant data, it is not possible to verify these claims.

Main data gaps - This product group shows a lack of public health and environmental data and insufficient information about product composition as well as the substances formed at the impregnation process.

7. Other

Various water repellents based on other chemistries are on the market. Table 1 lists a few repellent product details. Information was not available on how stain repellency was achieved; this information has also not been available from the manufacturer's websites. This information concerns Arristan HPC from CHT/Bezema, H2O Repel from Devan (the product may have been discontinued) and Careguard FF from Sarex. Information on a few other identified agents/types is provided below.

7.1 NEOSEED

7.1.1 Marketed products

NEOSEED from Nicca Chemical Co. is a water repellent based on a non-ionic unknown polymer and unknown ingredients (see Table below).

NICCA CHEMICAL CO.,LTD.	
Product name	NEOSEED NR-90
Chemical properties	Non-ionic Polymer, Ester Compound, Hydrocarbon compound, Organic Solvent and Water
Functional properties	• Water repellency • No oil repellency • Hand is a little stiffer than PFAS-based products
Application areas	Clothing and non-clothing textiles (polyester, nylon, cotton, all kind of fabric) carpet ・ table cloth ・ wallpaper ・ umbrella ・ suit, coat ・ surgical gown ・ uniform ・ automotive engine filter ・ outdoor garments ・ cardboard
Application process	Standard application: 2 to 6 % solution by pad application.
Wash resistance	No data
Price	About the same range as current PFAS-based water repellent (C_6)
Information on release/emissions of the substance during use and/or wash	No data
Classification	No data
Human health proper-	No data

ties	
Environmental fate properties	BOD_5 41 ppm (0.1%) COD (Mn) 115 ppm (0.1%)
Environmental effects properties	LC_{50} (Red killifish, 96 h) 250 ppm

7.1.2 Health assessment

Health data on specific impregnation agents

NEOSEED NR-90 is a white liquid offering water repellence. Its composition is only general and qualitatively known as a non-ionic polymer, with ester and hydrocarbon compounds. The active repellent ingredient is not identified. It is claimed that: "No reportable quantities of hazardous ingredients are present." No documentation for the claim is found, and no test results are given for toxicity, irritation, mutagenicity etc.

However, it is mentioned under Hazard Identification that the product:

- "May be irritating to eyes"
- "Prolonged or repeated contact may cause skin irritation"
- "May be harmful if swallowed".

In addition, some first-aid measures (precaution phrases) are mentioned, indicating that the product is not without health hazards. It is not possible to verify the producers' claim of a non-hazardous product.

Harmonised classification

None.

Risk of dangerous substances in the treated textile

No information is available.

7.1.3 Environmental assessment

Environmental data on specific impregnation agents

NEOSEED NR-90 from NICCA is a white water-soluble liquid offering water repellence. Its composition is only generally and qualitatively known as a non-ionic polymer, with ester and hydrocarbon compounds. The active repellent ingredient is not identified either. It is claimed that: "No reportable quantities of hazardous ingredients are present." The $^{96h}LC_{50}$ in red killifish (*Aphyosemion bivitattum*) was 250 ppm.

Harmonised classification

None.

Risk of dangerous substances in the treated textile

No information is available.

7.1.4 Summary

Availability and technical properties - The agents of this type are relatively new. Few types have been identified. Application areas cover various clothing and non-clothing textiles. The agents provide durable water repellency but not oil repellency. Price information for one product indicated that the price is comparable to PFAS-based products.

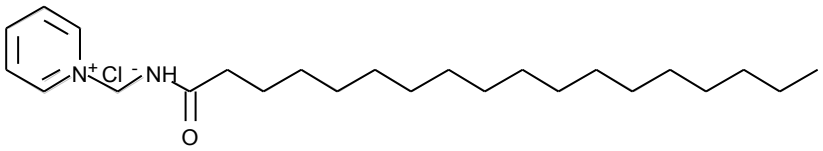
Health assessment - For one commercial product, described as a non-ionic polymer with ester and hydrocarbon compounds, it was claimed that: "No reportable quantities of hazardous ingredi-

ents are present." However, no documentation for that claim as regards health effects was given, and some risk phrases were mentioned, indicating skin- and eye-irritating properties and harmfulness if swallowed. Therefore, it was not possible to verify the producers' claim of a non-hazardous product.

Main data gaps - Documentation for the non-hazardous claim is lacking.
Environmental assessment - For one commercial product, described as a non-ionic polymer with ester and hydrocarbon compounds, it was claimed that: "No reportable quantities of hazardous ingredients are present."

7.2 Stearamidomethyl pyridinium chloride

A classic cationic textile surfactant is 1-(stearamidomethyl) pyridinium chloride, which was previously marketed by ICI as Velan PF:



This substance can react with cellulose at elevated temperatures to form a durable water-repellent finish on cotton. It was later found that the reaction was restricted to the surface of the fibres and that the high cure temperature weakened the fabric. Sodium acetate had to be added to prevent the decomposition of the cellulose by the hydrogen chloride formed. Also, the pyridine liberated during the reaction had an unpleasant odour, and the fabric had to be scoured after the cure. The toxicological properties of pyridine ended its use in the 1970s, when government regulation of such substances increased; however, it appears that it still is used in mixture with siloxanes (see above).

The health and environmental data are insufficient for an assessment.

7.3 Nanomaterial-based repellent chemistries

Repellent chemistries containing nano-materials are coated on fabrics to achieve desirable properties without a significant increase in weight, thickness or stiffness. As is the case with the dendrimer technology, the term "nanomaterials" does not disclose any information on chemical composition. According to a research report on water repellent (ZDHC, 2012), the use of nanomaterials to impart water repellency and stain resistance effects on textile is one of the most common ways nanotechnology is being used in the textile industry. These attributes are achieved by embedding fabrics with tiny fibres, called nano-whiskers, which form a cushion of air around fibre to repel water and stains. The treatment is believed to be durable to repeated home laundering cycles.

During the market research for this survey, no nanomaterial-based repellent products refraining from the use of fluorine technology were identified. A few companies (Schoeller, BASF, Nanotex) market products containing nanoparticles which are surface-treated with fluorine chemistries. In fact, the products actually form fluooroalkyl polymers at the surface. Further details on these chemistries have consequently not been obtained.

8. Conclusion

The obtained information on the alternatives is summarised in the following table.

It can be concluded that no alternatives matching the PFAS-based repellents on all technical parameters are available. The alternatives provide durable water repellency, but no repellency against oil, oil-based dirt and alcohol.

Regarding health and the environment, for most of the alternative impregnation agents reviewed, there is insufficient qualitative and quantitative public information about the ingredients. Only a few specific ingredients are stated and for these, limited data on health and environmental properties are available. The summary in the table is thus based on the limited information available.

