Rijksinstituut voor Volksgezondheid
en Milieu
*Ministerie van Volksgezondheid,
Welzijn en Sport*

Factsheet: silicon polymer use for pest control

RIVM

A. van Leeuwenhoeklaan 9
3721 MA Bilthoven
Postbus 1
3720 BA Bilthoven
www.rivm.nl

T 030 274 91 11
info@rivm.nl

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Authors
M. Marinković
M. Montforts

The use of silicone polymers for pest control is advancing. Generally, there are two types of applications: 1) mosquito control products that are spread on water bodies, and 2) products that are sprayed on crop plants to control herbivorous insects and mites. Both application types use silicone polymers as active substances and claim an exclusively physical/mechanical mode of action. Because of this type of action they are exempted from the registration as biocides/plant protection products under the current EU regulations.
RIVM presents an overview of the presently marketed silicone products, their compositions and their working mechanisms. Our risk assessment shows that risks cannot be excluded for the environment, consumers and workers owing to either physical effects of the polymer or effects of chemical processing agents (siloxanes) and monomers. Therefore, we recommend that the current use of these products is actively regulated to protect workers, consumers and the environment. We recommend that these types of pest control agents are included in the definition of active substances in the EU regulations for biocides and for plant protection products.

1. Mosquito control products

1.1 Products, applications and working mechanism

1.1.1 Products

There are two silicon-based liquid products on the market that are used to control mosquitos, i.e. Aquatain AMF™ Liquid Mosquito Film and Vazor® Liquid Mosquito Film. Aquatain Products Pty Ltd (Australia) has invented this product and markets it under the tradename Aquatain AMF since 2010[1]. In 2019, Bleu Line Group (Italy) gained exclusive rights to manufacture and distribute Aquatain AMF™ for the export market, including the EU. The other product, i.e. Vazor® Liquid Mosquito Film, is distributed by Killgerm Chemicals Ltd and is produced by Selecta Srl [2]. The latter company is an integral part of the Bleu Line Group specialized in providing product solutions under private label. Considering this, as well as the information provided in the safety data sheets of both products, it can be concluded that Vazor® Liquid Mosquito Film and Aquatain AMF™ Liquid Mosquito Film are most likely the same product. In the remainder of the factsheet the tradename Aquatain AMF™ will be used for both products. Please do note that, in addition to mosquito control products, Aquatain Products Pty Ltd offers two more silicone-based liquid products that either reduce the loss of water due to evaporation (WaterGuard) or control oil spills on water (Gladiator). The latter two products are not further discussed in this factsheet.
Aquatain AMF™ is marketed in bottles and tanks for professional use, but recently it has also become available as to the consumer market.

EnviroSafe Mosquito Drops are small dispensers (45 mL) with a drop-counter that are available in retail chains in Australia (www.bunnings.com.au/envirosafe-45ml-mosquito-drops_p3010444). They are intended for treating small domestic areas (e.g. vases, flowerpot saucers, etc.). Other consumer targeting products are Aquatain drops, DengueDrops and MalariaDrops (see Figure 1) where water-soluble capsules are filled with Aquatain AMF™ allowing the treatment of up to 0.25 m^2 water surface. There appears to be no difference between the different drop tradenames each allowing the treatment of 0.25 m^2 water surface.

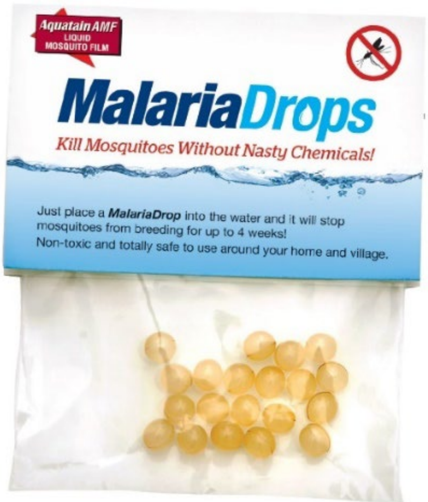


Figure 1. MalariaDrops (source: MalariaDrops flyer)

Aquatain AMF™ can also be obtained with a complementary biological larvicide (2% Bti; *Bacillus thuringiensis israelensis*) under the tradename Total Impact. This product rapidly kills all mosquito larvae, while larvae treated with only Aquatain AMF™ may take a few days to die (see section1.1.3). Upon request, a combination with a chemical larvicide (2% Temephos) is available from Aquatain Products Pty Ltd [1].

1.1.2 *Applications*

Aquatain AMF™ is poured or sprayed on standing or stagnant waters at an application rate of 0.5-1 mL per square meter of water surface. The application domain of Aquatain AMF™ has been expanding ever since the first approval in Australia in 2010. Initially it was intended for use on standing water in urban/semi industrial areas such as gutters, ponds, drains, water tanks, septic tanks and old tyres [3]. Aquatain Products Pty Ltd distinguishes now three categories[1]. Category A includes small areas of standing water such as water drums, puddles, gutters, pit latrines, blocked drains, construction sites and other standing water around the village or in urban environments, where Aquatain AMF™ is applied directly from squeeze bottles. Category B includes more difficult conditions, such as rubbish dumps and other situations where there is no continuous water surface. In these situations, Aquatain AMF™ is sprayed over the whole area, allowing a film to be formed over the pockets of water. Category C is defined as large areas of open water such as waterholes and swampy areas which have a water surface too large for treatment with squeeze bottles. In these cases, Aquatain AMF™ is recommended to be poured on to the water from 5 or 20 L drums, after which it will spread across the surface.
Bleu Line Group expanded the application domain now also recommending Aquatain AMF™ for treatment of amongst others lakes, rice paddies and drinking water tanks [4]. They also introduced the "Larvamatic" equipment for dispensing Aquatain AMF™, a portable 2L tank with GPS and a spray gun that dispenses 1 mL product per shot. On the Aquatain Export website no reference is made to dispersal by drones, but on the Pest-Protect event held in 2018 in Bremen (Germany) Stefano Scarponi, the export sales

director for Bleu Line, stated in an interview with Pest magazine UK that Aquatain AMF™ was applied using drones on rice paddy fields in Italy, and that trials were held in Kenya for malaria control [5]. Just recently, on 31 October 2019 researchers led by Bart Knols from the Radboud University (the Netherlands) used drones to spray rice fields in Zanzibar with an Aquatain AMF™ containing product in order to battle malaria (see Figure 2). This experiment (Anti-Malaria Drones) had wide media coverage (e.g. NY times, Reuters, Forbes magazine), and the results are expected to be published in peer-reviewed journals [6].

