Zero ozone - depletion potential, non - flammability, low toxicity, and high compatibility qualify viable alternatives* for *select cleaning applications.

Fluorocarbons and Supercritical Carbon Dioxide Serve Niche Needs

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Over the past decade, industry has been seeking replacements for the ozone-depleting chemicals (ODCs) used in various cleaning operations. For many applications, aqueous and semi-aqueous cleaners have been found to be good solvents for removal of contaminants such as solder flux, hydrocarbon oils, machining coolants, and particles.

These alternatives. used in many types of metal and printed circuit board cleaning, are mostly inexpensive, easy to use, and low in toxicity. However, there are certain precision cleaning applications, much of the type performed at Draper Laboratory, where aqueous and semi-aqueous cleaners cannot be employed.

Concerns about traces of water and detergent being left behind after aqueous cleaning, along with the non-volatile residues of semi-aqueous cleaners, make these unsuitable for cleaning of delicate, complex, and moisture-sensitive devices. These precision devices include certain gyroscopes, accelerometers, and ball bearing assemblies, many of which are constructed in part from beryllium. aluminum, and other reactive metals or metal alloys.

Some of these devices are lubricated with or contain exotic fluorinated organic compounds, including Krytox fluids (DuPont), FC fluids (3M). and bromotrifluoroethylene- and chlorotrifluoroethylene-based fluids (Halocarbon and PCR). Cleaning these fluids by aqueous and semi-aqueous systems is difficult or impossible in certain applications.

Niche Substitutes

Less common ODC replacements such as supercritical carbon dioxide (SC-CO_2) and fluorocarbon solvents have been found to have niche precision cleaning applications. Specific uses include replacement of CFC- 113 for removal of various sized particles during the manufacture of precision devices. and to clean the aforementioned fluorinated fluids.

SC-CO, and fluorocarbons are being touted as ODC replacements due to their zero ozone-depletion potential (ODP), non-flammability, low toxicity, and high compatibility. This article will discuss their advantages and limitations in precision cleaning, experimental results confirming their effectiveness, and corresponding equipment.

It's appropriate to address these two different approaches in the same article because, in some cases, they both have similar cleaning characteristics due to physical properties and solubility for removal of the fluorinated fluids.

In other situations, the two techniques can complement each other. For example, SC-CO_2 may remove gross amounts of a fluorinated lubricant, followed by a fluorocarbon solvent to remove any remaining traces of lubricant and particles.

CFC-113: Hard to Beat

CFC-113 has been the dominant solvent for the cleaning required for the assembly of precision devices at Draper Laboratory. Unique and desirable physical, chemical, and environmental properties that make CFC-113 ideal for this application are the reasons it has been difficult to replace.

- High-purity grades are available (i.e., Freon-113. PCA grade from DuPont). CFC-113 is not only chemically pure. it's available in grades containing very low non-volatile residues (NVR). typically <1 part per million (ppm) by weight in the solvent. This quality is crucial when large quantities of solvent are used. and complex parts must be precision cleaned with no residual surface contaminants remaining.
- CFC-113 has a low toxicity. is chemically stable. and nonflammable. These qualities are important, as large quantities are used in some power-spray cleaning applications where hazards to personnel must be minimized.

cyclic materials are of interest in that they are better solvents than the perfluoroalkanes, and will have use for cleaning some of the viscous bromotrifluoroethylene-based damping fluids.

DuPont's fluorocarbon solvent. Vertrel 245, is a mixture of the 1,2 and 1,3 perfluorodimethylcyclobutane isomers. Figure 4 illustrates structures.

Other fluorocarbon-based solvents include Perfluorosolv (PFS- 1) from Ausimont and HFC-4310 mee, an experimental material from DuPont. Both are excellent solvents for cleaning Krytox fluids.

Fluorocarbons have advantages as replacement solvents because some of their physical properties compare to those of CFC-113, as Tables 1-3 outline.