According to the producer's information, most of the products should not be labelled or classified as harmful to the environment, but on the basis of the available information, for many products it is not possible to verify these statements. Apart from the siloxanes, where it is unclear which cyclic or small linear siloxanes are present in the products, the agents do not appear to contain significant amounts of persistent substances.

Furthermore, very little information on trace levels of raw materials, intermediates and substances formed by decomposition in the final products is available.

TABLE 8
SUMMARY OF TECHNICAL MAIN TECHNICAL PROPERTIES REGARDING REPELLENCY, AVAILABILITY PRICE, HEALTH PROPERTIES AND ENVIRONMENTAL PROPERTIES.

Type	Technical properties	Availability; price *	Health properties of impregnation agents *	Environmental properties of impregnation agents **
Paraffin-based repellents	Durable water repellent - no oil and alcohol repellency	Many products on the market. The agents are cheaper compared to the PFAS-based, but requires a higher dosage	The main ingredient in most products is paraffin oil/wax, i.e. mixtures of long chain alkanes (linear aliphatic hydrocarbons), which is harmless in its pure form. The compositions of the products are mainly confidential, but some products also contain isocyanates, dipropylene glycol, metal salts or other unspecified substances, which may be harmful.	Most components are readily biodegradable, are not bioconcentrated or accumulated in organisms and food chains, and aquatic toxicity is insignificant

Type	Technical properties	Availability; price *	Health properties of impregnation agents *	Environmental properties of impregnation agents **
Silicone-based repellents	Durable water repellent - no oil and alcohol repellency	Many products on the market. Price approximately the same as PFAs-based	The silicones most used in textile impregnation agents are based on polydimethylsiloxanes (PDMS). These siloxanes are registered in REACH, they are inert and generally have no adverse effects. Unclear to what extent cyclic and small linear siloxanes may be present at trace levels in the agents. Specifically D4 is suspected of damaging fertility, and D5 is a potential carcinogen.	Not enough data for a detailed evaluation. Unclear which siloxanes may be present at trace levels in the agents. Some cyclic siloxanes are PBTs. Low-molecular-weight poly(dimethylsiloxanes) and polydimethylsiloxanes (PDMS) have low toxicity and are not considered PBT or vPvB substances.
Dendrimer-based repellents	Durable water repellent - no oil and alcohol repellency	Few products identified. Price range from approximately the same as PFAS-based to slightly more	According to the producer's information, these products should not be labelled or classified as harmful. The product compositions were not specified sufficiently for an assessment, but some of the products contain unknown siloxanes (likely among those discussed above), cationic polymers, isocyanates or powerful irritating organic acids.	Not enough data for a detailed evaluation. According to the producer's information, these products should not be labelled or classified as harmful for the environment.
Polyurethane-based repellents	Durable water repellent - no oil and alcohol repellency	One product identified. Price approximately the same as PFAS-based to slightly more	According to the producer's information, the product should not be labelled or classified as harmful to health. Nevertheless, several health hazard precaution phrases are mentioned in the MSDS.	Not enough data for a detailed evaluation. According to the producer's information, these products should not be labelled or classified as harmful for the environment.
Other repellents	Durable water repellent - no oil and alcohol repellency	Few products identified. Price approximately the same as PFAS-based	It is indicated by the manufacturer that the product include "no reportable quantities of hazardous ingredients". However, no documentation for this was provided, and some risk phrases were mentioned for the product indicating skin- and eye irritating properties and harmfulness if swallowed.	Not enough data for a detailed evaluation. For one commercial product it is indicated by the manufacturer that the product include "no reportable quantities of hazardous ingredients

* Price comparison is approximate as the price of PFAS-based repellents and the alternatives vary between specific repellents and also by specific applications.

** Concerns the substances in the agents and not trace levels of raw materials or degradation products.

Abbreviations and acronyms

3D	Three-dimensional
AATCC	American Association of Textile Chemists and Colorists
BCF	Bioconcentration Factor
BMF	Biomagnification Factor
BOD/BI5	Biochemical Oxygen Demand
BSI	Bundesverband der Deutschen Sportartikel-Industrie e.V.
Bw	body weight
CEFIC	European Chemical Industry Council
CHO	Chinese Hamster Ovary
CIR	Cosmetic Ingredient Review
CLP	Classification, Labelling and Packaging (Regulation(EC) No 1272/2008)
CNS	Central Nervous System
COD	Chemical Oxygen Demand
C&L	Classification and Labelling (Inventory under REACH)
D3	Cyclotrisiloxane
D4	Cyclotetrasiloxane
D5	Cyclopentasiloxane
D6	Cyclohexasiloxane
D7	Cycloheptasiloxane
DIN	Deutsches Institut für Normung (German Institute for Standardisation)
DNA	Deoxyribonucleic acid
DNEL	Derived No Effect Level
DOC	Dissolved Organic Carbon
Dw	dry weight
DWR	Durable Water Repellent
E_bC_{50}	Effect concentration at which 50% reduction of biomass is observed
EC	European Commission
EC_n	Effect concentration where n % of the species tested show the effect
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ECHA	European Chemicals Agency
EOG	European Outdoor Group
EPA	Environmental Protection Agency
EU	European Union
GC/MS	Gas Chromatography/Mass Spectrometry
GLP	Good Laboratory Practice
HMDSO	Hexamethyldisiloxane (elsewhere also abbreviated MM or HMDS)
IC	Inhibition Concentration
ICR	Imprinting Control Region
INCI	International Nomenclature of Cosmetic Ingredients
ISO	International Organization for Standardization
Koc	Organic carbon/water partitioning coefficient
Kow	Octanol/water partitioning coefficient
LAD	Laundry Air Dry
LC	Lethal Effect Concentration
LD	Lethal Effect Dose

LOAEL	Lowest Observable Adverse Effect Level
LOUS	List of Undesirable Substances (of the Danish EPA)
MDM	Octamethyl trisiloxane
MD2M	Decamethyl tetrasiloxane
MD3M	Dodecamethyl pentasiloxane
MM	Hexamethyldisiloxane
MSDS	Material Safety Data Sheet
NOAEC	No Observable Adverse Effect Concentration
NOAEL	No Observable Adverse Effect Level
NOEC	No Observable Effect Concentration
NOEL	No Observable Effect Level
OECD	Organisation for Economic Co-operation and Development
OIA	Outdoor Industry Association
OPPTS	Office of Prevention, Pesticides and Toxic Substance
PBT	Persistent, Bioaccumulative and Toxic (in the environment)
PDMS	Polydimethylsiloxanes
PFAS	Entire group of perfluoroalkyl and polyfluoroalkyl substances
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctane Sulfonic Acid
PNEC	Predicted No Effect Concentration
POPs	Persistent Organic Pollutants
ppm	parts per million
PU/PUR	Polyurethane
PVC	Polyvinylchloride
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (Regulation)
SCCP	The Scientific Committee on Consumer Products
SDS	Safety Data Sheet
STP	Sewage Treatment Plant
TDS	Technical Data Sheet
TOC	Total Organic Carbon
UNEP	United Nations Environment Programme
VOC	Volatile Organic Compound
vPvB	Very Persistent and very Bioaccumulative
ww	Wet weight
ZDHC	Zero Discharge of Hazardous Chemicals (concerted action)

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Appendix 1: Health data on selected siloxanes in registration dossiers

The following information has been extracted from the REACH registration dossiers available from ECHA's Dissemination Site Database (ECHA 2014, b).