Figure 2. Spraying of rice fields in Zanzibar with Total Impact, an Aquatain AMF^{TM} containing product (www.antimalariadrones.com)

1.1.3 *Working mechanism of Aquatain AMF™*

Once applied to water, the silicone-based liquid spreads and forms an ultra-thin silicone film (a mono molecular film (MMF)) on the water surface that lowers the water surface tension. While this application type was initially designed as an anti-evaporation liquid, it proved to be effective in disrupting the mosquito lifecycle. The low surface tension of the silicone film prevents the attachment of larvae and pupae to the water surface, leading to their suffocation. The low surface tension also prevents pupae from emerging and discourages female mosquitoes from laying eggs. Adult mosquitos that do touch the water surface layer become trapped and die. The reported efficiencies are: 100% mortality of the pupae of all mosquito species within 3 hours; 100% mortality of the L3 and L4 stage larvae within 3 days; 94% mortality of the L1 and L2 stage larvae within 10 days; 100% suppression of pupation; and egg deposition on treated water [4].

The film is reported to be unaffected by rainfall, is highly resistant to wind and wave action. The film is claimed to be highly permeable to gases, allowing oxygenation of the water. The film remains on the surface for up to 4 weeks, after which the application can be repeated [3].

1.2 Composition of Aquatain AMF™

Several safety data sheets were found for Aquatain AMF™, with varying levels of detail regarding composition. All safety data sheets report a viscosity of 100 cSt. Aquatain Products Pty Ltd reports the composition as "*Ingredients determined not to be hazardous to 100%*" [7]; Bleu Line Group reports the composition as 89% polydimethylsiloxane and 11% inert ingredients and carriers [8]; a New Zealand distributor reports the composition as >75% poly dimethyl siloxane (CAS No. 63148-62-9), <10% food grade white mineral oil (CAS No. 8042-47-5), and the rest as "other non-hazardous components [9]; an UK distributor reports the composition as 86-90% polydimethylsiloxane (CAS No. 63148-62-9) and 7-8% white mineral oil (CAS No. 8042-47-5) [10]. The same composition is reported in the safety data sheet of Vazor® Liquid Mosquito Film [2]. An Israeli distributor reports the composition as 87.5% (w/w) polydimethylsiloxane (CAS No. 63148-62-9) [11], thereby specifying the structure as containing 23 dimethylsiloxy units.

1.3 Identification of relevant substances

1.3.1 Polydimethylsiloxane

1.3.1.1 Substance properties and (self-)classifications

Searching ECHA's public dissemination site using polydimethylsiloxane as search term yields 65 hits of which five entries correspond to unmodified polydimethylsiloxane. Polydimethylsiloxane (PDMS) is also known as dimethicone in medical, pharmaceutical and cosmetic applications where it is used in lotions for treating head lice, as well as personal care products such as soaps and shampoos. Searching the latter term yielded one more additional entry. PDMS (CAS 8050-81-5) is approved as food additive 'E 900' being an anticaking and antifoaming agent. The latter CAS number yielded two more entries on ECHA's public dissemination site. PDMS is the most widely used silicon-based organic polymer but being a polymer, a REACH registration is not required. All entries are pre-registrations and as such there are no data available on ECHA's public dissemination site regarding the physical and chemical (physchem) properties of the PDMS (e.g. viscosity), the (eco)toxicity or the environmental fate. These substances do have self-classifications in the C&L database. Most notifiers do not self-classify PDMS (56-87%). The different PDMS entries all contain self-classification as Eye Irrit. 2 (6-36%). There are notifiers that self-classify for chronic aquatic toxicity, i.e. Aquatic Chronic 2 (0-2%), Aquatic Chronic 3 (0-6%), and Aquatic Chronic 4 (0-29%). Other self-classifications have also been given, including Repr.2 and Stot RE 2, but at much lower levels (0-1%). For more details, see Table 1 below.

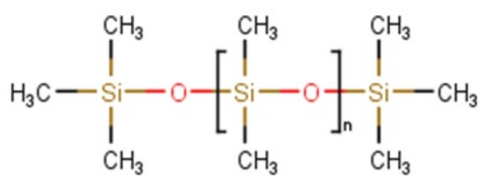
Table 1. Overview of polydimethylsiloxane self-classifications

Self-classifications	**Number of self-classifications per substance (EC name; EC No.; Cas No.)**							
	Dimethyl siloxane *EC No. 613-156-5* *CAS No. 63148-62-9*	Poly(dimethylsiloxane) *EC No. 615-070-3* *CAS No. 70131-67-8*	Polydimethylsiloxane polymer *EC No. 614-822-8* *CAS No. 68937-54-2*	Dimethylpolysiloxane *EC No. 613-154-4* *CAS No. 63148-60-7*	Poly(dimethylsiloxane) *EC No. 618-493-1* *CAS No. 9016-00-6*	Dimethicone *EC No. 618-433-4* *CAS No. 9006-65-9*	Simethicone *EC No. 617-098-1* *CAS No.8050-81-5*	Isopropanol-Silicon *EC No. 933-297-9* *CAS No.8050-81-5*
Not classified	1083	514	212	32	163	104	41	-
Flam Liq. 3	26	-	-	-	-	-	-	1
Acute Tox. 1	1	-	-	-	-	-	-	-
Acute Tox. 2	1	-	-	-	-	-	-	-
Acute Tox. 4	-	1	6	-	-	-	-	-
Skin Corr. 1A	13	-	-	-	-	-	-	-

Skin Irrit. 2	-	7	-	4	-	-	-	-
Eye Dam. 1	13	-	-	-	-	-	-	-
Eye Irrit. 2	143	65	26	4	44	59	3	1
STOT SE 3	-	1	-	-	-	-	-	1
Repr. 2	13	1	-	-	-	-	-	-
STOT RE 2	1	1	-	-	-	-	-	-
Aquatic Chr. 2	25	-	4	-	-	-	-	-
Aquatic Chr. 3	11	-	-	-	-	-	3	-
Aquatic Chr. 4	4	-	-	-	85	-	-	-

Information on PDMS is available from other sources though. In 2001, a silicone polymer homologue of PDMS was assessed under the Australian National Industrial Chemicals Notification and Assessment Scheme (NICNAS) including several toxicological studies with PDMS [9]. In 2010, the Australian Pesticides & Veterinary Medicines Authority (APVMA) assessed Aquatain AMF™[3], mostly referring to the NICNAS report for data of PDMS. In 2011, the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) published under the Joint Assessment of Commodity Chemicals (JACC) an updated report (2^{nd} edition) on linear polydimethylsiloxanes (CAS No. 63148-62-9) [12]. Especially, the latter report contains detailed information on PDMS, which has been included in Table 2, and is discussed in this section.

