The Search for Nonflammable Solvent Alternatives for Cleaning Aerospace Oxygen Systems

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Photo: NASA/SSC

Background

- Oxygen systems are susceptible to fires caused by particle and nonvolatile residue (NVR) contaminants, therefore cleaning and verification is essential for system safety.
- Cleaning solvents used on oxygen system components must be either nonflammable in pure oxygen or complete removal must be assured for system safety.
- CFC-113* was the solvent of choice before 1996 because it was effective, least toxic, compatible with most materials of construction, and non-reactive with oxygen.
- When CFC-113** was phased out in 1996, HCFC-225 was selected as *an interim replacement* for cleaning propulsion oxygen systems at NASA.
- HCFC-225 production phase-out date is 01/01/2015

*Chlorofluorocarbon **Hydrochlorofluorocarbon

The HCFC-225 Problem

- **NASA Propulsion Test Ops* use > 8000 lbs/year**
- **HCFC-225 is a Class II Ozone Depleting Substance**
  - **Montreal Protocol of 1987**
  - **Clean Air Act Amendments of 1990**
- **HCFC-225 will no longer be available for procurement or new use after 2014**
- **No use of stockpiled <u>new</u> solvent after 2014**
  - **Used/recycled HCFC-225 is permitted – fallback plan at MSFC & SSC**
  - **HCFC-225 has a long shelf life**
- ***Many users in the aerospace industry still rely on stockpiled CFC-113***

*Large scale test facilities at Marshall Space Flight Center, Huntsville, AL and Stennis Space Center, Hancock County, MS

Alternatives for Cleaning Oxygen Systems

Now in use on aerospace components

Alternative Approach	Limitations
Aqueous ultrasonic with verification of NVR by Total Organic Content or by analysis of the cleaning agent	Ultrasound does not scale up for large components, not practical for test stands, corrosion risk to some components
Flammable solvents such as cyclohexane, ethyl acetate, and isopropyl alcohol	High risk where complete drying to remove solvent cannot be assured
Two step process: Clean with a flammable solvent, rinse with a nonflammable solvent	Costly, requires additional equipment, not very practical for field cleaning operations.
Trichloroethylene (vapor degreasing, flush cleaning)	Carcinogen, Hazardous Air Pollutant (HAP), not permitted in some jurisdictions
Clean and/or verify with stockpiled CFC-113 or HCFC-141b	Stockpiles are limited, losses occur even with recapture and reuse
Clean and/or verify with HCFC-225 **MSFC and SSC propulsion test systems**	Must stockpile and use reclaimed material after 01/01/2015

Why HCFC-225 at NASA-MSFC and SSC ?

- **HCFC-225 (AK-225G) is used extensively at Marshall Space Flight Center and Stennis Space Center for cleaning and NVR verification on large propulsion oxygen systems, and propulsion test stands and ground support equipment.**
- **Many components are too large for ultrasonic agitation - necessary for effective aqueous cleaning and NVR sampling.**
- **Test stand equipment must be cleaned prior to installation of test hardware. Many items must be cleaned by wipe or flush in situ where complete removal of a flammable solvent cannot be assured.**
- **The search for a replacement solvent for these applications is ongoing.**

Replacement Solvent Considerations

Safety, Health, and Environmental Hazards

Environmental

ODP - ozone depleting potential

VOC - volatile organic compound

HAP – hazardous air pollutant

GWP – global warming potential (future)

Safety and Health

Toxicity

Flammability (human safety)

Performance Requirements and Cost Considerations

Materials compatibility

- Metals – corrosion
- Nonmetals – swelling, deterioration

Cleaning effectiveness

- Greases, oils, fingerprints, Krytox, etc.
- Effective cleaner in the use condition (hand wipe, cold flush, etc.)
- Dry by evaporation without residue

Oxygen compatibility/flammability

Solvent Volatility

- Must capture effluent to test for NVR

Business Considerations

- Solvent stability/recyclability/disposal - can it be captured and redistilled?
- Availability
- Cost per pound; Equipment modification costs

Ground Rules for Solvent Candidates

The replacement solvent cannot be:

- **Ozone Depleting Substance (ODS)**
  - **Per Montreal Protocol or likely based on chemical structure**
- **Hazardous Air Pollutant (HAP)**
  - Listed at http://www.epa.gov/ttn/atw/188polls.html
- **Carcinogen**

The replacement solvent must be:

- **A single component or a true azeotrope at the use conditions to assure that the performance properties will remain constant.**
- **EPA SNAP approved or approval anticipated**

