

A dark red rectangular box with a black border. Inside the box, the text "Aquatain AMF" is written in a large, white, italicized sans-serif font. Below it, the words "LIQUID" and "MOSQUITO FILM" are written in a smaller, white, bold, sans-serif font, stacked on two lines.

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Report On

ENVIRONMENTAL FATE & EFFECTS

OF

SILICONES

June 2009

SUMMARY

The attached paper reviews the chemistry and the environmental impact of silicones (Polydimethylsiloxanes or PDMS) - the main component of Aquatrain - in the environment.

Key points are:

- silicones are widely used in consumer and industrial applications
- they degrade in the environment to compounds of silicone dioxide, carbon dioxide and water
- they do not bioaccumulate ie. they do not build up in the bodies of living organisms, because they are too large to pass through cell membranes
- silicones entering wastewater treatment plants become adsorbed to the sludge
- tests on organisms which dwell in aquatic, soil or sediment have shown no adverse effects at concentrations well above those found in the environment.

Environmental Fate and Effects of: **POLYDIMETHYLSILOXANE**

Description

Polydimethylsiloxanes (PDMS) are fully methylated linear polysiloxanes and are also known as silicone fluids. The materials covered within this document fall within the table below:

<u>CAS#</u>	<u>Structure</u>	<u>Viscosity (centistokes)</u>	<u>CAS Name</u>	<u>Common Names</u>
63148-62-9	$\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_n\text{SiMe}_3$	5 to 10^6	Siloxanes and Silicones, di-Me, trimethylsiloxy terminated	Dimethicones, simethicone, etc.
70131-67-8	$\text{HO}(\text{Me}_2\text{SiO})_n\text{H}$	5 to 10^6	Siloxanes and Silicones, di-Me, hydroxyterminated	

Summary

PDMS fluids are used in a wide variety of consumer and industrial applications such as personal care products, food additives, medicinal products, release agents, antifoam additives and dielectric fluids. Most of these uses employ high molecular weight (>1000 Dalton) fluids. A large fraction of the total material produced is used in solid applications such as silicone rubbers and sealants, which are disposed as solid wastes at the end of their useful life, and therefore go to landfill or incineration. Nowadays, ~ 15% of the total is used in applications which may be discharged to waste water treatment systems. Following waste-water treatment, the majority of PDMS is adsorbed to sewage sludge and only a minor fraction is released to the environment. PDMS concentrations in wastewater treatment plant effluent are generally below the detection limit of 1-5µg/l. The subsequent fate of the sewage sludge-bound PDMS depends on local practice and regulations. Much of the sludge is now directed to landfill, incineration and soil amendment. Laboratory and field studies have demonstrated the potential for PDMS to degrade via mineral-catalyzed hydrolysis in soils and sediments, ultimately to form silicone dioxide (SiO₂), carbon dioxide (CO₂) and water (H₂O). No adverse effects were observed in terrestrial or aquatic organisms exposed to PDMS at concentrations that were many times higher than those observed in the field.

Note on References

This fact sheet is a condensation of information presented in "THE HANDBOOK OF ENVIRONMENTAL CHEMISTRY" Vol. 3 Part H, G. Chandra (Ed.), Organosilicon Materials, Springer-Verlag, Berlin, 1997.

comprehensive references should consult this book.

Readers who are interested in a comprehensive review of all published data and

Applications

Polydimethylsiloxanes (PDMS) are typically used as additives in personal care, household and automotive products to impart water repellency, shine and feel. In detergents, food processing and healthcare applications they are mainly used as antifoam additives. Other typical applications include the use as a lubricant, mold release, paper coating or textile finishing. PDMS are also used as electrical or mechanical fluids.

Ecologically relevant physical properties

Average Molecular weight: 700 to 300,000

Density (g/ml): 0.94 - 0.98

Vapor pressure (mmHg at 25°C): $<10^{-3}$ to negligible

Water solubility: not soluble ($\mu\text{g/l}$ range)