Table 2. Relevant parameters of polydimethylsiloxane

Name	Polydimethylsiloxane (PDMS)
EC name	Dimethyl siloxane
IUPAC name	Poly[oxy(dimethylsilene)]
Synonyms	Dimethicone, dimethylsiloxane, dimethylsilicone, silicone oil, dimethylpolysiloxane, dimethylpoly-siloxane hydrolyzate, E 900, Permethylsiloxane, Polydimethylsiloxane, Polydimethyl-siloxane, rnethyl end-blocked, Polyoxy(dimethylsilylene), Siloxane, dimnethyl-, α-(Trimethylsilyl)-ω-hydroxy, Siloxanes and silicones, di-Me
CAS name	Siloxanes and silicones, di-Me
CAS number	63148-62-9
EC number	613-156-5
Molecular formula	MD_nM where M = $-Si(CH_3)_3-O_{1/2}$, D= $-Si(CH_3)_2-O-$ and n=number
Molecular weight	62 + (74 x n) g/mol (where n≥13)
Structure	
Water solubility	< 1 ng/L at 23°C*
Log K_{ow}	>> 8.21**
Log K_{OC}	>> 5.16**
Vapour pressure	Not measurable (PDMS is non-volatile)

** predicted value based on measured data for pure octamethyltrisiloxane (MDM; L3; CAS No. 141-62-8) and decamethyltetrasiloxane (MD_2M; L4; CAS No. 141-62-8)*
*** value for decamethyltetrasiloxane*

PDMSs are linear silicone polymers with varying degree of polymerization and thus viscosity. The ECETOC report covers PDMS fluids of viscosities ranging from 10 to >100 000 cSt which corresponds to a polymerisation of 15 to >1000 dimethylsiloxy units and a molecular weight of 1125 to 74 000 g/mol. Aquatain AMF™ is reported to have a viscosity of 100 cSt [7], which would according to the ECETOC report correspond to an average number of 70 dimethylsiloxy units instead of the reported 23 units [11]. The latter would correspond to a lower viscosity of ~30 cSt. The ECETOC report notes that the physchem properties of PDMSs (>10 cSt) only slightly vary with increasing viscosity, and consequently this is not considered an issue.

1.3.1.2 Environmental fate and behaviour

At environmentally relevant conditions, PDMSs are clear, colourless and viscous liquids with a low vapour pressure. They have an extremely low water solubility, are highly hydrophobe and adsorb strongly to soil and sediment. The values presented in Table 2 are based on experimental data for the shorter chained linear siloxane oligomers (L3, L4 and L5), as exact values cannot experimentally be determined for PDMS. Older PDMS studies report higher water solubilities (and consequently lower octanol-water partitioning coefficient and soil adsorption constants), but this is likely because commercial products were tested that may have contained low molecular siloxane oligomer impurities and/or hydroxy terminated siloxanes, both which have higher water solubilities. Furthermore, the studies might have analysed suspensions rather than determining the truly dissolved concentrations.

PDMSs are chemically stable substances resistant to thermal degradation, oxidative degradation and radiation. The ECETOC report indicates that in case of an accidental spill of PDMS fluid to surface water (which occurs when Aquatain AMF™ is applied), the PDMS will spread rapidly forming a very fine film. This film will eventually break up to form tiny droplets which adsorb to suspended particles, eventually settling out of the water column and becoming part of the sediment compartment. In the sediment, degradation (hydrolysis) of PDMS has been shown to occur, but this is a very slow process. After 1 year, the principal degradation product dimethylsilanediol (DMSD; CAS No. 1066-42-8; EC No. 213-915-7) amounted to 5-10% of applied radioactivity (%AR) and CO_2 to 0.25 %AR (Carpenter, 1996 cited in [12]). While the surface water-sediment route is the most relevant one to assess the environmental fate of Aquatain AMF™, it worth noting that PDMS (35 and 1000 cSt) was shown not to degrade significantly in sludge (Palmer, 1992 cited in [12]). In soil, formation of CO_2 and other volatile substances was very low (≤0.11% AR). The primary transformation product was, just as in sediment, DMSD (percentage not reported). It was reported that over time the molecular weight of the extractable products decreased (from 7000 to ~160 g/mol) due to the scission of siloxane (Si-O-Si) bonds. This results in the formation of silanols of varying size with DMSD as the smallest possible degradation product.In a review paper, degradation of PDMS in soil (primarily hydrolysis) was reported to be within days with half-lives ranging 4 to 28 days in seven soils [13]. Under moist conditions (>10%), however, degradation can be very slow in soil, with the half-live for PDMS amounting to 2.4 to 3.9 years [12].

The molecular size and high Log K_{ow} of PDMS with viscosity of >10 cSt, make it unlikely that PMDS will bioaccumulate in fish. The ECETOC report indicates that linear PDMS with seven dimethylsiloxy units was not taken up by rainbow trout (Annelin and Frye, 1989, cited in [12]). In another study PDMS with a viscosity of 5 cSt (12 dimethylsiloxy units) was not taken up by goldfish after 67 days, and not in guppy after 20 days (Opperhuizen et al, 1987 cited in [12]). The latter study did report that lower molecular weight PDMS substances were detected in fish (no details provided).

1.3.1.3 *Environmental toxicity*

The NICNAS report contains no ecotoxicological data.

The ECETOC report concluded that PDMS has no effect on aquatic organisms (fish, daphnia, algae) and sediment-dwelling organisms (e.g. midge larva) and little or no effect on soil organisms (e.g. earthworm). The aquatic test were conducted at test concentrations greatly exceeding water solubility and effect concentrations were expressed as nominal, but as no detrimental effects were observed, it can be concluded that there was no toxicity up to water solubility. In a reproduction test with the springtail *F. candida* a NOEC of 230 mg/kg dry weight was reported based on reduction in offspring. Thus, terrestrial invertebrates appear to be susceptible to PDMS. Insects were also shown to be sensitive to PDMS when applied directly. In both cases, the toxicity appears to be the result of physical rather than toxicological action. A scanning electron microscopical study on the effects on the surface of insects war reported that showed that the mechanism indeed appears to be suffocation caused by PDMS filling the tracheal system (Richling and Böckeler, 2008, cited in [12]).