Current EPA Assessment

Per Section 612 of title VI of the Clean Air Act, the SNAP (Significant New Alternatives Policy) list of March 18, 1994 includes all acceptable ODC alternative solvents. Fluorocarbons are designated acceptable under narrow use limits, consistent with the type of precision cleaning discussed in this article.

The EPA has used the following language to describe usage of fluorocarbons such as PF-5060, PF-5070. and PF-5052:

Applications - Electronics and precision cleaning.

Decision - "Acceptable for high-performance, precision-engineered applications where reasonable efforts have been made to ascertain that other alternatives are not technically feasible due to performance or safety requirements."

User requirements - "Users must observe this limitation on fluorocarbon acceptability by conducting a reasonable evaluation of other substitutes to determine that fluorocarbon use is necessary to meet performance or safety requirements. Documentation of this evaluation must be kept on file."

Draper's fluorocarbon usage is strictly limited to the two areas discussed. both within the EPA SNAP restrictions: precision cleaning to remove particles and fluorinated fluids.

Evaluation of Fluorocarbon Purity

As discussed earlier, the presence of non-volatile residues in cleaning solvents is undesirable. Parts must be cleaned and the solvent must evapo-

Table 1
Comparison of PF-5052 and Vertrel 245
Physical Properties to Those of CFC-113

SOLVENT PROPERTY	CFC-113	VERTREL 245	PF-5052
Boiling Point (°C)	48	45	50
Surface Tension (dynes/cm)	17.3	11.6	13
Density (g/cc) 25°C	1.57	1.67	1.70

Table 2
Comparison of Physical Properties
of the 3M Perfluorocarbons

SOLVENT PROPERTY	PF-5050 (C_5F_{12})	PF-5060 (C_6F_{14})	PF-5070 (C_7F_{16})
Boiling Point (°C)	30	56	80
Surface Tension (dynes/cm)	9.5	12	13
Density (g/cc) 25°C	1.63	1.68	1.73
NVR Specification	10 micrograms/ml	10 micrograms/ml	10 micrograms/ml

Table 3
Comparison of Physical Properties
of Perfluorinated Morpholines

SOLVENT PROPERTY	PF-5052	PF-5062	PF-5072
Boiling Point (°C)	50	72	95
Surface Tension (dynes/cm)	13	—	—
Density (g/cc) 25°C	1.70	1.74	1.79
NVR Specification	10 micrograms/ml	10 micrograms/ml	10 micrograms/ml

Table 4
NVR Results

SOLVENT	RESIDUE IN PPM
Freon-113 PCA	0.3
Vertrel 245	0.8
FC-72 lot 625	0.8
FC-72 lot 646 #21	0.3
FC-72 lot 646 #22	0.2
FC-72 lot 646 #23	0.2
PF-5060	0.6
PF-5050	0.4
PF-5060 lot 653 #49	0.5
PF-5060 lot 653 #53	0.4
PF-5070 lot #173	0.1
PF-5052	0.3

rate without leaving residues. Several batches of fluorocarbons have been evaluated for NVR.

Table 4 lists the results of selected fluorocarbon replacement solvents in ppm by weight compared to Freon PCA. Note that with all samples analyzed, the fluorocarbon residues are <1 ppm, which has been the acceptable value for Freon PCA in the past.

Particle content of the solvents is also critical, and filtering methods must be developed to ensure that the solvent is free of particles. 0.45-micron filters in the power-spray equipment have worked successfully - necessary. as particle-free or HPLC-type grades of fluorocarbons are not available at this time.

Fluorocarbon Recovery and Recycling

Draper has employed two approaches for containment and recycling of the expensive fluorocarbon solvents.

The containment issue has been addressed through use of various contained power-spray apparatus. Specifically, Quadrex (Gainesville, FL) equipment has been used to remove particles in precision cleaning operations (see Figure 5).

Initially. the intent of Quadrex equipment implementation was to conserve CFC-113 losses. Now, with PF-5070 having replaced this agent in the Quadrex equipment at Draper, the technology limits the losses of expensive fluorocarbon solvents.