Octamethylcyclotetrasiloxane (D4) is registered under REACH (ECHA, 2014e). From the REACH dossier, the following information can be extracted:

- D4 was readily >75% absorbed orally in rats when dissolved in corn oil and diet. Most was excreted shortly again in exhaled air or in the urine as polar metabolites.
- In an *in vitro* study with human skin the dermal absorption was 8.2% of the D4 substance.
- About 5 % of D4 inhalation exposure was absorbed in the lungs after 6 hours' exposure.
- In male rats the acute oral LD_{50} was >4.8 g/kg bw.
- An acute inhalation $^{4h}LC_{50}$ value of >36 mg/L (2975 ppm) air was determined in rats.
- The acute dermal toxicity was low with a LD_{50} value of >2500 ml/kg (>2400 mg/kg bw).
- D4 was not skin irritating for rabbits in an acute dermal irritation test (OECD 404). D4 was neither eye irritating nor skin sensitizing in the guinea-pig maximisation test (OECD 406).
- In a two-week repeated dose oral toxicity study the NOAEL for D4 was < 500 mg/kg bw/day in rabbits.
- Inhalation exposure to D4 for up to 24 months induced the following notable effects in male and female rats:
    - Reduced two-year survival and terminal body weight of male rats exposed to 700 ppm.
    - Lymphocytic leukocytosis in both sexes of rats exposed to 700 ppm.
    - A dose-related decrease in selected serum enzymes in both sexes of rats.
    - Increases in absolute and/or relative weight of liver, kidney, and uterus of D4-exposed rats, especially at 700 ppm.
    - Increased incidence of rhinitis in males exposed to 700 ppm for 12 months.
    - Increased incidence and severity of changes in the nasal epithelium of both sexes of rats exposed to 700 ppm and females exposed to 150 ppm for 24 months.
    - Increased severity of chronic nephropathy in both sexes of rats exposed to 700 ppm for 24 months.
    - Increased incidence of hypertrophy of hepatocytes in male rats exposed to 700 ppm for 12 or 24 months.
    - Increased incidence of endometrial adenomas and endometrial epithelial hyperplasia in the uteri of rats exposed to 700 ppm for 24 months.
    - The NOAELs for carcinogenic effects were 150 and ≥700 ppm in females and males, respectively. The NOAEL for general toxicity was 150 ppm, based on chronic nephropathy. The NOAEL for local respiratory effects was also 150 ppm based on findings in the nasal cavity.
- In a three-week dermal exposure study in rabbits (OECD 410) the dermal NOAEL was greater than the highest dose tested: 1 ml/kg bw/day.
- D4 was not inducing chromosome aberrations in Chinese Hamster Ovary (CHO) cells *in vitro* (OECD 473).
- D4 was not mutagenic in mouse lymphoma L5178Y cells or in Ames test with *Salmonella typhimurium* or in other *in vitro* tests.
- D4 was also negative in *in vivo* studies such as the micronucleus assay and dominant lethal assay.

DNELs have been developed:

- For workers via inhalation the DNEL for systemic and local effects was estimated to 73 mg/m^3 based on a NOAEC = 915 mg/m^3 and an assessment factor of 12.5.
- For workers and the general population no hazard via dermal route or for the eye identified.
- For the general population via inhalation the DNEL for systemic effects was estimated to 13 mg/m^3 based on a NOAEC = 325 mg/m^3 and an assessment factor of 25.
- For the general population via oral route the DNEL for systemic effects was estimated to 3.7 mg/kg bw/day based on a NOAEL = 374 mg/kg bw/day and an assessment factor of 100.

Decamethylcyclopentasiloxane (D5) is registered under REACH. Data submitted show that in an inhalation toxicokinetics study with rats approximately 2% of the inhaled ^{14}C-labeled D5 was retained regardless of sex or exposure concentration. D5 was excreted in urine (metabolites: dimethylsilanediol and methylsilanetriol) and faeces (parent D5) in approximately equal proportions. The skin absorption in rats was also very low at <1.2%; in human skin *in vitro* even lower, at 0.04%. Approximately 20% of ^{14}C-D5 delivered in corn oil appeared to be absorbed after a single oral administration in rats. Oral rat LD_{50} was > 5 g/kg bw, thus no acute toxicity. In rats the inhalation $^{4h}LC_{50}$ was 8.67 mg/L air or >545 ppm (6.72 mg/L). The dermal LD_{50} in rats and rabbits was > 2 g/kg bw. D5 was not skin irritating in rats and rabbits, eye irritating in rabbits or skin sensitising in guinea-pigs.

In a repeated dose 90-day oral toxicity study with rats (OECD 408), the NOAEL of D5 was considered to be greater than or equal to the highest dose tested, 1000 mg/kg bw/day. In a two-year inhalation combined chronic toxicity and carcinogenicity study with rats, the NOAEC for general toxicity was ≥160 ppm (2.42 mg/L; the highest dose tested). Local effects on the nasal cavity and adaptive increases in liver weights in females were observed at 160 ppm. The NOAEC for carcinogenic effects was 40 ppm (0.6 mg/L) based on uterine tumours at 160 ppm. D5 was negative in *in vitro* mutagenicity tests with bacteria, mouse lymphoma cells, and Chinese hamster lung fibroblasts. *In vivo* there was no induction of unscheduled DNA synthesis in the hepatocytes of treated rats, and no observation of increased levels of micronuclei in the bone marrow cells of the treated rats.