In the APVMA assessment it was concluded that Aquatain AMF™ is safe for use in standing water in domestic/suburban areas such as gutters, ponds, drains, water tanks, septic tanks and old tyres. Warning were formulated, restricting the application area too less than 100 m^2, not allowing the application to drinking water, and indicating that it must be contained or not allowed to enter the wider aquatic environment. The reason being that there is little information available on the long term ecological impact of repeated applications on mono molecular film (MMFs) on natural wetland ecosystems and the organisms that inhabit aquatic ecosystems such as waterfowl, reptiles, rotifers, spiders, algae, annelids, nematodes, etc. It was further noted that especially bird species living in aquatic habitats may be susceptible to MMFs. If the products contact birds' feathers, this could result in wetting of feathers leading to a reduction in the ability to float on water surfaces, to fly and negatively affecting thermoregulation. Apparently this happened before with a MMF product licensed in Adelaide (Australia)[3].

1.3.1.4 *Human health*

The human health data will only be briefly discussed, as PDMS with a viscosity of 350-1050 cSt (CAS 8050-81-5) is approved as an anticaking and antifoaming food additive 'E 900' in the EU, at a maximum level of 10 mg/kg in solid foodstuffs and 10 mg/L in liquids [14]. The Joint FAO/WHO Expert Committee on Food Additives (JECFA) re-evaluated in 2011 the registration and withdrew the temporary ADI of 0–0.8 mg/kg bw day from

2008, and re-established for PDMS the ADI of 0–1.5 mg/kg bw, originally established at the eighteenth meeting [15]. It was concluded that PFDMS with and without silica (max 5%) does not pose a significant risk to human health.

The ECETOC report indicates that PMDS has a low potential for absorption via oral ingestion and dermal contact, with swallowed PDMS being rapidly excreted unchanged in faeces. Aerosolised PDMS may give rise to inhalation exposure, but no adverse effects were observed in laboratory animals. It was concluded that PDMS is not a skin irritant or a skin sensitizer and only mildly to non-irritating to the eyes. Regarding the latter study, the NICNAS report indicates that persistent irritation is associated with higher viscosity grades (tested were 2 to 12500 cSt). The ECETOC report notes that there are no significant adverse effects of PDMS in acute toxicity studies, repeated dose toxicity studies, chronic/carcinogenicity studies conducted with laboratory animals. PDMS was also concluded not to be mutagenic *in vitro*. Regarding effects on humans, the ECETOC report indicates that PDMS is used in treating humans, e.g. urology, ophthalmology and dermatology. There are no known effects on the immune system. Diseases (connective tissue, atypical connective tissue, rheumatic and autoimmune diseases, and breast cancer) have been reported after injection with PDMS for cosmetic purposes and placement of breast implants (made of high viscosity PDMS), but these diseases were apparently not associated with PDMS. The APVMA assessment, the NICNAS report and the ECETOC reports all concluded that PDMS does not pose a risk to human health.

1.3.1.5 Discussion on the risks associated with PDMS in Aquatain AMF™

PDMS with a viscosity of 350 to 1050 cSt has been assessed as safe for human consumption and has been approved as food additive E900. Considering the low viscosity of the PDMS used in Aquatain AMF™ (100 cSt), even slight eye irritation is not expected to occur when using the product. Overall, no risk to human health is expected from the PMDS present in Aquatain AMF™.

In the environment, the PDMS layer can affect non-target insects in a similar way as mosquitos. Other species that could be affected are birds that come into contact with the thin silicone layer on the water surface. Wetting of their feathers could impair their ability to float on water surfaces, to fly and would also negatively affect their thermoregulation. It should be noted that originally Aquatain AMF™ was approved in Australia for the control of mosquitos in standing water in urban/semi industrial areas. As the risks to the environment could not be excluded, the APVMA required the following cautions were on the label [3]:

- DO NOT allow the treatment area to exceed <100 m^2 and/or must be contained and not possible to flow into the wider aquatic environment.
- DO NOT allow chemical containers or spray to get into drains, sewers, streams or ponds.
- DO NOT treat drinking water, as this product has not been assessed for that use.

Since then, however, the application domain has expanded and the Bleu Line Group now also recommends application of Aquatain AMF™ for treatment of lakes, rice paddies and drinking water tanks. The expanded uses could cause a risk to the environment.

Due to the share molecular size of PDMS with a viscosity of >10 cSt there is no direct PBT/vPvB concern, as it will not bioaccumulate. However, the ECETOC report indicates that siloxane bonds can break (in clay containing soil) and that siloxane structures of varying molecular size can be formed (rearrangement), including octamethylcyclotetrasiloxane (Buch and Ingebrigston, 1979 cited in [12]). The ECETOC report notes that the outcome of this earlier study is in contradiction to later studies (e.g. Lehmann et al., 1994a; 1995; Traina et al., 2002) where silanols and especially PDMS were identified as degradation product. The discrepancy is likely due to the difference in experimental condition where the latter studies used more realistic environmental conditions in contrast to Buch and Ingebrigston (1979) who heated to the soil to 80 °C and used high PDMS loading rates, resulting in high concentrations of DMSD that apparently self-condenses leading to formation of D4. Overall, it seems unlikely that PDMS will degrade in the environment to cyclic or linear siloxanes. It should be noted though that these low molecular weight organosilicons are used as starting materials for the polymerization of PDMS [13], and can be presented as impurities in commercial PDMS. This is relevant as octamethylcyclotetrasiloxane (D4; CAS No. 556-67-2), decamethylcyclopentasiloxane (D5; CAS No. 541-02-6) and dodecamethylcyclohexasiloxane (D6; CAS No. 540-97-6) have been identified as PBT and vPvB substances under REACH [16], while the linear siloxane oligomers decamethyltetrasiloxane (L4; MD_2M; CAS No. 141-62-8) and dodecamethylpentasiloxane (L5; MD_3M; CAS No. 141-63-9) are currently investigated under the Substance Evaluation process under REACH regarding their PBT/vPvB properties. Decisions requesting sediment simulation testing and sediment toxicity testing have been issued in 2017 for both short chained linear siloxanes, and results are expected in 2020 [17, 18]. There is a restriction regarding the use of D4 and D5 in wash-off cosmetics products in concentrations ≥0.1% (w/w) [19]. At the moment a more elaborate restriction is ongoing that will prohibit the placing on the market of leave- on personal care products and other consumer/professional products (e.g. dry cleaning, waxes and polishes, washing and cleaning products) containing D4/D5/D6 in concentrations > 0.1% (as well as D6 in wash off cosmetic products). Concluding, if D4, D5 and/or D6 (and at a later stage possible also L4 and L5 if the same route is followed as for the cyclic siloxanes) are present as impurities in percentages above 0.1% (w/w) in Aquatain AMF™, its use will be prohibited in the EU.