No compatibility problems or major leaks have been identified when a fluorocarbon is used with this equipment as a simple drop-in replacement. However, containment is only one aspect of solvent use. Once vapors are contained they must be recovered and recycled, which the Quadrex equipment is capable of through distillation.

This equipment is essentially a glove box with a power-spray gun allowing parts spraying at pressures up to several hundred psi. All used solvent collected and returned to the reservoir tank is routinely distilled to remove NVR. The distilled material is then checked for the same.

Another method employed at Draper to recover expensive fluorocarbons is simple recovery and distillation, whereby volatile fluorocarbon is strip-distilled leaving non-volatile contaminants behind. This method is used when fluorocarbons are sprayed to clean parts and recovered using low-pressure (<100 psi) spray apparatus.

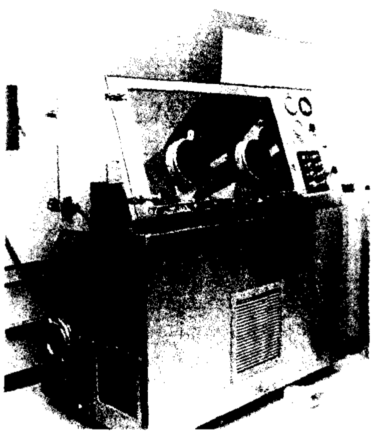
Hydrocarbon/ Fluorocarbon Mixtures

Fluorocarbons by themselves are poor solvents for removal of general contaminants, lubricants, oils, etc. Their solvency can be improved by adding a hydrocarbon such as alkanes, which have solubility with fluorocarbons Use of these mixtures will require a tradeoff: improved solvent character versus flammability/flash point issues as the amount of hydrocarbon in the fluorocarbon increases.

3M currently offers two experimental mixtures. each of which Draper has evaluated. These include L-12874, an azeotrope of = 10 percent methyl tertiary-pentyl ether and 90 percent PF-5060: and L-12862, an azeotrope of = 10 percent isooctane and 90 percent PF-5062. The latter mixture has been found to be more useful in cleaning due to the higher boiling point of 73°C versus 53°C.

The better solvent properties of the fluorocarbon in the mixture. PF-5062 compared to PF-5060, also improves the L-12862 material's cleaning ability. These mixtures can be used for light hydrocarbon oil and grease re-

Figure 5



Contained power-spray apparatus, essentially a glove box with a high-pressure spray gun, limits losses of expensive fluorocarbon solvents.

Table 5
Ring Tensile Strength

RING TENSILE TEST IDENTIFICATION	PEAK LOAD AT FAILURE (pounds)	RING TENSILE STRENGTH (psi)
Reference Ring #1	226	3600
Reference Ring #2	230	3650
Reference Ring #3	264	4200
Reference Ring Average	–	3817
SCF Cleaned #1	325	5100
SCF Cleaned #2	253	4000
SCF Cleaned #3	207	3300
SCF Cleaned Average	–	4133

moval along with extraction of some brominated/fluorinated viscous fluids not amenable to removal with 100 percent fluorocarbon.

Case Study

A study was initiated to replace the use of ODCs in a NASA satellite program for the cleaning of bearing parts lubricated exclusively with Krytox fluids. Removal of Krytox lubricants and greases is a unique and difficult clearing problem, because very few solvents dissolve Krytox adequately.

Solvents such as CFC-113 are currently used to clean Krytox 143 AB and AC from the bearing hardware, a duplex system where the balls are held in place with polyimide retainers.

The study was divided into three tasks: determination of Krytox solubility in ODC alternatives, determining polyimide compatibility with SC-CO_2, and performing fundamental studies of the cleaning effectiveness of ODC alternatives to remove Krytox from metal and polyimide coupons.

Cleaning studies applied metal coupons and polyimide rings to simulate the removal of contaminants from parts. Performing initial studies this way, on coupons instead of live hardware, is a common procedure. After completion of these tasks, information obtained from the alternative processes was applied to actual NASA bearing parts.

