NEW FLUORINATED SOLVENT ALTERNATIVES

by

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Abstract

The elimination of the ozone depleting substances CFC-113 and 1, 1, 1-trichloroethane has forced industry to use numerous substitute materials and not-in-kind processes. Acceptable alternatives have been found for many applications. However, some of these alternatives have resulted in a higher cost in terms of process complexity and economics or have substituted a future safety or environmental liability for the original problem. For many users, the search for a suitable alternative continues.

Ideal substitutes for ODS liquids should combine their beneficial safety and performance properties, e.g. non-flammability, acceptable toxicity, adequate solvency and high stability, with the additional desire of minimal environmental impact. Commercially available perfluorochemicals (PFCs) are a well-known class of materials that are non-ozone depleting and possess many of these desirable attributes. However, their use as ODS replacements will be limited to those applications requiring their extremely high stability and very low toxicity.

Development efforts are underway to create new fluorinated materials which complement perfluorochemicals and expand the capabilities of available alternatives. Results to date are promising and indicate that these materials should provide improved performance in some ODS replacement applications. This paper will discuss their physical and performance properties, their projected environmental impact, their developmental status, and their likely place in the ODS replacement market.

Introduction - The Changing Solvents/Cleaning Market

The solvents/cleaning market is changing in nature and scope. In 1989, the global market for CFC-113 and l,l,l-trichloroethane was nearly 1 billion lbs/yr. Since that time, the market for these materials and their in-kind HCFC replacements has been contracting into a much smaller specialty market for safe fluorinated liquids with reduced ozone depletion potential. By the year 2000, the fluorinated fluids market is estimated to be less than ten percent of its original volume.

The elimination of the traditional cleaning solvents has resulted in the use of numerous alternative materials. This has included a return to the hydrocarbon and chlorinated solvents which were replaced a generation ago as well as many not-in-kind processes such as aqueous and no clean. Alternatives have been identified for many applications, but some have been found to be less than ideal substitutes. Often success has been achieved at a high cost in terms of equipment complexity, process flexibility and overall economics. In some instances the alternative may substitute a future safety or environmental liability for the original problem.

Water based cleaning processes have been found to be acceptable for a number of applications. Nevertheless, some products contain water sensitive materials or are so geometrically complex that they are exceedingly difficult to dry. Chlorinated solvents have good solvency for a number of soils. However, they also generate concern due to their toxicological properties and the extensive practices required for workplace safety (e.g. more costly containment equipment, ventilation improvements, safety equipment and hazardous waste handling).

While some HCFCs exhibit lower toxicity, they can be considered only transitional solvents since they have an ozone depletion potential (ODP). The use of hydrocarbons and other organic solvents has been limited to those instances when the flammability, volatile organic compound (VOC) emission, and worker safety issues can be managed.

Desired Properties of Safe Alternatives

There are a number of the more demanding applications for which an acceptable alternative has yet to be identified. Typically, these are applications which require fluids that: are non-flammable, have very low toxicity, have high thermal and chemical stability, can evaporate leaving no residue, are non-corrosive and compatible with key materials, have low surface tension and viscosity, possess adequate solvency for the application, can be readily contained, and are economical to use. For these applications, a suitable solvent substitute must possess physical properties which closely resemble the ozone-depleting solvents they replace.

Ideal substitutes for ODS liquids should combine the beneficial safety and performance properties of the traditional solvents with the fundamental desire of minimal environmental impact. Perfluorochemicals are the only currently available non-ozone depleting alternatives which possess most of these desirable attributes. However, due to regulatory concerns with their long atmospheric lifetimes, their use as ODS replacements will be limited to those applications requiring their selective fluorochemical solvency, their extremely high stability and/or their very low toxicity. Consequently, there remains the need for safe, non-ozone depleting alternatives with broader use potential.

New Fluorinated Materials

For several years, the chemical industry which has supplied the solvents market has been attempting to develop an ideal alternative solvent. Recent efforts have focused on hydrofluorocarbons (HFCs) since they appear to possess many of the performance and safety properties required of alternatives and are expected to be more environmentally acceptable than the ODSs they replace. Efforts are underway to develop a family of new fluorinated liquids which complement perfluorochemicals and are superior in many aspects to other alternatives. Several promising product candidates have been developed which can be manufactured using 3M's installed production base, thus hastening commercial introduction.

Physical Properties

Results to date are very encouraging and indicate that these new materials should provide improved performance in many demanding ODS replacement applications, including precision cleaning. Until the completion of the patent portfolio, the composition of these materials cannot be disclosed. However, Table 1 provides information on a range of physical properties for two new materials, identified here as Liquids A and B, which are expected to be commercialized first,

Key features of these materials are that they will cover a range of higher boiling points which is desirable for cleaning efficacy and containment. In alternative cleaning systems such as the Advanced Vapor Degreasing (AVD™) process, higher boiling fluids have demonstrated improved cleaning performance and reduced loss rates. The fact that these compounds are non-flammable means that these materials can be used safely and should not require expensive explosion-proof equipment.