1.3.2 White mineral oil

1.3.2.1 Substance properties and (self-)classifications

CAS number 8042-47-5 is registered under REACH as white mineral oil (petroleum) at Annex X level (100 000+ tpa). It is described as a highly refined petroleum mineral oil consisting of a complex combination of hydrocarbons obtained from the intensive treatment of a petroleum fraction with sulfuric acid and oleum, or by hydrogenation, or by a combination of hydrogenation and acid treatment. Additional washing and treating steps may be included in the processing operation. It consists primarily of alkanes in the range of C_{15} through C_{50}, but, as specified on ECHA's dissemination sit under the summary of the 'environmental fate & pathways' endpoint, isoalkanes, cycloalkanes, aromatic compounds and polyaromatic compounds (PAH) can be present. It should be noted that PAHs are not specified under the composition section. Please see table below for the self-classification.

The same CAS number is allowed as a pesticide active substance. The EFSA peer reviews from 2008 for: Paraffin oil (CAS 8042-47-5, chain lengths C_{17}-C_{31}, boiling point 280-460°C) [20] and Paraffin oil (CAS 8042-47-5, chain lengths C_{18}-C_{30}, reliable boiling point range not available) [21], both conclude indicate a concern with regarding to the presence of relevant impurities. It was therefore concluded that until high purity is demonstrated paraffin oils have to be considered as T "Toxic", carcinogenic category 2, R45 "May cause cancer". The standing committee on the food chain and animal health finalized in its meeting on 28 January 2011 the review report for the active substance paraffin oil CAS No 8042-47-5 and concluded that paraffin oils of high purity raise no toxicological concern as regards the exposure to humans. The active substance paraffin oil was included in Annex I of Directive 91/414/EEC [22].

Table 3. Relevant parameters of white mineral oil

EC name	White mineral oil (petroleum)
IUPAC name	-
CAS number	8042-47-5
EC number	232-455-8
Molecular formula	not applicable - UVCB
Molecular weight	-
Structure	C_{15-50} alkanes
Log K_{ow}	4.3 – 18.02 (QSAR estimates)
Water solubility	2.69×10^{-12} - 11.55 mg/L (QSAR estimates)
Vapour pressure	≤0.01 kPa at 20°C (OECD TG 104)
Harmonized classification	-
Self-classifications (C&L Inventory accessed 2-12-2019)	▪ Not classified [1355 notifiers] ▪ Flam. Liq. 3 (H226) – Flammable liquid and vapour [2 notifiers] ▪ Asp. Tox 1 (H304) – May be fatal if swallowed and enters airways [815 notifiers] ▪ Eye Irrit. 2 (H319) - Causes serious eye irritation [17 notifiers] ▪ Acute Tox.4 (H332) - Harmful if inhaled [18 notifiers] ▪ Acute Tox.4 (H312) - Harmful in contact with skin [3 notifiers] ▪ Acute Tox.4 (H302) - Harmful if swallowed [1 notifier] ▪ Skin Irrit. 2 (H315) – Causes skin irritation [3 notifiers] ▪ Skin Sens. 1 (H315) – May cause an allergic skin reaction [2 notifiers] ▪ Muta 2 (H341) – Suspected of causing genetic defects [17 notifiers] ▪ STOT SE 2 (H371) – May cause damage to lungs [17 notifiers] ▪ STOT RE 1 (H372) – Causes damage to lung and skin through prolonged or repeated exposure [17 notifiers]

	▪ STOT RE 2 (H372) – May cause damage to lung through prolonged or repeated exposure [4 notifiers] ▪ STOT RE 2 (H372) – May cause damage to blood system through prolonged or repeated exposure [1 notifier] ▪ Aquatic Chronic 2 (H411) - Toxic to aquatic life with long lasting effects [11 notifiers] ▪ Aquatic Chronic 4 (H411) – May cause long lasting harmful effects on aquatic life [72 notifiers]

1.3.2.2 Environmental fate and behaviour

White mineral oil is a complex petroleum UVCB. Such a mixture if difficult to test and the environmental fate and behaviour of the constituents can differ greatly. Generally, the alkanes are expected to be poorly water soluble and non-volatile at ambient temperature and pressure.

1.3.2.3 Environmental toxicity and human health

Depending on the purity of the substance relevant impurities (e.g. PAHs) could pose a risk to the environment and human health.

1.3.2.4 Discussion on the risks associated with white mineral oil in Aquatain AMF™

White mineral oil could contain relevant impurities (e.g. PAHs), some of which have been identified as CMR and PBT. This could pose a risk to human health and the environment. Considering that for pesticide use paraffin oils (same CAS number) of high purity are available, it is likely that this will also be the case for Aquatain AMF™, and as such risks are dependent on specific exposure situations.

1.4 Current regulatory status of Aquatain AMF™

In 2010, the Australian Pesticides & Veterinary Medicines Authority (APVMA) approved Aquatain AMF™ for the control of mosquitos in standing water in urban/semi industrial areas in Australia [3].

In Europe, Belgium requested on 16 May 2014 the Commission to decide, pursuant to Article 3(3) of Regulation (EU) No 528/2012, whether a polydimethylsiloxane-based formulation for controlling mosquitoes is a biocidal product for the purposes of Article 3(1)(a) of that Regulation. According to Article 3(1)(a) of Regulation (EU) No 528/2012, only products that are intended to destroy, deter, render harmless, prevent the action of, or otherwise exert a controlling effect on any harmful organism by any means other than mere physical or mechanical action, constitute biocidal products. In response to the above request Bleu Line Srl prepared a position paper providing arguments that Aquatain AMF™ is not a biocidal product as it does not provoke any chemical or biological action on harmful organisms at any stage of the process. More specifically, it was argued that Aquatain AMF™ is purely physical/mechanical and there is no causal chain or connection between an active substance provoking chemical action and the control exerted over the mosquitoes. As such, Bleu Line Srl concluded in the position paper that Aquatain AMF™ is not a biocidal product pursuant to Article 3(1) of the BPR as interpreted by the EU Court in Case C-420/10 Söll GmbH v Tetra GmbH. The European Commission considered the information provided by Bleu Line Srl and concluded that the polydimethylsiloxane-based formulation constitutes a physical barrier to the reproductive capabilities of mosquitoes. Therefore, the European Commission adopted on 23 April 2015 decision (EU) 2015/655 with Article 1 stating: *"A polydimethylsiloxane-based formulation for controlling mosquitoes by adding a silicone film of lower surface tension on water bodies, and which is placed on the market for that purpose, is not a biocidal product for the purposes of Article 3(1)(a) of Regulation (EU) No 528/2012"* [23]. This decision effectively exempted Aquatain AMF™ from registration as biocide due to its physical action. As a consequence, potential risks to human health and the environment have not been assessed.

