A Comparison of Hydrofluoroether and Other Alternative Solvent Cleaning Systems

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Abstract

In the early 1980s, solvents, in particular chlorofluorocarbons (CFCs), were the cleaning medium of choice in the disk drive industry. Due to their high ozone depletion potential (ODP), environmental regulations on CFCs were tightened resulting in a phaseout of these solvents in the mid-1990s. At that time, no other solvents were able to match the properties of CFCs and the industry transitioned to aqueous cleaning. However, as the complexity and sensitivity of components increase along with areal density, manufacturers are looking at alternatives to aqueous cleaning to resolve issues with cleaning performance, drying and corrosion.

In evaluating the new generation of solvents, it is important to find one with the right balance of properties. Segregated hydrofluoroethers (HFEs) are a new class of solvent. In these molecules all of the hydrogen atoms reside on carbons with no fluorine substitution and are separated from the fluorinated carbons by the ether oxygen, i.e. R_fOR_h. HFEs offer safety and performance properties similar to CFCs but offer a superior environmental profile.

Cleaning Solvents: A Balance of Properties

Cleaning alternatives to CFCs and aqueous processes need to have the right balance of safety, environmental and performance properties. Some of the key components for each of these properties are listed in Table 1. In deciding on a cleaning chemistry for your application, it is important to consider how all of these factors will contribute to the overall cost of ownership. Less expensive solvents can have hidden costs that negate the initial low raw material price.

HFEs offer a good balance of these three properties. Cleaning systems incorporating HFEs help address worker safety and environmental concerns – while offering performance comparable to CFCs. 3M has developed a family of HFE-based solvents that offer this balance.

Table 1.
The Right Balance of Properties

Safety	Environmental	Performance
Low toxicity	Regulatory sustainability	Cost effectiveness
Nonflammable	Zero ozone depletion	Selective solvency
	Non-VOC	Compatibility
	Short atmospheric lifetime	Stability
	Low global warming	Stringent quality
	Low solubility in water	

Neat HFEs

These are used for cleaning light oils, halogenated compounds and particulate.

- HFE-7100 (methyl nonafluorobutyl ether, b.p. 61°C)
- HFE-7100DL
- HFE-7200 (ethyl nonafluorobutyl ether, b.p. 76°C)
- HFE-7200DL
- HFE-7500 (2-trifluoromethyl-3-ethoxydodecafluorohexane, b.p. 130°C)

HFE-7100DL and HFE-7200DL are high purity versions of HFE-7100 and HFE-7200 for sensitive applications. These products have specifications for ions, metals and non-volatile hydrocarbons, esters and silicones.

Azeotropes and Blends

Azeotropes are used for cleaning medium weight oils, flux residues, hydrocarbon lubricants, and silicone oils.

- HFE-71IPA (HFE-7100 and isopropanol azeotrope)
- HFE-71DE (HFE-7100 and trans- 1,2-dichloroethylene azeotrope)
- HFE-71DA (HFE-7100, trans- 1,2-dichloroethylene and ethanol azeotrope)
- HFE-71D90 (HFE-7100 and trans-1,2-dichloroethylene blend)

An azeotrope is a mixture of two or more components that vaporises without a change in composition. Azeotropes offer significant advantages in process safety and control due to their consistency in composition during cleaning processes.

Co-solvent system

A co-solvent system uses neat HFEs, typically HFE-7100, as a carrier solvent and rinse agent for a low-volatility organic solvent. The organic solvent increases the cleaning power of the system, while the HFE is used to rinse the organic solvent off the parts and provide an inert nonflammable vapour blanket. Co-solvent cleaning systems are used for cleaning heavy oils, greases, flux residues, adhesives and hot melts.

SAFETY PROPERTIES

The key safety properties of HFEs and other common solvents are shown in Table 2. The HFEs have a safety profile superior to alternative solvents. A tangible benefit of solvents with a good safety profile is lower equipment costs. HFE cleaning systems do not require the equipment safety add-ons (i.e. explosion proofing, extinguishing equipment and inert atmosphere) needed with some other solvents. The low toxicity of HFEs also means greater margins of safety in the event of a spill.

