VOLATILE METHYL SILOXANES (VMS) AS REPLACEMENTS FOR CFCs AND METHYL CHLOROFORM IN PRECISION CLEANING

Richard F. Burow Dow Corning Corporation Midland, Michigan 48686-0994

ABSTRACT

Low molecular weight silicone fluids are finding use as replacements for CFCs and methyl chloroform in a variety of cleaning applications. These fluids are described as volatile methyl siloxane (VMS) fluids. They are very low in toxicity and do not contribute to depletion of the ozone layer.-

The linear VMS fluids, available commercially as Dow Corning(R) OS Cleaning Fluids, will remove most surface contaminants found in precision metal working, such as cutting fluids, greases and silicone fluids. They evaporate to leave no residue. They do not harm most elastomers or plastics.

OS Cleaning Fluids are currently being used as cleaning agents by manufacturers of optics and precision aerospace components, and evaluations are underway at a large number of manufacturers of precision parts and electronic components.

INTRODUCTION

Since the drafting of the Montreal Protocol, users of chlorofluorocarbons (CFCs), methyl chloroform (1,1,1 trichloroethane or TCA), and other ozone depleting substances have been searching for acceptable alternatives for their cleaning and carrier applications. Although many alternatives are being offered, it has become evident that there are no one-for-one replacements for CFCs and TCA. There are no replacements that are "ozone safe" and also have all the same properties and performance characteristics as these substances used formerly. In the past, a whole plethora of applications were served by TCA and a few CFCs, but now the user must identify the specific alternative that best meets the requirements of his or her specific cleaning or carrier application.

In precision cleaning, the user can choose from many aqueous, semi-aqueous and non-aqueous alternatives. While aqueous and semi-aqueous cleaning systems are often chosen, there are cases where non-aqueous systems are preferable. Non-aqueous systems offer excellent cleaning, no potential for corrosion, simpler processing, and easy recyclability.

Dow Corning Corporation has recently introduced a new non-aqueous chemistry offering all of these benefits. This new chemistry is a family of low

molecular weight silicone fluids described as volatile methyl siloxane (VMS) fluids and having either a linear or a cyclic structure:

$$CH_{3} = \begin{bmatrix} CH_{3} & CH_{3} & CH_{3} \\ & & & \\ & & \\ CH_{3} & Si-O + Si-O + Si-CH_{3} \\ & & \\ & & \\ CH_{3} & CH_{3} & nCH_{3} \end{bmatrix}$$

$$CH_{3} = \begin{bmatrix} CH_{3} & CH_{3} & CH_{3} & CH_{3} \\ & & \\ &$$

These VMS fluids are known commercially as DOW CORNING(R) OS fluids. The linear VMS fluids, known as OS-10, OS-20 and OS-30 Cleaning Fluids, are rapidly gaining acceptance as precision cleaning agents and are now being used in the cleaning of aerospace guidance system components, optics, and electronic components.

PROPERTIES OF VOLATILE METHYL SILOXANE FLUIDS

Dow Corning OS Cleaning Fluids are pure distilled methyl polysiloxanes containing no additives. They are crystal clear and almost odorless. Evaporation rates are slower than CFC-113 and are in the range of butyl acetate. Like CFC-113, the OS Cleaning Fluids evaporate completely at room temperature and leave no residue.

The physical properties of three linear OS Cleaning Fluids are summarized on Table I. Note that the surface tensions are very low. This allows the OS fluids to spread rapidly and to creep into tight places to remove soils in the same manner as CFC-113 does.

VMS fluids are combustible or flammable. OS-10 Cleaning Fluid has the lowest molecular weight, is the most volatile, has the lowest flash point, and is classed as flammable. The highest molecular weight OS fluid has a higher flash point (135 degrees F, closed cup) and is classed as combustible.

VMS fluids have a low order of toxicity. OS Cleaning Fluids are non-irritating to the skin and respiratory tract and are non-sensitizing to the skin. They can cause mild eye irritation similar to wind burn ("dry eye"). OS Cleaning Fluids have not been found to be genetically active in a battery of in vitro tests. They have low oral and dermal toxicity and have not produced significant toxicity in any animal studies to date.

CLEANING ABILITY

OS Cleaning Fluids will remove most surface contaminants found in precision metal working and optics processing, and will remove most non-ionic soils in electronics processing. They are milder than most other solvents (low Kauri-Butanol values), but are excellent solvents for surface soils such as oils, greases, cutting fluids, and silicone fluids. Figure I compares the effectiveness of OS Cleaning Fluids and TCA in removing grease and cutting

fluid at room temperature. Waxes can be removed provided the VMS fluid is heated. Mechanical agitation or ultrasonics will speed the cleaning process.

After cleaning with VMS fluids or any other cleaning agent, parts can be rinsed with OS Cleaning Fluids. The very low surface tension (-17 dynes/cm) promotes rapid draining from surfaces. The most volatile VMS fluid (Dow Corning OS-10) can function as a drying agent; parts rinsed in this VMS fluid will dry in less than a minute at room temperature. The less volatile OS Cleaning Fluids take longer to dry and application of moderate heat will speed the drying process.

COMPATIBILITY

VMS fluids are very mild solvents and are safe for cleaning almost any substrate. OS Cleaning Fluids have practically no effect on plastics and elastomeric materials during the cleaning process. Tables II and III show the effect of soaking coupons of various plastics and elastomers in OS Cleaning Fluids for extended periods of time.

CLEANING EQUIPMENT

VMS fluids can be used in existing cleaning equipment provided it is designed to safely handle flat-tunable or combustible liquids. Vapor degreasers have been modified by some users to utilize OS-30 Cleaning Fluid. Cleaning equipment designed for use with IPA can be easily adapted to use OS-10 or OS-20. Contact Dow Corning or your equipment manufacturer for specific recommendations.