2. Products against crop pests

2.1 Products against crop pests

There are three silicon-based products on the market that are sprayed on crop plants to control herbivorous insects and mites feeding on these plants, i.e. Siltac® EC, Siltac® SF and ProTAC SF® (with SF standing for Special Formulation). ICB Pharma (Poland) invented the product and markets it under the tradename Siltac® EC since 2014[24]. Since 2018, ISA Nanotech BV (the Netherlands) markets it as Siltac® SF via local distributors in the Netherlands, Belgium and several Scandinavian countries [25]. ProTAC SF® is a registered trademark of ISA Nanotech BV and is distributed since 2019 by the Biobest Group NV (Belgium) [2]. Based on the safety data sheets it appears that all three tradenames concern the same product [26-28]. This is certainly the case for Siltac® SF and ProTAC SF® as the safety data sheet of the latter product notes that is was according to the ICB Pharma safety data sheet for the identical product Siltac® SF edition 1.0 of 01.08.2017. The labels of the EC and SF products do differ slightly with respect to the application instructions, i.e. mixing with other products, and with respect to the species that can effectively be controlled[2, 29]. While this could be the result of differences in formulation, it is more reasonable to reflect the result of ongoing product testing. The website and label of Siltac® EC appear to represent the most recently updated information sources. In the remainder of the factsheet the tradename Siltac® EC will be used for all three products.

2.2 Application and working mechanism of Siltac® EC

Siltac® EC is effective against spider mites, rust mites, aphids, scale larvae, psylids and whiteflies on fruit trees, berries, (greenhouse) vegetables, ornamental plants and cereals, with the efficacy of a treatment ranging 80-95%. The product can also be used to reduce the population of thrips on vegetables with effectiveness reaching 55% after a second treatment. While the SF products advise against mixing with other plant protection products, Siltac® EC provides instructions for tank mixtures with insecticides or acaricides [2, 24].

Siltac® EC is not intended as a preventive product and is to be used when the first colonies of pests appear. The product is added to water (0.05 - 0.2% depending on the pest, plant and application time) and the mix should be sprayed within 24 hours on crops. The highest dose corresponds to 1 L Siltac® EC per 500 L water per hectare. The instructions note that after spraying the crop, it is important that the product dries quickly. Slow drying can pull the leave edges (of fruits) together resulting in phytotoxicity and can result in reduced efficiency. Spraying should therefore not be performed if rain is expected within several hours (4-6), and not in the evening before night dew. After spraying the silicone polymers undergo crosslinking (condensation), and a sticky net-like polymeric structure is created on the body surfaces of the treated insects, immobilizing them immediately. The shrinking net structure crushes the insects, and blocks their trachea leading to suffocation[30]. Dead insects may remain attached to leaves for a few days, after which they fall off. The technology is referred to as 3D-IPNS™ (three-dimensional Immobilising Polymeric Net Structure) by ICB Pharma.

There are several claims made regarding Siltac® EC that deserve attention. Firstly, it is claimed that due to the physical mode of action of the product pests are not able to develop resistance to it. Consequently, it is indicated that the product can be used multiple times during a season and for consecutive years without losing any of its effectiveness. The only restriction laid down is that there should be sufficient time, i.e. 5 to 7 days between successive treatments to avoid phytotoxicity. Assuming that pest indeed cannot acquire resistance, frequent application would still result in the build-up of the product on fields. How this will affect non-target organisms over time has not been investigated. A second claim is that the product does not leave chemical or burdensome residues in crops [25]. As such no restrictions are laid down regarding the latest time of application, and crops could be treated just before harvest. Consequently, workers and consumers could come in contact with the (cured) product. To our knowledge it has not been investigated how this could affect either. A third claim is that Siltac® EC is not toxic to bees and has little effect on (predatory) beneficial insects. The provided reasoning is that these species are stronger and more mobile, and consequently the polymer network does not get a grip on them [31]. The latter claim is not supported by scientific data.

2.3 Composition of Siltac® EC

The composition of Siltac® EC is specified in the safety data sheets as a mixture of polymeric silica compounds, other polymers, siloxanes and anti-oxidants. One hazardous constituent is specified, namely polyalkyleneoxide modified heptamethyltrisiloxane (CAS No. 67674-67-3) that is present in a concentration of <75% w/w [26-28]. Regarding the other constituents, no information is provided, except the statement on the Siltac® EC website that all ingredients meet the requirements as set out by the REACH Regulation (EC) No. 1907/2006.

Further information was obtained from a public literature study that tested the effectiveness of Siltac® EC on spider mites and aphid [32]. The composition of Siltac® EC was reported as a mixture of organomodified trisiloxane and sol-gel (tertaetoxysilane). The paper describes the condensation reaction that occurs upon spraying (i.e. Stöber process) as being catalysed by acid secretions of the insect body with the rate being determined by 1-(etoksylopropoksylotrisiloksylo) triethoxysilane, yielding a branched polysiloxane chain on the arthropods body (see Figure 3).

It should be noted that the Stöber process generally yields polymers with diameters ranging 50 to 2000 nm [33]. This would imply that the formed polymers fall within the scope of the proposed restriction for intentionally added microplastics that is currently under review.

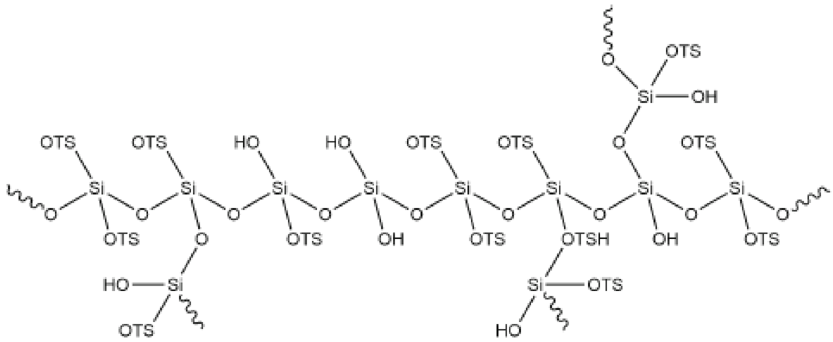


Figure 3. Scheme of polysiloxane chain spatial structure (from Patrzałek et al. [32]). From the article it is not clear what the exact group is refered to as OTS.