In a two-generation reproductive toxicity study no parental toxicity in the F0 and F1 generations was observed at air exposure concentrations of 30, 70, and 160 ppm. The NOAEL was determined to be > 160 ppm. D5 was an inhibitor of human and rat cytochrome P450 enzymes.
DNELs have been developed:

- For workers via inhalation the DNEL for systemic effects was estimated to 97.3 mg/m^3 based on a NOAEC = 1216 mg/m^3 and an assessment factor of 12.5.
- For workers via inhalation the DNEL for local effects was estimated at 24.2 mg/m^3 based on a NOAEC = 1216 mg/m^3 and an assessment factor of 12.5.
- For the general population via inhalation the DNEL for systemic effects was estimated at 17.3 mg/m^3 based on a NOAEC = 432 mg/m^3 and an assessment factor of 25.
- For the general population via inhalation the DNEL for local effects was estimated at 4.3 mg/m^3 based on a NOAEC = 432 mg/m^3 and an assessment factor of 25.
- For the general population via oral route the DNEL for systemic effects was estimated at 5 mg/kg bw/day based on a NOAEL = 1000 mg/kg bw/day and an assessment factor of 200.
- No hazards to skin and eyes were foreseen.

Dodecamethylcyclohexasiloxane (D6) is registered in REACH (ECHA, 2014g). From the dossier, the following information can be extracted:

- In a toxicokinetic study a single oral dose of labelled D6 (1000 mg/kg bw/day) given to male and female rats was largely excreted as D6 in the faeces within 48 h, with less than 12% having been absorbed. Radioactivity recovered in the urine (0.3-0.4% of the adminis-

tered dose) was present exclusively as polar metabolites; two major metabolites, methylsilanetriol (50-70%) and dimethylsilanediol (30-50%), were identified. Low levels of radioactivity were detected in organs and tissues (liver, fat, bone marrow), and small amounts of metabolites were present in the blood.
- An *in vitro* study (OECD 428) found virtually no penetration (0.003%) by D6 through samples of human skin in 24-h semi-occluded contact. Most of the substance evaporated.
- The oral (gavage) LD_{50} for acute toxicity (OECD 423) in female rats has been determined at >2 g/kg bw.
- An acute dermal single application LD_{50} value of >2000 mg/kg was determined for male and female rats in a study according to OECD Guideline 402.
- The substance was not skin irritating in a study (OECD 404) with rabbits or eye irritating in rabbits (OECD 405).
- D6 was not causing skin sensitisation in the guinea-pig maximisation test.
- In an oral combined repeated dose/reproductive and developmental toxicity study in the rat (OECD 422) the NOAEL for systemic toxicity of D6 via the oral route was determined to be 1000 mg/kg/day (highest dose tested).
- In a 90-days inhalation study with rats, hyperplasia and inflammation in the nasal tissue were observed at 10 and 30 ppm but not at 1 ppm. Thus the NOAEL was 1 ppm (182 mg/m^3) and the lowest observable adverse effect level (LOAEL) was 10 ppm (182 mg/m^3).
- D6 was not mutagenic in *in vitro* bacteria tests (OECD471) with *Salmonella typhimurium* strains TA1535, TA1537, TA100 and TA98 (Ames test) and *Escherichia coli WP2uvrA*.
- In an *in vivo* micronucleus assay in ICR mice (OECD474) no increases in micronucleated polychromatic erythrocytes was observed.

DNELs have been developed for D6:
- For workers via inhalation the DNEL for systemic effects was estimated at 11 mg/m^3 based on a NOAEC = 274 mg/m^3 and an assessment factor of 25.
- For workers via inhalation the DNEL for local effects was 1.22 m/m^3 based on a LOAEC = 10 ppm = 182 mg/m^3 and an assessment factor of 75.
- For workers no hazard via dermal route was identified.
- For the general population via inhalation the DNEL for systemic effects was estimated to 2.7 mg/m^3 based on a NOAEC = 137 mg/m^3 and an assessment factor of 50.
- For the general population via inhalation the DNEL for local effects was 0.3 mg/m^3 NOAEC = 18.2 mg/m^3 and an assessment factor of 75.
- For the general population via dermal route no hazard was identified.
- For the general population via oral route the DNEL for systemic effects was estimated to 1.7 mg/kg bw/day based on a NOAEL = 1000 mg/kg bw/day and an assessment factor of 600.
- No hazards to skin and eyes were identified.

Hexamethyldisiloxane (HMDSO) is registered under REACH (ECHA, 2014h). From the dossier, the following information can be extracted: (the acronym HMDS is used)
- In an *in vivo* toxicokinetics study with rats exposed nose-only for 14 days (OECD 417). The majority of systemically absorbed HMDS (MM?) was eliminated in the urine as polar metabolites during 24 hours or was expired. Of the about 3% retained most was found in fat, kidneys and ovaries.
- In an in vitro dermal absorption 24-h study only 0.023% of the applied dose of hexamethyldisiloxane was absorbed through human cadaver skin. The majority of the dose volatilised from the application site (97.5%).
- The acute oral (gavage) rat LD_{50} (OECD 401) was determined to be > 3200 mg/kg bw,
- An acute inhalation $^{4h}LC_{50}$ of 15,956 ppm (equivalent ca. 106 mg/l) was determined in a study according to OECD Guideline 403.

- An acute dermal single application LD_{50} value of >2000 mg/kg was determined for male and female rats in a study according to OECD Guideline 402.
- The substance was not skin irritating in a study (OECD 404) with rabbits or eye irritating in rabbits. However, in a clinical assessment inhalation of the vapour of MM by humans was reported to produce a slight irritation of the lungs, skin and eyes.
- In a human patch test hexamethyldisiloxane was not sensitising to the skin.
- In a 28-day repeated oral gavage study with rats the NOAEL was 160 mg/kg bw/day based on reduced food consumption, reduced body weight gain, reduced liver weight, changes to white cell count and corpuscular parameters in male rats.
- In a two-generation reproductive inhalation rat toxicity study the NOAEC for parental toxicity relevant to humans was 400 ppm based on microscopic liver findings in the F0 males of the 5000 ppm group and F1 males and females in the 5000 and 1600 ppm groups.
- In a 28-day repeated dose dermal toxicity study in rats, the no observable effect level (NOEL) for MM was considered to be 500 mg/kg/day, based on reduced kidney and liver weights in males.
- MM did not induce chromosome aberrations in Chines hamster lung cells.
- MM was not mutagenic *in vitro* in the Ames test with *Salmonella typhimurium* bacteria, *Saccharomyces cerevisiae* yeast or in mouse lymphoma L5178Y cells.
- MM did not induce chromosome aberrations in rat bone marrow cells *in vivo*.
- In a long-term (2 years) inhalation study with rats exposed to 100, 400, 1600 and 5000 ppm MM, in the highest exposed, a statistically significant increase in benign Leydig cell tumours in testes of males and enlarged livers in females were observed.
- In a two-generation reproductive toxicity rat study the NOAEC for parental toxicity relevant to humans was 400 ppm based on microscopic liver findings in the F0 males of the 5000 ppm group and F1 males and females in the 5000 and 1600 ppm groups. F0 and F1 reproductive performance was not affected at any concentration. The NOAEC for neonatal toxicity was considered to be 1600 ppm due to decreased F2 offspring weights at 5000 ppm in the F2 generation. The NOAEC for developmental effects was 1600 ppm.