The low solubility of water in these materials is quite desirable in many applications such as displacement drying and the cleaning of water sensitive components. This is especially important for applications in humid environments. The low solubility of these materials in water is also desirable in order to minimize losses into any contacting water stream.

The high densities, low viscosities and low surface tensions of these materials are all very important properties in precision cleaning applications, especially for particulate removal and for penetrating complex geometries. Also of importance are their heats of vaporization which are even lower than CFC- 113. A low heat of vaporization will allow rapid, residue-free drying of parts and will minimize liquid drag-out losses, facilitating their recovery and containment.

Table 1
Physical Properties of New Fluorinated Fluids vs. CFC-113

Property	Liquid A	Liquid B	CFC-113
Boiling Point (°C)	50 - 60	70 - 80	48
Freezing Point (°C)	< - 79	< -79	-35
Flash Point (°C)	None	None	None
Solubility for Water (ppm)	< 100	< 100	170
Solubility in Water (ppm)	< 20	< 20	110
Liquid Density (g/ml)	1.4 - 1.6	1.4 - 1.6	1.56
Viscosity (cp)	< 0.7	< 0.7	0.68
Surface Tension (dynes/cm)	< 14	< 14	17.3
Heat of Vaporization (cal/g)	< 30	< 30	35

Environmental Properties

The challenge for the chemical industry has been to develop solvents which have not only the physical properties to function as ODS substitutes but also the characteristics to be considered environmentally acceptable. One of the surprising features of these new fluorinated fluids is that they were found to excel in both of the areas.

The environmental properties of these fluids are listed in Table 2. The new fluorinated materials do not contain chlorine or bromine and therefore do not contribute to the catalytic cycles which cause ozone depletion. As a result, the compounds will have no ozone depletion potential. The atmospheric lifetimes of these compounds are long enough that they are not precursors to photochemical smog (i.e. should not be considered VOCs) but short enough to preclude concerns over accumulation in the atmosphere. Like all organic compounds, these materials absorb infrared energy. However, due to the short atmospheric lifetimes, they will have low global warming potentials, particularly when compared to CFCs and the currently available alternatives.

Table 2
Environmental Properties of New Fluorinated Fluids vs. CFC-113

Property	Liquids A & B	CFC-113
ODP (CFC-11 = 1.0)	0	0.8
VOC	No	No
Atmospheric Lifetime (years)	≤ 5	110
Global Warming Potential (100 year ITH)	< 500	4500

Stability

Although this new class of fluorinated fluids degrades readily in the environment, they have exhibited relatively high stability during use. As Table 3 indicates, the new fluorinated fluids are quite hydrolytically stable, even at elevated temperatures. While many partially fluorinated compounds have been found to have measurable decomposition rates at temperatures near or above their boiling points, these new fluids are comparable in stability to CFC- 113. However, these new fluorinated materials are not as chemically or thermally stable as PFCs such as perfluorohexane. Thus, for the most demanding applications requiring extremely high stability, PFCs will likely remain the only viable alternative.

Table 3
Hydrolytic Stability of New Fluorinated Fluids vs. CFCs and PFCs

	Liquid A	Liquid B	C_6F_{14}	CFC-113
HF Generation @ BP (µg/g/hr)	<0.5	<0.1	<0.01	0.02
HF Generation @110 °C (µg/g/hr)	<0.7	<0.3	<0.01	0.44

Toxicity

An important factor by which ODS alternatives must be judged is their toxicological properties. In nearly all applications some degree of worker exposure is likely to occur either through routine operation or accidental release. The toxicological testing program for the new compounds is presented in Table 4. Based on acute testing results to date, these new fluorinated materials are practically non-toxic by inhalation and orally with no observable effects at 10,000 ppm (inhalation) or 5 g/kg (oral). Toxicity evaluations are continuing, including higher concentration and longer exposures.

Table 4
Toxicological Testing Plan

Test	Status
Phase I	
Acute Oral Toxicity	Practically non-toxic
Acute Inhalation Toxicity (4 Hour)	No Observable Effects @ 10,000 ppm
Primary Dermal Irritation	In Progress
Primary Ocular Irritation	In Progress
Ames Assay	In Progress
Phase II	
Cardiac Sensitization Study	Planned
Two Week Repeat Dose Inhalation Study	Planned
Sub-chronic (90 Day) Inhalation Study	Planned

Materials Compatibility

Initial compatibility testing indicates these new fluids will be very compatible with a wide variety of metals, plastics and elastomers - similar to the wide ranging compatibilities observed with PFCs. Table 5 lists the materials with which the new fluids have been found to be compatible to date. The good compatibility of these fluids with especially sensitive plastics such as polycarbonate and polymethyl methacrylate indicates they should have good utility in the precision cleaning of assemblies containing many composite materials. The new fluids will have compatibility for some elastomers and plastics which is superior to CFC-113. However, as with most fluorinated liquids, these materials will absorb into fluorinated plastics and elastomers over longer exposure periods.