Essential Performance Requirements

- **Effective** at removing high risk contaminants
  - The critical cleaning process is ambient flush of complex surfaces
  - Critical contaminants are hydrocarbon oils and greases
    - Hydraulic fluid, tube bending oil, gauge oil, fingerprint, etc.
    - Silicone oils and halogenated greases also of concern
- **Compatible** with metals and critical nonmetals used in propulsion oxygen systems
- **Non-reactive** in liquid and gaseous oxygen (LOX/GOX)
  - LOX impact test – no reactions at 72 ft-lb
    - Reconsideration of the threshold acceptance limit has been suggested.
  - Non-reactive at elevated pressures in GOX

Additional Desired Properties

- Less toxic
- Lower VOC or exempt
- Boiling point 100°F < BP < 160°F
- Higher Kauri-butanol (Kb) value has been a useful indicator of expected cleaning performance
  - Solvents with Kb < 20 performed poorly in previous tests
  - Questionable measure for solvents with BP < 40 C (104°F)
- Higher Wetting Index
  - Wetting Index = (1000 x density) / (surface tension x viscosity)
- Higher compatibility with common nonmetals used in SSC/MSFC oxygen systems
  - Many nonmetals can be removed prior to cleaning but this drives cost and risk of damage.

The Search for New Options

- Performed extensive literature search
- Contacted solvent manufacturers and blenders
  - DuPont, 3M, AGC Chemicals, Honeywell, Dow Chemical, Lyondell, Solvay, Arkema, Zeon Chemicals (Japan)
  - Microcare, Petroferm
- Consulted with other aerospace cleaning experts
  - NASA Precision Cleaning & Contamination Control Team
  - Joint Service Solvent Substitution Working Group
- Contacted DOD users of HCFC-225
  - USAF, NAVAIR, NAVSEA (no identified Army users)

Initial Solvent Search Conclusions

- **No bio-based cleaners are potential candidates**
  - **All are flammable, high boiling point, and/or leave residues**
  - **Good industrial solvents, not suitable for precision cleaning**
- **The most effective non-ODS hydrocarbon solvents are flammable, not candidates**
  - **Ethyl acetate, cyclohexane, trans-dichloroethylene (tDCE), nPB**
  - **Nonflammable solvents are all halogenated**
- **Newer nonflammable degreasing solvents are azeotropes of halogenated solvents with tDCE**
  - **tDCE added to improve solvency**
  - **NASA data indicates tDCE > 35-40% unlikely to pass LOX impact test**
  - **Azeotropes with low tDCE% have low boiling points**

Matrix of Solvent Characteristics
40+ solvents compared

Solvents re LOX/GOX cleaning

	A	C	D	E	F	G	H	I	J	K	L	M	N	O
1	**NVR Solvent**	**Availability Risk**	**LOX Comp?**	**MAPTIS code**	**Notes**	**Clean Air Act HAP?**	**ODS?**	**VOC %**	**100 year GWP**	**OSHA AEL (PEL) (ppm)**	**Flash Point**	**Upper explo limit per ASTM E681**	**Lower explo limit per ASTM E681**	**AIT per ASTM E659**
14	3M HFE 7300		No data		HFE-64-13, High BP 208 F	No	No	No	200	100 TWA	None	None	None	408 C
15	3M HFE 7200		Yes			No	No	No	55	200	None	2.4	2.4	375 C
16	3M HFE 72FL	Blend			Not Azeo	No	No	20%	75	200	None	13.7	6.7	396 C
17	3M L-14780	BP 82 F SNAP App'd parts	Yes		78% HFE7000/ 22% tDCE	No	No	22%	87	75 (HFE)	None			
18	Ethyl acetate(47%)/Cyclo hexane(53%)	flammable	No											
19	Ethyl Acetate HPLC grade	flammable	No											
20	DuPont Vertrel XF (see KSC-Spec-P-0021)	Weak NVR solvent KB=9	Yes-WSTF		HC-431 mee				1640					
21	DuPont Vertrel MCA (see KSC-Spec-P-0019)	Good NVR solvent. LOX data is variable SNAP app'd	variable	04091		No`	No	38%	806	200	None	None	None	
22	Isopropyl Alcohol	Not a good NVR solvent/ flammable	No											
23	Perfluoro-n-Butyl Iodide (PFBI)	Impure PFBI form won't pass LOX test	Rated C	04034	Discontinued									
24	Acetone (Spectro grade)	flammable	No	01370										
25	Cyclohexane	very flammable	No											
26	Asahiklin AE3000	SNAP App'd			KB=13	No	No	exem?	540	50	None	None*	None*	
27	Asahiklin AE3000AT	SNAP app'd			KB=32	No	No	46% +	540 (HFE	100 est.	None	None*	None*	
28	Asahiklin AE3000ATE	Prob. won't pass LOX test									None	None*	None*	
29	DuPont Vertrel SDG	Prob. won't pass LOX test									None	14%	7%	
30	DuPont Vertrel MCA Plus	Prob won't pass LOX test			BP 100 F	No	No	50%	650	214	None	11%	6%	