DNELs have been developed for MM:

- For workers via inhalation the DNEL for systemic effects was estimated to 53.4 mg/m^3 based on a NOAEC = 1335 mg/m^3 and an assessment factor of 25.
- For workers via inhalation the DNEL for local effects showed no hazard was identified.
- For workers hazard via dermal route the DNEL for systemic effects was 333 mg/kg bw/day based on a NOAEL = 100 g/kg bw/day and an assessment factor of 300. The NOAEL used was surprisingly high and based on a skin absorption of 0.023% of dose.
- For the general population via inhalation the DNEL for systemic effects was estimated to 13.3 mg/m^3 based on a NOAEC = 664 mg/m^3 and an assessment factor of 50.
- For the general population via inhalation the DNEL for local effects showed no hazard was identified.
- For the general population via dermal route the DNEL for systemic effects was estimated to 167 mg/kg bw/day based on a NOAEL = 100 g/kg bw/day and an assessment factor of 600.
- For the general population via oral route the DNEL for systemic effects was estimated to 0.27 mg/kg bw/day based on a NOAEL = 160 mg/kg bw/day and an assessment factor of 600.
- No hazards to skin and eyes were foreseen.

Octamethyltrisiloxane (MDM) is registered in REACH (ECHA, 2014i). From the dossier the following information can be extracted:

- The oral (gavage) LD_{50} for acute toxicity (OECD 423) in female rats has been determined at >2 g/kg bw.

- The acute inhalation toxicity (OECD 403) in rats was determined as a $^{4h}LC_{50}$ of 2350 ppm (22.6 mg/L).
- The acute dermal toxicity (OECD 402) in rats was determined as $^{24h}LD_{50}$ > 2 g/kg bw.
- MDM was not skin irritating in rabbits with a 72-h observation period.
- MDM was not sensitising in a guinea-pig maximisation test (OECD Guideline 406).
- In repeated dose 28-day oral (gavage) toxicity with rats (OECD 407) NOAELs were 25 mg/kg/day in the males and 250 mg/kg/day in the females.
- In a sub chronic 90-days inhalation toxicity study (OECD 413) with rats the NOAEL value was 400 ppm. Serious liver and kidney effects were seen at a concentration of 800 ppm in males and 3200 ppm in females.
- MDM was negative in an *in vitro* test of chromosome aberrations in CHO cells (OECD 473).
- MDM was negative with and without metabolic activation in the Ames bacterial mutagenicity test with *Salmonella typhimurium,*
- In a developmental toxicity screening test (OECD422) with rats exposed by inhalation the NOAEC was 3146 ppm.
- MDM did not induce estrogenic or anti-estrogenic effects in the rodent uterotrophic assay following inhalation exposure of rats at 3500 ppm.

DNELs have been developed for MDM:

- For workers via inhalation the DNEL for systemic effects was estimated to 78 mg/m^3 based on a NOAEC = 1945 mg/m^3 and an assessment factor of 25.
- For workers via inhalation the DNEL for local effects no hazard was identified.
- For workers hazard via dermal route the DNEL for systemic effects was 11 mg/kg bw/day based on a NOAEL = 1103 mg/kg bw/day and an assessment factor of 100.
- For the general population via inhalation the DNEL for systemic effects was estimated to 19 mg/m^3 based on a NOAEC = 968 mg/m^3 and an assessment factor of 50.
- For the general population via inhalation the DNEL for local effects showed no hazard was identified.
- For the general population via dermal route the DNEL for systemic effects was estimated at 5.6 mg/kg bw/day based on a NOAEL = 1113 mg/kg bw/day and an assessment factor of 200.
- For the general population via oral route the DNEL for systemic effects was estimated to 0.04 mg/kg bw/day based on a NOAEL = 25 mg/kg bw/day and an assessment factor of 600.
- No hazards to skin and eyes were identified.

Decamethyltetrasiloxane (MD2M) is not classified due to lack of data but it is registered under REACH (ECHA, 2014j). Absorption through intact human skin *in vitro* was insignificant at <0.1%. It is neither skin (OECD404) nor eye irritating. In a seven day oral dose rat study the NOAEL for MD2M was 1000 mg/kg bw/day. In a 28 days oral gavage rat study according to OECD407, the NOAEL was 25 mg/kg bw/day in males and at least 1000 mg/kg bw/day in females. In a rat uterotrophic assay similar to OECD 440, decamethyltetrasiloxane exposure (400 ppm, 6 h/d for 3 days) resulted in a very weak estrogenic response in the luminal epithelial cells only. MD2M was not mutagenic in a mouse lymphoma cell test or in the Ames bacteria test.
DNELs have been developed for MD2M:

- For workers via inhalation the DNEL for systemic effects was estimated at 102 mg/m^3 based on a NOAEC = 2554 mg/m^3 and an assessment factor of 25.
- For workers via inhalation the DNEL for local effects no hazard was identified.
- For workers hazard via dermal route the DNEL for systemic effects was 15 mg/kg bw/day based on a NOAEL = 1449 mg/kg bw/day and an assessment factor of 100.
- For the general population via inhalation the DNEL for systemic effects was estimated at 25 mg/m^3 based on a NOAEC = 5083 mg/m^3 and an assessment factor of 50.

- For the general population via inhalation the DNEL for local effects showed no hazard was identified.
- For the general population via dermal route the DNEL for systemic effects was estimated at 7.3 mg/kg bw/day based on a NOAEL = 1461 mg/kg bw/day and an assessment factor of 200.
- For the general population via oral route the DNEL for systemic effects was estimated at 0.04 mg/kg bw/day based on a NOAEL = 25 mg/kg bw/day and an assessment factor of 600.
- No hazards to skin and eyes were foreseen.

Dodecamethylpentasiloxane (MD3M) is not classified due to lack of data, but it is registered in REACH (ECHA, 2014k). DNELs have been developed on the basis of read across from an inhalation study with MD2M but that is too uncertain. The oral absorption of MD3M in rats is about 25% of administered dose. The elimination was rapid and in 2 days most was excreted, mainly in faeces.