I. Solubility Studies

The solubility of Krytox 143 AB and AC was determined in ODC replacement solvents such as PF-5052. The Krytox 143 AB and AC were found to be soluble in all fluorocarbon solvents at levels of at least 50 grams Krytox to 100 milliliters of solvent.

Qualitative solubility studies for Krytox were performed using SC-CO_2 extraction. SC-CO_2 cleaning for Krytox removal was found to be an acceptable evaluation technique for coupon studies in later tasks.

The preliminary SCF studies, strictly visual, simply involved cleaning the Krytox-contaminated metal plates using SC-CO_2. Visual examination revealed that this process effectively removed Krytox.

II. Compatibility Studies: Polyimide with SC-CO_2

Thermal analyses were used to check polyimide's compatibility with SCF. With polyimide rings exposed to SC-CO_2 cleaning conditions to remove Krytox. structural integrity was evaluated using differential scanning calorimetry (DSC) and thermal mechanical analyses (TMA).

TMA and DSC revealed no major differences upon comparison of an unexposed polyimide ring and one exposed to SC-CO_2 (3000 psi and 200°F for 45 minutes).

The coefficient of the thermal expansion of the rings (by TMA) above and below the glass transition temperature compare favorably. The only differences in the initial part of the DSC curves relate to the absorbed CO_2 coming out of the SCF-cleaned retainer and differences in amount of atmospheric moisture absorbed.

An additional evaluation, tensile strength measurement, compared SCF-exposed and unexposed polyimide rings. A total of six rings were pulled to failure, three having been cleaned with SCF and three which hadn't.

On average. no significant difference was observed between the two groups, as shown in Table 5. All test specimens easily exceeded the 2000 psi ring tensile strength, indicating that SCF cleaning does not adversely affect the average ring tensile strength of porous polyimide.

III. Metal Coupon Cleaning Study

440C stainless steel coupons were passivated, polished, and solvent-cleaned for Krytox removal studies with candidate ODC-free processes. All coupons were baselined using grazing angle reflectance (GAR). fourier transform infrared (FTIR). before contamination and cleaning studies.

The stainless steel coupons were used as the test pieces to simulate the

Table 6
ODC-Free Coupon Cleaning Procedures for Krytox 143 AB and AC Removal

ODC-FREE OPERATION	TIME	CONDITIONS
1) PF-5052 soak	15 min.	100 ± 5°F
2) PF-5052 soak	15 min.	100 ± 5°F
3) PF-5052 dip	–	Room temperature
4) Blow dry N_2	–	–
SC-CO_2 cleaning	45 min. cycle	Extractor pressure: 3000 psi Extractor temperature: 150°F CO_2 flow rate: 0.5 liter/minute

Table 7
Polyimide/SCF Cleaning Procedure

OPERATION	TIME	CONDITIONS
SC-CO_2 cleaning (2 cycles initially)	45 min.	Extractor pressure: 3000 psi, Extractor temperature: 200°F CO_2 flow rate: 0.25 liter/minute

removal of Krytox 143 AB and AC from ball bearings- and races. Table 6 outlines the cleaning procedures.

FTIR analyses of coupons from ODC-free procedures revealed complete Krytox removal to the detection limits of the FTIR technique. Coupon cleanliness was determined by grazing angle FTIR. The coupons were analyzed for the characteristic strong IR bands found in the Krytox. Figures 6 and 7 compare the FTIR of the Krytox-contaminated coupon before and after cleaning with PF-5052.

$SC\text{-}CO_2$ cleaning evaluated as an ODC-free process for Krytox removal was also found to remove the bulk Krytox from the coupons. Figure 8 shows a coupon's FTIR spectrum after cleaning with $SC\text{-}CO_2$.

IV. Krytox Removal from Polyimide Retainers

Studies to evaluate $SC\text{-}CO_2$ and PF-5052 solvents, the ODC-free alternatives used for extraction, were performed with polyimide rings.