Table 5
Materials Compatible with New Fluorinated Fluids

Elastomers	Plastics	Metals
Natural Rubber	Polymethyl methacrylate	302 Stainless Steel
Nitrile Rubber	Polyvinylchloride	Carbon Steel
Neoprene	Polypropylene	Aluminum
Urethane	Polyethylene	Copper
EPDM	Polycarbonate	
SBR		

Solvency

A number of precision cleaning applications involve the removal of halogenated lubricants or dampening fluids such as perfluoropolyethers, polybromotrifluoroethylene (BTFE) fluids and polychlorotrifluoroethylene (CTFE) fluids. Consequently, it is necessary to have ODS alternatives with solvency for such compounds. As would be expected with any highly fluorinated solvent, Liquid A and Liquid B have very high solubility for other halogenated materials. The results of initial solvency screening tests are provided in Table 6.

Table 6
Solubility of Halogenated Compounds in New Fluorinated Fluids

Solute	Liquid A	Liquid B
Perfluoropolyether	Miscible	Miscible
Functionalized Perfluoropolyether	Miscible	Miscible
Polybromotrifluoroethylene (BTFE)Fluid	Miscible	Miscible
Polychlorotrifluoroethylene (CTFE) Fluid	Miscible	Miscible

Miscibility is defined as solubility > 50 percent by weight.

The majority of cleaning applications require the removal of hydrocarbon based soils. Unfortunately, the most difficult challenge for the chemical industry has been to develop an ODS alternative with adequate solvency for hydrocarbons which is non-flammable, low in toxicity and has no ODP. The new family of materials has achieved a balance between these requirements.

Typically a liquid's solubility for a solute will increase with temperature. Since the new fluorinated fluids have boiling points which are higher than many of the available alternatives, they are able to be used at temperatures which enhance their solubility for hydrocarbons. The new materials display solvency for hydrocarbons which is significantly greater than PFCs, particularly at the boiling point of the fluids. As Table 7 indicates, their hydrocarbon solvency can be measurably greater than other partially fluorinated solvents as well. Although the new fluids do not exhibit the solvency of CFC-113, evaluations in cleaning processes have demonstrated that complete miscibility for a soil is not required to successfully clean a surface.

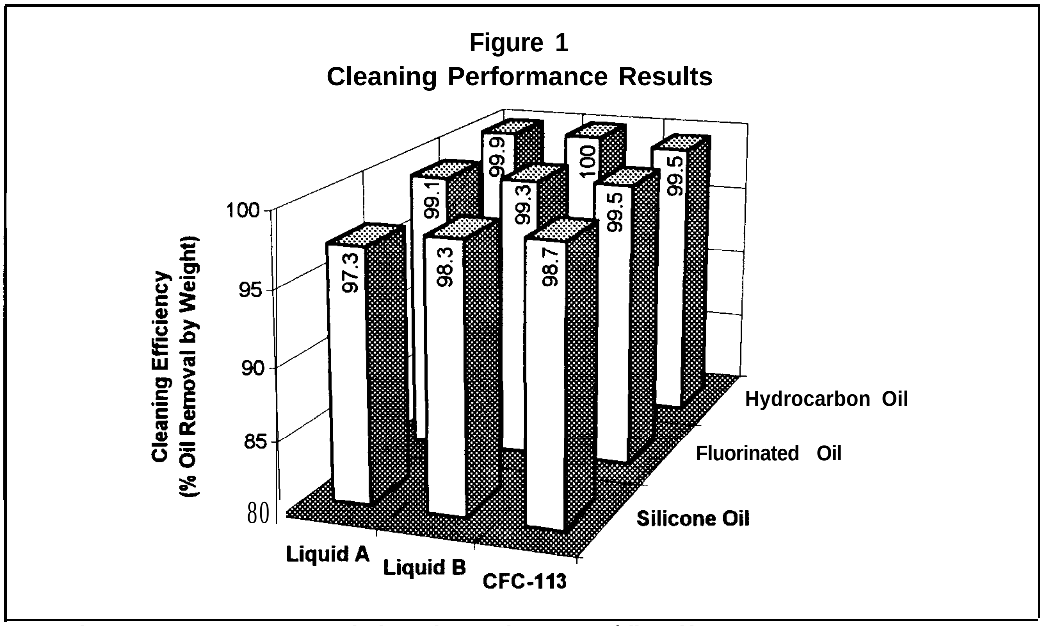
Table 7
Solubility of Hydrocarbon Oil in Fluorinated Fluids
(percent by weight at the boiling point)

Liquid A	Liquid B	$C_6F_{13}H$	C_6F_{14}	CFC-113
3	3	<0.3	<0.2	miscible

Hydrocarbon Oil: aliphatic hydrocarbon alkanes ranging from $C_{16}H_{64}$ to $C_{31}H_{64}$
Miscible indicates solubility greater than 50 percent by weight.