Appendix 2: Environmental assessment for selected siloxanes

Octamethylcyclotetrasiloxane (D4)
The environmental risk assessment reports from the UK Environment Agency concluded that D4 potentially meets the criteria for a PBT substance, when the persistence in sediment is considered, but this conclusion was based on a poorly reported preliminary study (Brooke et al., 2009a). Furthermore, the report mentioned that the half-life for degradation by OH-radicals in the atmosphere was estimated at 12.7-15.8 days. The main degradation process for D4 in water was hydrolysis with a half-life in fresh water (pH 7, 12°C) of 16.7 days, and in sea water (pH 8, 9°C), it was shorter at 2.9 days. The main degradation product formed during the abiotic degradation of D4 was dimethylsilanediol. The properties of D4 mean that it is volatile and also adsorbs strongly onto soil and sediment. A sediment half-life of 123 days at 12°C was determined. Transport to remote areas via air is likely to occur but the substance has a low potential for subsequent deposition to surface media in such regions. Experimental data show that D4 bioconcentrates in fish and is taken up from food. The most reliable value for the steady state BCF was 12,400 in fathead minnow (*Pimephales promelas)* based on total ^{14}C measurements. D4 was not toxic to algae, *Daphnia* and fish at concentrations up to its water solubility limit (0.056 mg/L) (Brooke et al., 2009a).
In November 2008, Environment Canada (2008a) published a screening assessment of D4 with similar conclusions and that D4 had the potential to cause ecological harm.

According to the CLP regulation D4 is classified as aquatic chronic 4 with H413 (ECHA, 2014d). D4 is registered in REACH and has been evaluated as PBT/VPvB (ECHA, 2014e). The vP criterion was fulfilled on the basis of sediment degradation studies. The BCF is above 5,000 in fish. The B and vB criteria were therefore also fulfilled. The T criterion was fulfilled on the basis of both aquatic and mammalian toxicity studies. Thus, D4 met the criteria for a PBT and a vPvB substance in the environment. This conclusion was endorsed by the ECHA PBT Expert Group in November 2012.
In the REACH registration dossier, a hazard assessment was made for aquatic and terrestrial organisms and predators:

- The PNEC for fresh water organisms was 0.44 µg/L with an assessment factor of 10.
- The PNEC for marine water organisms was 0.044 µg/L with an assessment factor of 100.
- The PNEC for STPs was 10 mg/L with an assessment factor of 100.
- The PNEC for freshwater sediment was 0.59 mg/kg sediment dw with an assessment factor of 50.
- The PNEC for marine water sediment was 0.059 mg/kg sediment dw with an assessment factor of 500.
- The PNEC for soil was 0.15 mg/kg soil dw from partition coefficient.
- The PNEC oral for secondary poisoning of predators was 41 mg/kg food with an assessment factor of 90.

Decamethylcyclopentasiloxane (D5)
An environmental risk assessment report from the UK Environment Agency concluded that D5 met the screening criteria for vPvB substances (Brooke et al., 2009b).

The UK Environment Agency assessment also mentioned that D5 had a hydrolysis half-life of 315 days in fresh water at pH 7 and 12°C, but that it was only 43 days in sea water at pH 8 and 12°C. D5 was highly adsorptive to organic matter in sediments and soils. The degradation half-life in sediment was estimated at 800-3100 days. The measured fish BCF was between 2000 and 10.000, but the biomagnification factor (BMF) was small, between 1 and 4. D5 was not toxic to algae, *Daphnia* and fish at concentrations up to its water solubility limit (0.017 mg/L at 23°C) (Brooke et al., 2009b).

In 2009, Environment Canada published a screening study of D5 concluding that D5 could have long-term harmful effects on the environment (EHS Journal, 2011). Later, a Board of Review concluded the opposite: "that Siloxane D5 does not pose a danger to the environment" (Siloxane D5 Board of Review, 2011).

D5 is registered in REACH (ECHA, 2014m). The results of the evaluation of PBT/vPvB properties in REACH was based on the available information, D5 meets the Annex XIII criteria for a vPvB substance in the environment due to its persistence in sediment and high bioconcentration factor in fish. This conclusion was endorsed by the ECHA PBT Expert Group in November 2012 (ECHA, 2014n). D5 is intended to be classified, according to CLP, as Aquatic Chronic 4 (H413) (ECHA, 2014d).

According to a later unpublished 90-days study (OECD 219) on rainbow trout (*Oncorhynchus mykiss*), referred from the REACH dossier, a NOEC of ≥ 14 µg/L was found, and a published 65-days study on fathead minnow (*Pimephales promelas)* found a NOEC ≥ 8.66 µg/L (Parrott et al., 2013). D5 has been shown to cause effects on plants, springtails and earthworms. The lowest reported IC_{50} was 209 mg/kg dry weight in a study with barley (Velicogna et al., 2012).

In the REACH registration dossier, a hazard assessment was made for aquatic andterrestrial organisms and predators. There was no potential hazard for air.
Hazards for aquatic organisms were as follows:

- The PNEC for STPs was 10 mg/L with an assessment factor of 100.
- The PNEC for freshwater sediment was 11 mg/kg sediment dw with an assessment factor of 10.
- The PNEC for marine water sediment was 1.1 mg/kg sediment dw with an assessment factor of 100.

Hazards for terrestrial organisms were as follows:

- The PNEC for soil was 3.77 mg/kg soil dw with an assessment factor of 100.

Hazard for predators were as follows:

- The PNEC oral for secondary poisoning of predators was 16 mg/kg food with an assessment factor of 90.

Dodecamethylcyclohexasiloxane (D6)
In 2008, Environment Canada and Health Canada published a screening study of D6 (Environment Canada, 2008b). It was concluded that D6 was persistent in air with calculated atmospheric half-lives of more than 2 days. D6 has the potential to be transported over long distances in the atmosphere. However, it has a low potential to be deposited in water or soil in remote regions. The hydrolysis half-life for D6 is expected to be longer than that of its structurally similar analogues, D4 and D5. D6 was considered persistent under typical Canadian water conditions. In sediment, D6 was expected to have a half-life longer than 49 to 588 days under realistic Canadian sediment conditions, indicating that D6 may be persistent in sediment. D6 was not considered persistent in soil. It was concluded that D6 met the persistence criterion but not the bioaccumulation criterion as set out in the Persistence and Bioaccumulation Regulations.

D6 is classified according to CLP as Aquatic Chronic 4 (H413) (ECHA, 2014d). D6 is registered in REACH (ECHA, 2014g).
In the dossiers the following data was found:

- D6 was not considered a PBT or vPvB substance.
- It was stable in water with a hydrolysis half-life of 42h at pH4, 401 days at pH7 and 125 h at ph9 and 25°C. The degradation product was dimethylsilanediol.
- In a sludge test according to OECD 310, 4.47% of the substance was biodegraded in 28 days.
- A degradation half-life in soil with 32% RH was determined to be 1.38 days.