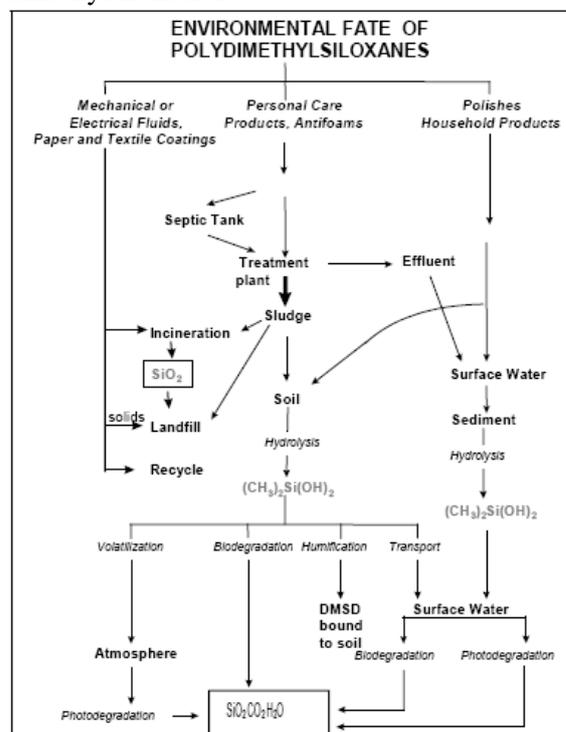
Octanol/water partition coefficient (Log K_{ow}): > 9 .

Environmental Fate

A large fraction of the total material produced is used in solid applications such as silicone rubbers and sealants, which are disposed as solid wastes at the end of their useful life, and therefore go to landfill or incineration.

Between 10-20% of the total is used in applications such as personal care products and detergent antifoam agents which may be discharged to waste-water treatment systems. Following wastewater treatment, the majority of PDMS is adsorbed to sewage sludge and only a minor fraction is released in the effluent to the environment. Some applications such as polishes and other household products are ultimately likely to become a component of household waste. By virtue of its extreme water insolubility and high sludge-water partition coefficient, greater than 97% (based on wastewater treatment plant models and laboratory studies) of the PDMS entering wastewater treatment plants becomes a component of the sludge. The remaining fraction which is bound to suspended solids is released with the treated effluent and will become part of the sediment compartment. The fate of PDMS, therefore, is largely linked to the fate of the sludge. Sludge is usually land-filled or incinerated using controlled environmentally sound processes. If PDMS is incinerated, the degradation products are

amorphous silicon dioxide, carbon dioxide and water. The silicon dioxide in the resulting ash is land filled. The sludge may also be applied to soil, either as a disposal option or to improve the quality of the soil. PDMS is known to hydrolyze in soil to dimethylsilanediol.



Recent monitoring and modeling studies have revealed several facts about PDMS hydrolysis in soil:

- The hydrolysis is catalyzed by clay.
- The hydrolysis is thermodynamically favored.
- The most important factor in determining the rate of hydrolysis is the moisture content of the soil.
- The laboratory half-life of PDMS in dry soil is about 1-4 weeks, depending on the soil type. In the field, conditions are far more variable, and the degradation rate of PDMS will vary extensively with variations in the weather. In temperate regions, PDMS will degrade most rapidly during the warm, dry conditions of summer. In tropical regions, PDMS degradation will be fastest during the dry season.

Dimethylsilanediol formed by the hydrolysis of PDMS, can bind to soil, volatilize (and oxidize) or biodegrade. Volatilized dimethylsilanediol will either photo-degrade

or be re-deposited in the soil during rain. The ultimate degradation product of dimethylsilanediol is silicon dioxide, water and carbon dioxide.

Suspended solids present in the effluent of wastewater treatment may contain trace amounts of PDMS. These trace amounts may be found in the sediments downstream from the treatment plant. In the sediments, PDMS will hydrolyze to dimethylsilanediol as it does in soil; however, the rate is slower, with an initial estimated half-life of several years. Once formed, the dimethylsilanediol is released to the water because of its high water solubility. There is also evidence for rapid degradation of dimethylsilanediol in the water phase by sunlight.

To summarize: PDMS degrades in the environment and the degradation process results in the formation of naturally occurring compounds of silicon dioxide, carbon dioxide, and water.

Environmental Exposure

Soil and sediment, which are the relevant compartments when considering the environmental fate of PDMS, have been monitored in the USA, Europe and Japan; typical concentrations are generally less than those shown below (all values are on a dry weight basis):

- Soil, sludge amended soil: 15 mg/kg
- Soil, from industrial areas: 5 mg/kg
- Soil, from remote areas: <0.25 mg/kg
- River Sediment, from highly populated or industrialized areas: 25 mg/kg
- River Sediment, from rivers in remote areas: <0.1 mg/kg.