RECOVERY AND RECYCLE

OS Cleaning Fluids can be readily cleaned and recycled by distillation and/or filtration, depending on the contaminants present. Recycle of OS Cleaning Fluids makes their use more economical and reduces the potential for entry into the environment.

REGULATORY STATUS

Studies conducted at the University of California, Riverside, demonstrated that OS Cleaning Fluids have an atmospheric lifetime of 10 to 30 days. Thus OS fluids will not rise and accumulate in the stratosphere to deplete the ozone layer and they do not contribute to global warming. Ultimate breakdown products are carbon dioxide, silicic acid, and water.

Dow Corning has made a voluntary submission to the United States Environmental Protection Agency (EPA) requesting inclusion in the list of acceptable substitutes as precision and electronics cleaning substances in the Significant New Alternatives Policy (SNAP). The Dow Corning submission is still under review, but EPA has stated that "preliminary indications are that this substitute merits approval" (58 Fed. Reg. pg. 28175).

Further studies at University of California, Riverside, have shown that OS Cleaning Fluids do not contribute to tropospheric ozone formation. (Low level

ozone formation is a proven contributor to smog formation and is the main reason for current VOC regulations.) Citing these University of California results and other relevant studies, Dow Corning petitioned the EPA in 1992 for an exemption from VOC regulations. The review of this petition is pending.

SUMMARY

Of all of the CFC alternatives available today, VMS fluids come closer than any other to matching the performance capabilities of CFCs. OS Cleaning Fluids and CFCs offer similar cleaning performance, low surface tension, excellent material compatibility, no-residue drying, and excellent toxicological properties. In addition, the OS Cleaning Fluids have not shown any adverse environmental effects. For these reasons, VMS fluids are becoming the cleaning-agent-of-choice in a growing number of precision cleaning applications.

TABLE I. PROPERTIES OF VMS FLUIDS

	CFC-113	TCA	OS-10	OS-20	os-30
MOLECULAR WEIGHT	187	133	162	236	310
FLASH POINT closed cup (°F)	NONE	NONE	30	94	135
FREEZING POINT °C	- 35	- 37	- 68	- 86	-76
BOILING POINT °C	47	74	100	149	192
EVAPORATION RATE butyl acetate = 1.0	17	6	3	1	0.1
VISCOSITY at 25°C,cst	0.68	0.79	0.65	1.0	1.5
SPECIFIC GRAVITY at 25°C	1.56	1.31	0.76	0.82	0.85
SURFACE TENSION at 25°C, dynes/cm	17.3	25.5	15.9	16 (est)	18
HEAT OF VAPORIZATION cal/gm at 150° F	35	56.7	46 (est)	44 (est)	36 (est)
KAURI-BUTANOL VALUE	31	124.8	16.6	15.1	13.4

TABLE II COMPATABILITY OF VMS FLUIDS WITH ELASTOMERS l-week immersion at 50° C, percent swell

POLYMER	COMMON NAME	HYDROCARBON ESTER	OS-10	os-20	os-30
ACRYLONITRILE- BUTADIENE	BUNA N	4	8.1	0	.4
CHLOROSULFONATED POLYETHYLENE	HYPALON	12.8	2.4	-1.8	-1.9
EPDM RUBBER	NORDEL	24.6	-3.9	-6.6	-8.6
FLUOROELASTOMER	VITON A	0	-1.7	0	0
	VITON B	~.8	-1.2	-1.2	0
ISOBUTYLENE- ISOPRENE	BUTYL RUBBER	28.9	3.5	-5.8	-4.0
NATURAL POLYISOPRENE	NATURAL RUBBER	50.3	16.0	11.5	4.9
POLYCHLOROPRENE	NEOPRENE	41.2	58.5	56.9	53.9
POLYSILOXANE	SILICONE	13.6	-7.1	-8.3	-8.3

TABLE III. COMPATIBILITY OF VMS FLUIDS WITH PLASTICS

1-day immersion at 50° C, percent weight change

POLYMER	BRAND NAME	HYDROCARBON ESTER	OS-10	OS-20	OS-30
NYLON	ZYTEL	-0.3	-0.5	0	-0.3
ACRYLIC	LUCITE	-0.1	-0.2	0	-0.1
POLYSULPHONE	-	-0.1	-0.1	0	-0.1
PET	RYNITE	0	0	0	0
POLYCARBONATE	TUFFAK	-0.1	-0.1	0	-0.1
POLYVINYL CHLORIDE	PVC	-0.1	-0.1	0	. 0
ACETAL	DELRIN	-0.1	-0.2	0	-0.1
ABS	KRALASTIC	- 0	-0.3	0	-0.1
POLYPROPYLENE	-	1.5	0.6	0	0-1
PBT	VALOX	0	-0.3	0	-0.1
POLYETHERIMIDE	ULTEM	-0.1	-0.1	0	0
PVDF	KYNAR	0	. 0	0	0
POLYSTRYENE	STYRON	1.4	0.4	0	0.1
CHLORINATED POLYVINYL CHLORIDE	PVC	0	0	0	0
PTFE	TEFLON	0	0	0	0
IONOMER	SURLYN	7.1	0.6	0	0
ACRYLIC CLEAR	LUCITE	-0.1	-0.2	. 0	0
HIGH IMPACT POLYSTRYENE	STYRON	17.3	0	0	0
POLYCARBONATE B	TUFFAK	0	-0.1	0	-0.1
POLYPRO	-	0.9	0.3	0	0.1
PVC	PVC -	0	-0.1	0	0
NYLON B	ZYTEL	-0.1	-0.2	0	0.2
WHMW POLYETHYLENE	ALATHON	2.7	0.6	0	0.1
HPDE	•	1	0.2	0	-0.6