Cleaning Performance

The high solubility for halogenated compounds makes the new fluorinated fluids well suited for precision cleaning applications which require removal of such compounds, such as in the case of navigational instruments. The results of cleaning evaluations, in which the new fluorinated fluids are compared to CFC- 113 for the removal of a perfluoropolyether oil, are shown in Figure 1.



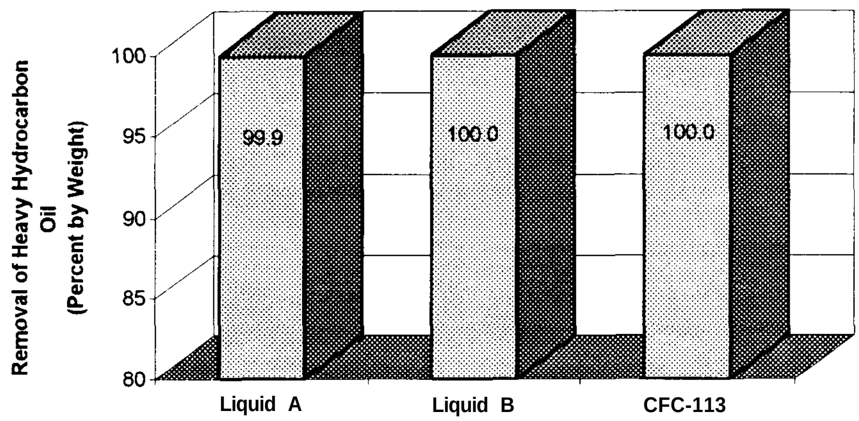
Test conditions: one minute immersion in boiling solvent with sonication followed by one minute vapor rinse.
Fluorinated Oil: Perflouropolyether Carboxylic acid (Krytox 157FSM)
Hydrocarbon Oil: Heavy White Mineral Oil (Aldrich)
Silicone Oil: AK 350 (Wacker Chemie)

Most highly fluorinated solvents have very low hydrocarbon solubility and consequently are typically poor cleaning solvents for such soils. However, as shown in Figure 1, the level of hydrocarbon solubility at the boiling point of these new fluids provides the capability of performing light to intermediate duty cleaning of hydrocarbons using the neat liquids. For such soils, the results obtained with the new fluorinated fluids are essentially identical to CFC-113. Similar results have been obtained when cleaning light to moderate molecular weight silicone oils from substrates. The results are summarized in Figure 1.

Although these new fluorinated fluids are better solvents than PFCs, they are not the solvent equivalent of CFC-113 or 1,1,1-trichloroethane. For applications in which heavier hydrocarbon oils or greases must be removed, the use of a co-solvent is required.

A number of co-solvent cleaning processes are currently employed as alternatives to ODSs. For example, the AVD™ process combines the use of low volatility, hydrocarbon solvating agents with a perfluorocarbon rinsing agent to clean a wide variety of soils. Figure 2 displays the results of using these new fluids as a rinsing agent in combination with a solvating agent in a co-solvent cleaning process. The cleaning performance is comparable to CFC- 113.

Figure 2
Cleaning Perfomance Results



Test conditions for Liquids A and B: one minute immersion with sonication in Petroferm Solvating Agent 24 followed by 30 second immersion rinse in Liquid A or B.
Test Conditions for CFC-113: one minute immersion with sonication.
Heavy Hydrocarbon Oil: Duo Seal Pump Oil (Sargent-Welch Scientific Co.)

Summary

It is evident that the post-ODS solvent market is changing dramatically. A number of alternative solvents as well as not-in-kind processes are being used to replace the ODSs. However, for some of the more demanding applications an acceptable alternative has yet to be identified. These applications require a solvent which combines the advantageous performance and safety properties of the ODSs with improved environmental acceptability.

A new family of fluorinated fluids has been identified which can satisfy the requirements for many of these demanding applications. These new materials have physical properties which closely resemble the ODS solvents covering a range of boiling points with solvency for a number of soils. Consequently, the new fluids can be used in precision cleaning processes which produce results equivalent to the ODSs. In addition, this class of compounds has no ODP, are not VOCs, have short atmospheric lifetimes and low global warming potentials, resulting in broader environmental acceptability.

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