A ring is SCF-cleaned until the Krytox residue detected in the SCF separator's glass collection liner is <0.1 ppm. The NVR level is based on 1000 ml of PF-5052 used to retrieve the residue in the liner. A clean separator liner is used in each cleaning cycle after the initial two-cycle cleaning procedure shown in Table 7.

The PF-5052 cleaning process involves placing the polyimide ring in 1000 ml of boiling PF-5052. This procedure is continued in 1000 ml of fresh PF-5052 solvent until the NVR is <0.1 ppm. Before the ring is placed into the first 1000 ml of PF-5052, it's rinsed quickly with PF-5052 to remove the gross external Ktytox.

V. Particle Removal Evaluation

To gauge alternative agent performance in the Quadrex equipment, selected precision parts contaminated with typical airborne contaminants such as lint, fibers, body hair, and dust were spray-cleaned with PF-5070 and compared to the currently used CFC-113.

Particle removal was evaluated two ways: comparison of high-magnification photographs of parts before and after cleaning, and particle count (tyndall) of solvent effluent after cleaning. In both cases the PF-5070 compared favorably to the CFC-113.

Synopsis of Results

- Fluorocarbons such as the PF-5052 solvent were found to be adequate ODC solvent alternatives for Krytox removal from metal coupons and polyimide rings.
- $SC\text{-}CO_2$ cleaning was also found to be an adequate ODC alternative - this one solvent-free - for the same application.
- Fluorocarbons such as PF-5052 and PF-5070 are the best alternatives for removal of particles from metal parts and polyimide retainers. This cleaning operation will be the final step in an ODC-free cleaning sequence after fluids are removed.
- $SC\text{-}CO_2$ cleaning involved the exposure of parts to elevated pressures (3000 psi) and elevated temperatures (200°F). Polyimide rings were found to be undamaged after exposure to the $SC\text{-}CO_2$ cleaning conditions required to remove Krytox.

Confirmed Alternatives

This article has presented a fundamental review of fluorocarbons and $SC\text{-}CO_2$ as ODC replacements for specific precision cleaning applications. These alternatives have been found to be useful for removal of fluorinated lubricants and damping fluids along with particles from precision devices not amenable to the common ODC-free procedures used in industry.

Both appear to be excellent cleaners

Figure 6
FTIR Spectrum
of Krytox 143 AC

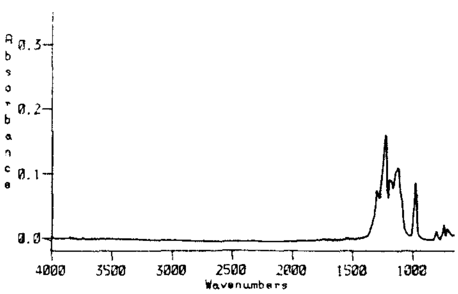


Figure 7
FTIR Spectrum of Coupon
After PF-5052 Cleaning
to Remove Krytox

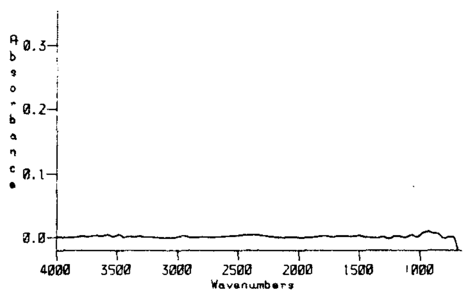


Figure 6
FTIR Spectrum of Coupon
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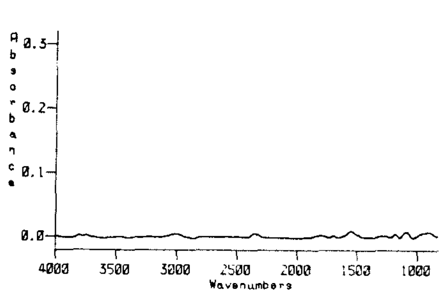

for fluorinated oils and lubricants, materials which are not readily removed by other alternatives.

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