- A steady-state BCF value of 1160 was determined for fathead minnow (*Pimephales promelas)* and a BCF of 2400 in *Daphnia magna*.
- The partition coefficients air-water and octanol-water were determined as LogKaw = 3.01±0.14 and LogKow = 8.87±0.14.
- In a flow-through fish test (OECD 305), a 49-day NOEC of ≥ 4.4 µg/L was determined for the effects of D6 on mortality of fathead minnow (*Pimephales promelas*).
- In a reproduction test (OECD 211), a 21-day EC_{50} of >4.6 µg/L and a NOEC ≥ 4.6 µg/L were determined for the effects of D6 on reproduction of *Daphnia magna*.
- A 72-hour EC_{50} value of > 2.0 µg/L and a NOEC ≥ 0.1 µg/L have been determined for the effects on growth rate of the alga *Pseudokirchnerella subcapitata*.
- In a respiration inhibition test with activated sludge (OECD 209) the $^{3h}EC_{50}$ was >100 mg/L.
- A 28-day EC_{50} value of 37 mg/kg dw sediment was determined for mortality of the harlequin fly *Chironomus riparius*. A NOEC < 22 mg/kg dw was determined for the effect on development rate and time.
- Data on terrestrial ecotoxicity was either absent or read across.

In the REACH registration dossier for D6, a hazard assessment was made for aquatic and terrestrial organisms and predators. There was no potential hazard for air.
Hazards for aquatic organisms were as follows:

- The PNEC for STPs was 1 mg/L with an assessment factor of 100.
- The PNEC for freshwater sediment was 8.3 mg/kg sediment dw with an assessment factor of 10.
- The PNEC for marine water sediment was 0.8 mg/kg sediment dw with an assessment factor of 100.

Hazards for terrestrial organisms were as follows:

- The PNEC for soil was 3.77 mg/kg soil dw with an assessment factor of 100.

Hazards for predators were as follows:

- The PNEC oral for secondary poisoning of predators was 67 mg/kg food with an assessment factor of 300.

Hexamethyldisiloxane (HMDSO)
Hexamethyldisiloxane has been suggested to be classified as Aquatic Acute 1 (H400), Aquatic Chronic 1 (H410) in the notified classification and labelling proposals according to CLP criteria (ECHA, 2014d). MM is registered in REACH (ECHA, 2014h).
In the dossiers the following data was found:

- MM is not considered a PBT or vPvB substance.
- MM is transformed in the air. The dominant gas-phase chemical loss process is by reaction with the OH radical (half-life 11.5 – 17.8 days).
- Hydrolysis half -lives of 1.5, 116 and 12 hours at pH 5, 7 and 9, respectively, were determined at 25°C.
- Biodegradation in water of MM was determined in a test according to OECD Guideline 301 C to 2% in 28 days.
- The rate of degradation in soil increased as the soil became drier, as expected. Degradation half-lives (closed tubes) ranged from 1.8 d at 32% relative humidity and at 22.0°C to 407.6 d at 100% RH and at 22.0°C. The degradation product was mainly trimethylsilanol. The volatilisation was the predominant process for removal of the test substance from soil at 100% RH with a volatilisation half-life of around 3 hours.
- BCF values of 1290 - 2410 L/kg (at 40 µg/L); 776 - 1660 L/kg (at 4 µg/L) have been determined with carp in separate exposures at two concentrations.
- The acute toxicity (mortality) in rainbow trout (*Oncorhynchus mykiss*) was determined as $^{96h}LC_{50}$ of 0.46 mg/L and NOEC of 0.11 mg/L, lower than the water solubility of MM of about 1 mg/L at 23°C.

- In a reproduction test (OECD 211) a 21-day EC_{50} of 0.30 mg/L and a NOEC of 0.08 mg/L were determined as regards the effects of MM on reproduction of *Daphnia magna*.
- A 70-hour EC_{50} value of > 0.55 mg/L and NOEC of 0.1 mg/L have been determined for the effects of MM on growth rate of the microalgae *Pseudokirchnerella subcapitata*.
- In a respiration inhibition test with activated sludge (OECD 209), the $^{3h}EC_{50}$ was >100 mg/L.

In the REACH registration dossier for MM, a hazard assessment was made for aquatic and terrestrial organisms and predators:

- The PNEC for fresh water organisms was 0.002 mg/L with an assessment factor of 10.
- The PNEC for marine water organisms was 0.0002 mg/L with an assessment factor of 100.
- The PNEC for intermittent releases to water was 0.003 mg/L with an assessment factor of 100.
- The PNEC for STPs was 10 mg/L with an assessment factor of 10.
- The PNEC for freshwater sediment was 1.7 mg/kg sediment dw with an assessment factor of 50.
- The PNEC for marine water sediment was 0.17 mg/kg sediment dw with an assessment factor of 500.
- The PNEC for soil was 0.083 mg/kg soil dw from partition coefficient.
- The PNEC oral for secondary poisoning of predators was 67 mg/kg food with an assessment factor of 300.

Octamethyltrisiloxane (MDM)

MDM is not classified or classified as Aquatic Chronic 4 with H413 in the EU notified classification and labelling according to CLP criteria (ECHA, 2014d). MDM is registered in REACH (ECHA, 2014i). In the dossiers the following data was found:

- MDM was not considered a PBT or vPvB substance.
- In a fish acute toxicity test (OECD203), a 96-hour NOEC for mortality of ≥19.4 µg/L was determined for rainbow trout (*Oncorhynchus mykiss*).
- In an early-life stage toxicity test (OECD 210) with rainbow trout the 90-days LOEC was >27 µg/L.
- In a 14-days prolonged toxicity test (OECD204) with juvenile rainbow trout the NOEC was >34 µg/L (saturated solution!).
- In a flow-through fish test (OECD 305) a 42-day NOEC for mortality of ≥34 µg/L (nominal), ≥21 µg/L (mean measured) was determined for fathead minnow (Pimephales promelas).
- In an acute immobilisation test with *Daphnia magna* (OECD 202) the ^{48h}NOEC was > 20 µg/L.
- In a *Daphnia magna* reproduction test (OECD 211) a 21-day EC_{50} (survival and mobility) of >14.3 µg/L was determined, and a NOEC of ≥14.3 µg/L has been determined for effects on growth and reproduction.
- A 72-hour EC_{50} value of >9.4 µg/L and NOEC of ≥9.4 µg/L have been determined for the effects of MDM on growth rate and biomass (yield) of the alga *Pseudokirchnerella subcapitata*.
- A 28-dayEC_{50} of >38 mg/kg dw sediment was determined for the effects on reproduction and biomass of the California blackworm *Lumbriculus variegatus*. A NOEC of 38 mg/kg dw sediment dry weight was determined for the same endpoints.