Mixing inert solvents, for example HFEs or hydrofluorocarbons (HFCs), with more aggressive solvents is done to enhance cleaning performance. The more aggressive solvents often have less desirable safety properties, particularly flammability. The presence of HFEs or HFCs can "inert" the more aggressive solvent. However, it is important to ensure the inert composition is maintained during actual use. Due to the difference in the evaporation rates of the two solvents, the composition of the mixture will change with time. If the vapour is rich with the more aggressive solvent, the liquid cleaning solution will become concentrated with the inert solvent and the cleaning efficiency of the mixture will decrease with time. If the vapour is rich with the inert solvent, the liquid cleaning solution will become concentrated over time with the more aggressive solvent. This could result in a flammable mixture of the two solvents being formed.

To overcome these composition change issues, azeotropes are used. An azeotrope is a mixture of two or more solvents that has the same composition upon vaporisation at the boiling point. Since the vapour has the same concentration as the liquid, evaporative losses will not result in decreased cleaning performance or safety concerns. Additionally, HFEs can inert more flammable solvents, resulting in a non-flammable, constant composition cleaning solution. The flammability characteristics of the HFE azeotropes and blends along with their components are shown in Table 3. Mixing these solvents with HFE improves the flammability characteristics and exposure guidelines.

Another common cleaning method is based on co-solvent systems. These systems are a mixture of an inert solvent and a low volatility organic solvent. The organic solvent increases the cleaning aggressiveness, while the inert solvent is used to rinse the organic solvent off the parts and form a non-flammable vapour blanket. The concentration of the organic solvent can be adjusted to the needs of the cleaning application.

TABLE 3.
FLAMMABILITY MITIGATION OF HFE AZEOTROPES AND BLENDS

	Flammable*	Explosion limits in air	Exposure guideline**
HFE-7100	No	None	750 ppm
Trans- 1, 2-dichloroethylene	Yes	9.7 – 12.8%	200 ppm
HFE-71DE 50% HFE-7100 50% trans-1,2-dichloroethylene	No	None	750/200 ppm
HFE-71D90 *** 10% HFE-7100, 90% trans	No	Not determined	750/200 ppm
Ethanol	Yes	3.3 – 19%	1000 ppm
HFE-71DA 53% HFE-7100 45% trans-1,2-dichloroethylene 2% ethanol	No	5.1 – 12.7%	750/200/1000 ppm
Isopropanol	Yes	2.5 – 12%	400 ppm
HFE-71IPA 95% HFE-7100, 5% isopropanol	No	4.0 – 16.7%	750/400 ppm

* Based on closed cup flash point

** 8-hr time weighted exposure

*** HFE-71D90 is a blend and should not be used in a vapour degreaser environment

HFE azeotropes and co-solvents offer similar solvency to more aggressive solvents, while having superior safety and environmental properties. Kauri-Butanol (KB) values for several common solvents are compared with HFE azeotropes and co-solvents in Table 4.

ENVIRONMENTAL PROPERTIES

HFEs have the best environmental profile of alternative solvents. The key environmental properties of HFEs and the common solvents are shown in Table 5. HFEs have zero ozone depletion potential, short atmospheric lifetimes and low global warming potential. This simplifies the product waste streams, which reduces operating costs. Additionally, this reduces regulatory concerns now and for the foreseeable future, and facilitates transfer of cleaning processes to manufacturing or processing operations located outside the U.S.

PERFORMANCE PROPERTIES

The performance of a cleaning solvent is critical in deciding which solvent is right for your application. The solvent must provide a cost-effective method to clean the components without damaging them. The HFE solvents provide a range of solvency power as shown in Table 4. These materials are also compatible with a large range of materials including most metals, numerous plastics, flex circuits and glues.

The cost of ownership of a solvent cleaning process is greatly impacted by the solvent losses during operation. Solvent cleaning is typically performed in a vapour degreaser. There are two primary modes of solvent loss in vapour degreasing equipment: diffusive loss and drag-out loss.

Diffusive loss occurs during operation as the solvent molecules move from the saturated vapour zone through the freeboard region to the degreaser's opening. The diffusive loss rate is a function of the solvent's boiling point and molecular weight. As boiling point and molecular weight increase, the diffusive loss rate decreases. Incorporating the following alterations to the degreaser can minimise diffusive losses:

Table 4. KB Values per ASTM D1133-86 for HFE Products and Common Solvents

Solvent	Kauri-Butanol Value
HFC-4310	9
HFE-7100	10
HFE-71DE	27
HCFC-225	31
CFC-113	32
HFE-71DA	33
HCFC-141b	56
1,1,1-TCA	123
n-Propyl bromide	125
Solvating Agent 24 *	> 150
NMP	> 300

* Solvating Agent 24 is a typical low volatility organic solvent used in the HFE co-solvent process and is available through Petroferm. Other organic solvents may be used depending upon the application.