Challenges in Evaluating Solvent Data

- Incomplete data on many solvents
- The most effective cleaners are either flammable in air or banned for new use
- Reporting of toxicity data is inconsistent
  - AEL, PEL, TLV, different measures, or incomplete
- Published flammability data in air is not a conclusive indicator of LOX/GOX reactivity
  - UEL, LEL, AIT in air not always indicative of LOX/GOX data
  - % tDCE threshold to pass LOX impact not established
  - Reactivity of azeotropes at elevated pressures unknown

Potentially Viable Solvent Candidates

- No “drop-in” replacements identified
- Three candidates have boiling points below 100°F
  - Difficult to use in flush applications and degreasers
  - Difficult to recapture for NVR testing or reuse
  - Evaporative cooling may result in excessive condensation
  - Must transport and store in pressurized containers
- Four candidates are questionable for LOX compatibility
- One may not be compatible with required metals
- Two previously tested solvents worth a second look

Potential Solvent Candidates

Single Component	Kb	AEL-8hr	Caveats
AGC Chemical AE3000 (new) HFE-347pc-f2 1,1,2,2-tetrafluoro-1-(2,2,2-trifluoroethoxy)-ethane	13	50 ppm	Low Kb may not clean well, toxicity
Honeywell Solstice PF (new) (1233zd(E)) Trans-1-chloro-3,3,3,-trifluoroprop-1-ene	25	300 ppm	Boiling point of 66°F – must use as aerosol
DuPont Capstone 4-I Perfluorobutyl iodide	No data	375 ppm	Not compatible with AL? expensive, short supply
Solvay Solkane 365mfc 1,1,1,3,3 Pentafluorobutane	14	1000 ppm	Unusual flammability characteristics
Azeotrope			
AGC Chemical AE3000AT (new) 45% tDCE / 55% AE3000	32	200 ppm / 50 ppm	Expected to clean well, may not pass LOX test
3M L-14780 (re-eval) 22% tDCE / 78% HFE-347mcc3 (3M HFE-7000)	Similar to MCA	200 ppm / 75 ppm	Boiling point of 82°F – must use as aerosol Performed well in past tests
DuPont Vertrel MCA (re-eval with new stabilizer) 38% tDCE/ 62% HFC-43-10mee 1,1,1,2,2,3,4,5,5,5-Decafluoropentane	20	200 ppm	Cleans well but borderline LOX compatible on past tests. Low AIT at high GOX pressure.
Solvay Solvokane (new) 30% tDCE/ balance HFC-365mfc 1,1,1,3,3 Pentafluorobutane	25	200 ppm / 1000 ppm	Kb of 25, Boiling point of 97°F, individual components are flammable

Highlighted solvents are low-boiling point (below 100°F) – use in aerosol form

Candidate Solvent Tradeoffs

Single Component	Kb ≥ 20	Should pass LOX	BP > 100°F	AEL-8hr ≥ 200	Metals Compat	VOC exempt
AE3000		✓	✓		✓	(✓)**
Solstice PF	✓	✓		✓	✓	(✓)**
Capstone 4-I	✓*	✓✓	✓	✓	? - Al	
Solkane 365mfc		?	✓	✓	✓	✓
Azeotrope						
AE3000AT	✓	?	✓		✓	!
L-14780	✓*	✓✓			✓	!
Vertrel MCA	✓	?	✓	✓	✓	!
Solvokane	✓	?		✓	✓	!

* No Kb data but other data shows good cleaning performance
** New solvent, VOC exemption expected
! Contains trans-DCE which is not VOC exempt

Solutions may be Use-Specific

- **Field cleaning potential options:**
  - **Lower boiling point solvents delivered in pressurized containers if handling, condensation, and cost can be managed (limited recovery for reuse)**
  - **Less effective solvents with increased cleaning time**
  - **Two step cleaning**
- **NVR sampling may need an array of options:**
  - **Accept lower LOX Impact threshold**
  - **Use PFBI where compatible (high cost)**
  - **Accept options with lower solvency and calculate NVR using an efficiency factor**
  - **Use non-flush sampling methods where feasible**

Conclusions

- No true drop-in replacement is expected.
- Many performance parameters are trade-offs.
- Potential alternatives are either:
  - Lower boiling point than required for NVR sampling or recovery/reuse
  - Higher flammability risk
  - Ineffective cleaners in ambient flush application
  - Potentially corrosive to key metals
- Solvent replacement is an ongoing process due to changing environmental requirements and increasing understanding of human toxicity issues.