Biological Effects

The toxicity of PDMS to environmental organisms is low.

Bioaccumulation: PDMS is a polymer with molecular weight typically in the range of 900 to 300,000 Dalton. Materials with molecular is greater than 1000mg/L. In a sub-chronic study where *Oncorhynchus mykiss* (rainbow trout) were fed PDMS in food, it was estimated that the fish ingested 10 mg of

weights greater than about 700 Dalton generally do not bio-accumulate, even if they have high octanol-water partition coefficients, because they are too large to pass through cell membranes.

Studies in earthworm (*Eisenia foetida*), midge (*Chironomus tentans*), and various fish species confirm that PDMS does not bioaccumulate. Similar conclusions were reached in rodent toxicity studies.

Microorganisms: PDMS has been shown to have no effect at high concentrations on the growth and reproduction of several bacterial, fungi and phytoplankton species. It has also been shown to have no effect on the activity of aerobic and anaerobic sludge microorganisms from waste-water treatment plants and on selected pure strains of fungal and bacterial colonies.

In model ecosystem studies, hydroxy- end-blocked PDMS had no adverse effects on the development of aerobic and anaerobic bacteria, algae or protozoa after a 24 week exposure. No adverse effects were found on growth of four species of algae during a 9-day exposure to saturated water solutions of PDMS.

Aquatic invertebrates and mollusks: No mortality was found in a variety of mollusks at high PDMS concentrations. When PDMS was tested for aquatic toxicity using the freshwater crustacean, *Daphnia magna*, it had no effect at concentrations below the water solubility. However, organisms may become trapped and immobilized if a surface film of insoluble PDMS is present. In experiments with PDMS concentrations in sediment of 600 mg/kg dry weight, no adverse effects on *Daphnia magna* survival, reproduction or growth were observed.

Fish: The low level of water solubility of PDMS makes it difficult to conduct aquatic tests. Numerous fish species have been tested with PDMS at concentrations well above the limit of solubility. Generally the acute toxicity

PDMS per day, corresponding to 10,000 mg/kg of body weight. No mortality, growth effects or abnormalities were noted.

Sediment dwelling organisms: The primary route of exposure in the aquatic environment is through contact with PDMS sorbed to sediments. *Chironomus tentans* (midge), *Hyallela azteca*, *Ampelisca abdita*, *Nereis diversicolor* (polychaete worms) have all been tested using a variety of protocols including chronic and sub-chronic exposure, partial lifecycle and bioaccumulation. The results confirm that PDMS has a low order of toxicity to sediment-dwelling organisms.

Terrestrial organisms: As wastewater treatment plant sludge containing PDMS may be applied to soil either as a disposal option or to improve the quality of the soils, its effect on soil macro- and microinvertebrates was studied. There was no observed effect of PDMS on *Eisenia foetida* (earthworms) up to the test limit of 1000 mg/kg in a chronic reproduction study. *Folsomia candida* (springtail) exposed to PDMS had a NOEC of 250 mg/kg in a chronic exposure study. There was no effect on *Triticum aestivum* (spring wheat) and *Glycine max* (soybeans) in a microcosm study with 9.5 mg/kg dry weight PDMS in soil (it is not

possible to mix higher concentrations of PDMS with sewage sludge, as the sludge will not absorb the PDMS).

Finally, there was also no effect on soil microflora respiration and nitrogen transformations up to the dosing limits of 1000 mg/kg dry weight.

To Summarise: PDMS effects testing with aquatic, soil and sediment dwelling organisms have shown no adverse effects at concentrations well above those actually found in the environment.

Conclusions

Only a minor fraction of the total usage of PDMS is released to the environment. Greater than 97% of this is removed via adsorption onto sewage sludge during wastewater treatment, and subsequently disposed with the sludge. Polydimethylsiloxanes do not bioaccumulate. Testing with both aquatic and terrestrial organisms has shown no adverse effects even at concentrations much higher than those found in field monitoring. PDMS is not expected to pose a risk to the environment.

The following producers of organosilicon materials have contributed funds and expertise to the study of the environmental fate and effects of PDMS: Bluestar Silicones (formerly Rhodia Silicones), Degussa, Dow Corning., Momentive Performance Materials (formerly GE Bayer Silicones and GE Silicones), Shin-Etsu, and Wacker Chemie. Expertise was also provided by Procter and Gamble Co.

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