- Increase the height of the freeboard region to decrease vapour diffusion out of the degreaser.
- Add a secondary chilling unit to condense the vapurs in the freeboard region.
- Use a sealed vapour degreaser to reduce openings for diffusive loss rate.

Drag-out loss occurs when solvent remains on parts as they are removed from the degreaser. Drag-out losses are related to the solvent's heat of vaporisation, surface

Table 5. Environmental Properties of Common Solvents

	Ozone Depletion Potential	Atmospheric Lifetime (years)	Global Warming Potential *	Volatile Organic Chemical
HFE-7100	0	4.1	320	No
HFC-4310	0	17.1	1,700	No
n-Propyl bromide	0.026	0.03	0.31	Yes
HCFC-225 ca/cb	0.03	2.1/6.2	180/620	No
HCFC-141b	0.1	9.4	630	No
1,1,1-TCA	0.1	4.8	140	Yes
NMP	0	N/A	N/A	Yes
Isopropanol	0	N/A	N/A	Yes
CFC-113	0.8	85	6,000	No

* 100 year Integrated Time Horizon, CO_2 = 1

Table 6. Key Properties of Common Solvents for Diffusive and Drag-Out Losses (at ambient conditions, unless otherwise noted)

	Boiling Point (Celsius)	Molecular Weight	Vapor Pressure (mm Hg)	ΔH_{vap} @ bp (cal/g)	Viscosity (cps)	Surface Tension (dynes/cm)
HFE-7100	61	250	202	30	0.61	13.6
HFC-4310	55	252	226	31	0.67	14.1
n-Propyl bromide	71	123	111	59	0.49	25.9
HCFC-225	54	203	285	35	0.59	16.2
HCFC-141b	32	117	548	53	0.43	19.3
1,1,1-TCA	74	133	132	58	0.65	25.6
NMP	202	99	0.3 @ 20°C	127	1.8	45.6
Isopropanol	82	60	44	159	2.0	20.8
CFC-113	48	187	333	35	0.65	17.3
	Higher is better.		Lower is better.			

Table 7. Effect of Solvent Diffusive and Drag Out Loss on Operating Costs*

Process Fluid	Solvent Cost ($/lb)	Usage Rate** (lb/hr*ft²)	Operating Cost+ ($/hr)
HFE-7100	15	0.03-0.1	1.80 – 6.00
HCFC-141b++	3	0.06-0.7	0.72 – 8.40
C_3H_7Br (n-PB)	3	0.04-0.6	0.48 – 7.20

* For a machine having an extended freeboard, secondary chilling.

** Low usage rate – simple parts, diffusive loss only.
High usage rate – very complex parts, diffusive and drag-out losses.

+ Machine assumed to have an opening of four square feet.

++ Diffusive loss rate of HCFC-141b with secondary chilling assumed to be the same as HCFC-123. Physical properties and measured loss rates of 141b and 123 similar with primary chilling only. Loss rate of HCFC-141b typically 5x higher than HFE-7100 based on field data

tension and viscosity. A lower heat of vaporisation will allow the solvent to more easily evaporate off the part. Solvents with lower surface tension and viscosity more easily run off the part and are less likely to be held up in complex geometry. To minimise drag-out loss:

- Increase the hold time of the part in the freeboard region to allow solvent retained on the component to evaporate.
- Superheat the vapour zone to drive off the solvent retained on the parts.
- Incorporate a vacuum system onto the degreaser to collect fluid retained on the component.
- Use properly designed baskets that do not retain solvent.

Due to their good balance of physical properties, HFEs have exceptionally low diffusive and drag-out losses compared to most solvents used in vapour degreasing equipment. The key physical properties for diffusive and drag-out losses for several standard solvents are shown in Table 6.

Diffusive and drag-out losses have a dramatic impact on the operating cost of a cleaning operation. A more expensive solvent with lower diffusive and drag-out losses can have a lower operating cost than lower priced solvent with higher losses. This is illustrated in Table 7.

Conclusion

The best cleaning solution for an application requires a solvent that has the right balance of performance, value, environmental and safety properties. It is important to look beyond the price per pound of a solvent in determining your cost of ownership. The performance properties of a solvent, specifically diffusive and drag-out loss, can have a significant impact on the operating cost of using a particular solvent system. Additionally, the safety and environmental properties of the solvent can have tangible and intangible affects on the cost of ownership model. Hydrofluoroethers offer an excellent balance of performance, safety and environmental properties, making them ideal for cleaning applications.

About the Author

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