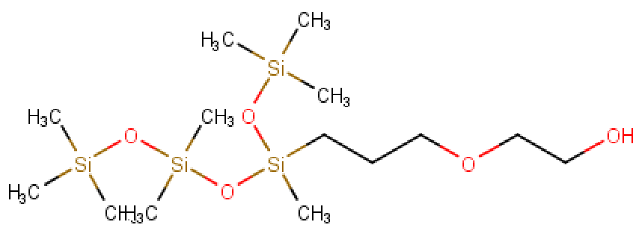
2.4 Substance properties, hazards and classifications

2.4.1 Polyalkyleneoxide modified heptamethyltrisiloxane

2.4.1.1 Substance properties and (self-)classifications

The substance is only pre-registered under REACH and as such there are no data available on ECHA's public dissemination site.
Please do note that the substance is self-classified by most notifiers as hazardous (Acute Tox.4 (H332); Eye Dam. 1 (H318); Aquatic Chronic 2 (H411)), which suggests that there are (eco)toxicological data available.

Table 4. Relevant parameters of polyalkyleneoxide modified heptamethyltrisiloxane

EC name	1,1,1,3,5,5,5-Heptamethyl-3-(propyl(poly(EO))hydroxy) Trisiloxane
IUPAC name	Polyalkyleneoxide modified heptamethyltrisiloxane
CAS number	67674-67-3
EC number	614-100-2
Molecular formula	$C_{14}H_{38}O_5Si_4$
Molecular weight	398.79 g/mol
SMILES	C[Si](C)(C)O[Si](C)(C)O[Si](C)(CCCOCCO)O[Si](C)(C)C
Structure	

Log K_{ow}	0.45 (BioLoom ClogP v1.5 estimate) 7.40 (Kowwin v1.67 estimate)
Water solubility	0.01357 mg/L at 25°C (WSKOW v1.42 estimate) 0.0112 mg/L (Wat Sol v1.01 estimate)
Vapour pressure	0.00092 Pa at 25°C (MPBPVP v1.43 estimate)
Harmonized classification	-
Classification in the Siltac® EC safety data sheet	▪ Acute Tox.4 (H332) - Harmful if inhaled ▪ Eye Irrit. 2 (H319) - Causes serious eye irritation ▪ Aquatic Chronic 2 (H411) - Toxic to aquatic life with long lasting effects
Self-classifications (C&L Inventory accessed 2-12-2019)	▪ Not classified [48 notifiers] ▪ Eye Dam. 1 (H318) - Causes serious eye damage [110 notifiers] ▪ Eye Irrit. 2 (H319) - Causes serious eye irritation [51 notifiers] ▪ Acute Tox.3 (H331) – Toxic if inhaled [1 notifier] ▪ Acute Tox.4 (H332) - Harmful if inhaled [115 notifiers] ▪ Aquatic Chronic 2 (H411) - Toxic to aquatic life with long lasting effects [118 notifiers] ▪ Aquatic Chronic 3 (H412) - Harmful to aquatic life with long lasting effects [1 notifier]

2.4.1.2 *Environmental fate and behaviour*

Searching the QSAR Toolbox (v4.2) yielded no physchem or (eco)toxicological data for the substance. QSAR estimates have been included in the above table to obtain a general picture of the substance characteristics. There appears to be a large discrepancy regarding the octanol water partitioning coefficient estimates of two different models. The substance is poorly water soluble and is not volatile.

2.4.1.3 *Environmental toxicity*

No data, except for the self-classification as Aquatic Chronic 2, indicating that the substance is toxic to aquatic organisms with long lasting effects.

2.4.1.4 *Human health*

No data, except for the self-classification as Eye Dam.1, indicating that the substance causes serious eye damage, and Acute Tox.4 indicating the substance is harmful if inhaled

2.4.1.5 *Discussion on the risks associated with polyalkyleneoxide modified heptamethyltrisiloxane in Siltac® EC*

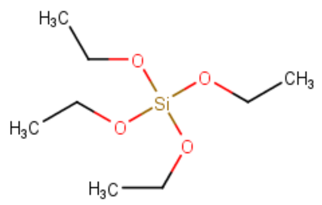
Self-classifications indicate that the substance could be toxic to the environment and human health. The substance is a (reactive) monomer, and during spraying workers could get exposed, as well as bystanders if drift occurs. The label instructions are clear requiring the rapid drying of to product to allow polymer formation. It remains unclear if unreacted polymers can remain on the crop plants, especially in cases where the products does not dry fast enough due to rainfall or high humidity. Unreacted polymers could pose a risk to consumers, especially it the crop plants are treated just before harvest. The latter scenario is per se not worst-case as the producers market Siltac® EC as not having MRLs (Maximum Residue Levels set), which allows treatment just before harvest.

2.4.2 *Tertaetoxysilane*

2.4.2.1 *Substance properties and (self-)classifications*

Patrzałek et al. [32] reports tertaetoxysilane as constituent of Siltac® EC. This is likely to be tetraetoxysilane (TEOS; CAS No. 78-10-4), which is registered under REACH at Annex X level (1000 – 1000 tpa). Please see the table below for relevant substance characteristics and classifications under CLP. It should be noted that the Siltac® EC safety data sheet does not specify this substance, even though it has harmonized classifications as Eye Irrit. 2 (H319) - Causes serious eye; Acute Tox.4 (H332) - Harmful if inhaled; and STOT SE 3 (H335) – May cause respiratory irritation.

Table 5. Relevant parameters of tetraetoxysilane

EC name	Tetraethyl orthosilicate
IUPAC name	Tetraethyl silicate
CAS number	78-10-4
EC number	201-083-8
Molecular formula	$C_8H_{20}O_4Si$
Molecular weight	208.33 g/mol
Structure	
REACH status	Registered at Annex X level
Log K_{ow}	3.18 (HPLC estimate; substance hydrolytically unstable)
Water solubility	258 - 1490 mg/L (non-GLP exp. studies; substance hydrolytically unstable)
Vapour pressure	1.1 hPa at 20°C (QSAR estimate)
Harmonized classification	Index number: 014-005-00-0 ▪ Flam. Liq. 3 (H226) – Flammable liquid and vapour ▪ Eye Irrit. 2 (H319) - Causes serious eye irritation. ▪ Acute Tox.4 (H332) - Harmful if inhaled ▪ STOT SE 3 (H335) – May cause respiratory irritation
Self-classifications (C&L Inventory accessed 2-12-2019)	One out of 737 notifiers additionally self-classifies as ▪ STOT SE 1 (H370 -blood) ▪ STOT RE 2 (H373 -kidneys and liver)

2.4.2.2 *Environmental fate and behaviour*

The substance was shown to be hydrolytically unstable in a GLP-compliant hydrolysis study according to OECD TG 111 at 25°C, yielding ethanol and the inorganic substance silicon tetrahydroxide. The half-lives amounted to 0.11, 4.4 and 0.22 hours at ph4, 7 and 9, respectively. The substance was also shown to be readily biodegradable with 98% degradation after 28 days in a GLP-compliant DOC die away test according to EU Method C.4-A (OECD TG 301A). There are no concerns with regard to persistence.