In the aquatic tests, the concentrations tested were very low and close to the water solubility of MDM of 35 µg/L; therefore, these test results are not very useful.

Environment Canada has developed a Risk Management Scope for MDM in which it was concluded that MDM meets one or more of the criteria as a persistent, bioaccumulative and inherently toxic

substance (Environment Canada, 2011). However, in the EU dossier, MDM is not considered a PBT substance.

The important PBT-information about MDM in the dossier was:

- A hydrolysis half-life of 13.7 d (329 h) at pH 7 and 25°C was determined.
- A biodegradation rate of 0% in 28 days was determined.
- The half-lives in soils depend on soil type and relative humidity and ranged from 0.32 days to 120 days.
- In nature, volatilisation was the predominant removal process (half-life <1d).
- In fathead minnows, steady-state BCF values of 5030 l/kg (1.7 µg/l) and 7730 l/kg (21 µg/l) and kinetic BCF values of 3610 l/kg (1.7 µg/l) and 5600 l/kg (21 µg/l) were determined.

In the REACH registration dossier for MDM, a hazard assessment was made for aquatic and terrestrial organisms and predators. There was no potential hazard for air.
Hazards for aquatic organisms were as follows:

- The PNEC for STPs was 1 mg/L with an assessment factor of 100.
- The PNEC for freshwater sediment was 8.3 mg/kg sediment dw with an assessment factor of 10.
- The PNEC for marine water sediment was 0.83 mg/kg sediment dw with an assessment factor of 100.

Hazards for terrestrial organisms were as follows:

- The PNEC for soil was 0.5 mg/kg soil dw from partition coefficient.

Hazards for predators were as follows:

- The PNEC oral for secondary poisoning of predators was 0.08 mg/kg food with an assessment factor of 300.

Decamethyltetrasiloxane (MD2M)
MD2M is registered in REACH (ECHA, 2014j). The following information is extracted from the dossier:

- MD2M was not considered a PBT or vPvB substance.
- A hydrolysis half-life of 30.3 days (728 h) at pH 7 and 25°C was determined for MD2M. Other tests for degradations were read across from other substances.
- A specific study of bioconcentration with a Flow-through Fish Test (OECD 305) with fathead minnow (*Pimephales promelas)*. Steady-state BCF values of 3870 L/kg (0.43 µg/L) and 1610 L/kg (5.3µg/L) and kinetic BCF values of 3830 L/kg (0.43 µg/l) and 1760 L/kg (5.3 µg/L) were determined.
- Adsorption and desorption constants for MD2M were determined as an overall average over three different soils. At 23.7 °C, an adsorption log Koc value of 5.16 and a desorption log Koc value of 5.33 were determined.
- In a fish acute toxicity test (OECD 203) with rainbow trout (*Oncorhynchus mykiss*) a $^{96h}LC_{50}$ and NOEC value of > 6.3 µg/L was determined based on mean measured concentrations.
- In a 35 days study with fathead minnow (*Pimephales promelas)* the NOEC was about the same as above (6.7 µg/L = water solubility).
- In a 21-days *Daphnia magna* Reproduction Test (OECD 211), the NOEC was > 4.9 µg/L.
- In the alga *Pseudokirchnerella subcapitata* growth inhibition test (OECD 201) the ^{72h}NOEC was >2.2 µg/L.
- In all these toxicity tests, the applied concentrations were very low and probably too low to have any chance of causing an adverse effect.
- In a respiration inhibition test with activated sludge (OECD 209), the $^{3h}EC_{50}$ was >100 mg/L.

- No effects on growth and survival were reported when testing MD2M at a loading rate of 100 mg/kg dw sediment (68 mg/kg dwt mean measured) with the freshwater amphipod *Hyallela azteca*. Therefore, a 28-day NOEC value of ≥68 was determined in sediment containing 3.7% organic carbon.
- The tests for terrestrial organisms registered were either data waived, read across or planned studies.

In the REACH registration dossier, a hazard assessment was made for aquatic and terrestrial organisms and predators. There was no potential hazard for air.
Hazards for aquatic organisms were as follows:

- The PNEC for STPs was 1 mg/L with an assessment factor of 100.
- The PNEC for freshwater sediment was 8.3 mg/kg sediment dw with an assessment factor of 10.
- The PNEC for marine water sediment was 0.83 mg/kg sediment dw with an assessment factor of 100.

Hazards for terrestrial organisms were as follows:

- The PNEC for soil was 3.77 mg/kg soil dw with an assessment factor of 100.

Hazards for predators were as follows:

- The PNEC oral for secondary poisoning of predators was 0.08 mg/kg food with an assessment factor of 300.

Dodecamethylpentasiloxane (MD3M)
Dodecamethylpentasiloxane (MD3M) is not classified due to lack of data, but it is registered in REACH (ECHA, 2014k). Some relevant information is available from the dossier:

- MD3M was not considered a PBT or vPvB substance.
- MD3M has extremely low water solubility. At 230C it is 70.4±8.3 ng/L.
- In an acute fish toxicity study, according to OECD 203, there was no mortality, and the $^{96h}LC_{50}$ in rainbow trout (*Oncorhynchus mykiss*) was >75 ng/L.
- In a long-term (35-days) test (OECD 305) with MD3M there was no mortality, and the LC_{50} value for fathead minnow (*Pimephales promelas*) was estimated to >39 ng/l.
- In both cases concentrations used in the tests were extremely low (lower than the previous siloxanes); therefore, the relevance of the data for evaluation of MD3M is questionable.

The ecological hazard assessment for aquatic and terrestrial organisms was:

- PNEC for STPs was 1 mg/L with an assessment factor of 100.
- PNEC for freshwater sediment was 1.66 mg/kg sediment dw with an assessment factor of 50.
- PNEC for marine sediment was 0.17 mg/kg sediment dw with an assessment factor of 500.
- PNEC for soil was 3.77 mg/kg soil dw with an assessment factor of 100.

Alternatives to perfluoroalkyl and polyfluoroalkyl substances (PFAS) in textiles
The objectives of this study are to identify non-fluorinated alternatives available for surface treatment and impregnation of textiles and to provide environmental and health assessments for the chemical alternatives.

Denne rapport undersøger hvilke tilgængelige ikke-fluorerede alternativer til overfladebehandling og imprægnering af tekstiler der findes, samt deres mulige miljø og sundhedseffekter.

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