2.4.2.3 *Environmental toxicity*

Short-term toxicity data are available for fish (LC_{50} >245 mg/L) , invertebrates (>75 mg/L) and algae (>22 mg/L) indicating that the substance is not very toxic. Considering the rapid hydrolysis it is likely that exposure to degradation products occurred. However, as there was no analytical monitoring, this cannot be determined.

2.4.2.4 *Human health*

Substance has harmonized classifications as Eye Irrit. 2 (H319) - Causes serious eye irritation; Acute Tox.4 (H332) - Harmful if inhaled; and STOT SE 3 (H335) – May cause respiratory irritation. Clearly there is a risk to human health.

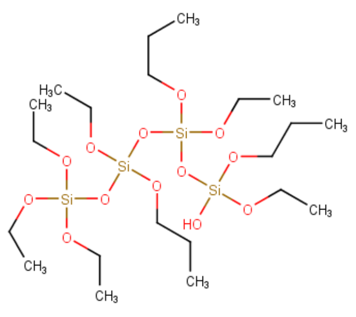
2.4.2.5 *Discussion on the risks associated with tertaetoxysilane in Siltac® EC*

The same argumentation applies as for with polyalkyleneoxide modified heptamethyltrisiloxane (see section 2.4.1.5) with the differences that in this case there are harmonized classifications, and the risk to human health is thus more concrete.

2.4.3 *1-(etoksylopropoksylotrisiloksylo) triethoxysilane*

Patrzałek et al. (2019) report 1-(etoksylopropoksylotrisiloksylo) triethoxysilane as a constituent of Siltac® EC. This is not a standardized chemical name, and it is expected to refer to 1-(ethoxypropoxytrisiloxyl) triethoxysilane. No information could be retrieved for this substance.

Table 6. Relevant parameters of 1-(ethoxypropoxytrisiloxyl) triethoxysilane

Common name	1-(etoksylopropoksylotrisiloksylo) triethoxysilane
name	1-(ethoxypropoxytrisiloxyl) triethoxysilane
CAS number	-
EC number	-
Molecular formula	$C_{21}H_{52}O_{13}Si_4$
Molecular weight	624.9 g/mol
Structure	

2.5 Current regulatory status

The product has been developed in Poland and is certified by the Polish National Institute of Public Health under number: PZH/ HT-3292/ 2017. This document could not be retrieved, and as such it remains unclear for what it has been certified.

On 23 -24 January 2017, the standing committee on plants, animals, food and feed discussed in Brussel in response to a question posed by Belgium if Siltac® EC is within the scope of Regulation (EC) No 1107/2009. The following was concluded: "*This product is at the limit between products that only have sticking properties and those of which the mode of action is more invasive (suffocation). From the elements of the dossier (i.e. the molecular structure) it shows that the action is rather immobilisation (trapping) until death follows, than suffocation. As a consequence, this product is not considered a PPP, which is in line with other similar decisions taken in the past*" [34]. This decision effectively exempted Siltac® EC from registration as plant protection product due to its physical action. As a consequence, potential risks to human health and the environment have not been assessed.

2.6 Potential alternatives

During research on Siltac® EC an alternative product named Afik® was identified that acts in a similar way by creating a membrane covering and immobilizing the pests. This product is, however, not based on silicon compounds but on natural polysaccharides (sodium salt of dioksylo-sulfon-succinate) [35].

3. Conclusion

The two application types both use silicone polymers to control pests, still they differ considerably. In conclusion, both products can pose a risk to human health and/or the environment.

The mosquito control products work on the basis of PDMS, an inert polymer. Risks to human health are not expected from PDMS. A risk to the environment cannot be excluded, as the increased application domain now also includes natural waters and rice paddies. In these ecosystems non-target aquatic invertebrates can be affected via the same physical mechanisms as mosquitos. Furthermore, the thin silicone layer on the water surface can negatively affect birds. These scenarios should be investigated on short notice, as large-scale experiments are already ongoing. In addition to these quantifiable risks, there might also be a PBT hazard associated with Aquatain AMF™. The PDMS can be contaminated with short chained cyclic (D4, D5, D6) and linear (L4, L5) siloxanes that are used as building blocks during polymerization of PDMS. If the cyclic siloxanes are present in concentrations ≥0.1% (w/w) the placement of the market of Aquatain AMF™ will be prohibited once the ongoing restriction for the D4, D5 and D6 in personal care products and other consumer/professional products (e.g. dry cleaning, waxes and polishes, washing and cleaning products) containing D4/D5/D6 in concentrations > 0.1% w/w, has been adopted. In the future the same might apply for the linear siloxanses L4 and L5 that are now under Substance Evaluation regarding their PBT/vPvB properties.

The product against crop pests is sprayed on plants in order to immobilize the insects feeding on these plants. In this case the product consists of reactive monomers that polymerize on the insects. During spraying the workers could get exposed to the monomers. Bystanders can also get exposed if drift occurs. Considering that one of the monomers has harmonized classifications as: Eye Irrit. 2 (H319) - Causes serious eye irritation; Acute Tox.4 (H332) - Harmful if inhaled; and STOT SE 3 (H335) – May cause respiratory irritation, there is a risk for worker and general public.
The manufacturer claims that immobilized insects fall off the plants after a few days, and that the product does not leave any residues of plant protection products. Considering that Siltac® EC has been exempted from registration as plant protection product it is clear that no residues of plant protection products will be left on the plant. This does not mean that there will be no silicone monomers or polymers left on the plants. Residues of monomers could especially be an issue when Siltac® EC is applied under less optimal conditions (rainfall; high humidity) where rapid drying does not occur, and polymerization (partially) fails. This could pose a risk to the workers, but also consumers. Another issue with Siltac® EC is that the formed polymers are likely in the range of 50 to 2000 nm, which would fall within the scope of the proposed restriction for intentionally added microplastics that is currently under review. If the proposal is approved, this could have implications on the placement of Siltac EC on the market.

A more general remark is that the current interpretation of the biocides and plant protection regulations is limiting, as only products containing active substances that act (indirectly) via a chemical/biological mode of action are required to register. This excludes the applications described in this factsheet, while those chemical substances are introduced into the environment with the aim to control certain pest species, and residues are left on products/ in the environment. The overall impact is thus rather similar compared to that of 'proper' biocides and plant protection products, and the legal distinction made appears to be rather artificial from the life sciences point of view.

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