Advanced Testing of Safe-Solvent Replacements for CFC-113 For Use in Cleaning Oxygen Systems

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Background

- *Use and Production of CFC-113 Restricted*
- *Replacement Cleaning Solvent Needed*
  - *Solvency As Good or Better Than CFC-113*
  - *Non-Flammable*
  - *Compatible With Liquid and Gaseous Oxygen*
  - *Low Toxicity or Non-Toxic*
  - *Acceptable Environmental Properties*
  - *Similar Volatility and Other Physical Properties*
  - *Manufacturable at Reasonable Cost*

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Phase I Compound Screening

- *Screened 247 Untested Halogenated Compounds*
  - *Solubility Parameter Solvency Screening Property*
    - *Predicted Using Structure-Property Relationships (SPRs)*
    - *Compounds With Similar Solubility Parameters Have Similar Solvency*
  - *Other SPRs Used to Predict Atmospheric Properties, Toxicity, Boiling Point*
- *5 Pure Compounds and 3 Mixtures Recommended*
  - *Solvency and Materials Compatibility Tests Performed*

Solvent Candidates

- *Solvent Candidates*
  - *4-bromo-3-chloro-3,4,4-trifluoro-1-butene, CH_2=CH-CFCl-CF_2Br*
  - *1-chloro-2,2,2-trifluoroethyl difluoromethyl ether, CHF_2-O-CHCl-CF_3*
  - *2-chloro-1,1,2-trifluoroethyl difluoromethyl ether, CHF_2-O-CF_2-CHFCl*
  - *methyl 2,2,2-trifluoroethyl-1-trifluoromethyl ether, CH_3-O-CH-$(CF_3)_2$*
  - *1-bromo-2-(trifluoromethyl)-3,3,3-trifluoropropene, CHBr=C-$(CF_3)_2$*
  - *mixtures of CH_2=CH-CFCl-CF_2Br and CHF_2-O-CHCl-CF_3*
- *Baseline Solvents For Comparison*
  - *1-iodononafluorobutane, CF_2I-CF_2-CF_2-CF_3 (Ikon P)*
  - *1,3-dichloro-1,1,2,2,3-pentafluoropropane, CF_2Cl-CF_2-CHFCl (AK-225G)*
  - *CFC-113, $CFCl_2$-CF_2Cl*

Objectives

- *Perform Solvency Tests Against Selected Contaminants*
- *Determine Compatibility With Liquid and Gaseous Oxygen*
- *Measure Flammability*
- *Determine Atmospheric Impact*
- *Determine Toxicity Characteristics*
- *Measure Key Thermophysical Properties*
- *Recommend Replacement Solvent*
- *Determine Cleaning Effectiveness in an Oxidizer System*
- *Assess Manufacturability of Recommended Solvent*

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Solvency Tests

- *Apply Approximately 0.1 grams of Contaminant on 1" Square Stainless Coupon*
- *Clean Static and Using Ultrasonics in 15 ml. of Solvent*
- *Mass of Contaminant Removed Determined By Weight Difference of Coupon Before and After Cleaning*
- *Most Solvent Candidates Cleaned As Good or Better Than CFC-113*

- *Selected Contaminants:*
  - *Mil-Spec 83232 Hydraulic Oil*
  - *Mil-Spec 7808 Engine Oil*
  - *Mil-Spec 81322 Hydrocarbon Grease*
  - *Krytox*
  - *Simple Green Aqueous Cleaner*

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Compatibility With Gaseous Oxygen

- *ASTM G72, "Standard Test Method for Autogenous Ignition Temperature of Liquids and Solids in a High-Pressure Oxygen Enriched Environment"*
  - *AIT < 250°F, Not Recommended for O_2 Systems*
  - *AIT 250°F - 400°F, Use Caution in O_2 Systems*
  - *AIT > 400°F, Recommended for O_2 Systems*
- *Performed by Wendell Hull & Associates*

GO_2 Compatibility Results

Solvent	Average AIT	Category
methyl 2,2,2-trifluoroethyl-1-trifluoromethyl ether	451°F	Recommended
1-bromo-2-(trifluoromethyl)-3,3,3-trifluoropropene	725°F	Recommended
4-bromo-3-chloro-3,4,4-trifluoro-1-butene	378°F	Caution
1-chloro-2,2,2-trifluoroethyl difluoromethyl ether	390°F	Caution
2-chloro-1,1,2-trifluoroethyl difluoromethyl ether	464°F	Recommended
1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113)	no ignition @ 50 psia and 2000 psia	Recommended
1-iodononafluorobutane (Ikon P)	345-355°F @ 2000 psia	Caution
1,3-dichloro-1,1,2,2,3-pentafluoropropane (AK-225)	no ignition @ 50 psia and 2000 psia	Recommended

Compatibility With Liquid Oxygen

- *ASTM G86, "Standard Test Method for Determining Ignition Sensitivity of Materials to Mechanical Impact in Pressurized Oxygen Environments"*
  - *Pass if No Reactions in 20 Impacts*
  - *Pass if Not More Than One Reaction in 60 Impacts*
- *Performed By NASA-WSTF Personnel*

LOX Compatibility Results

Solvent	Results	Category
methyl 2,2,2-trifluoroethyl-1-trifluoromethyl ether	1 Reaction/60 Impacts	***Passed***
1-bromo-2-(trifluoromethyl)-3,3,3-trifluoropropene	2 Reactions/28 Impacts	***Failed***
4-bromo-3-chloro-3,4,4-trifluoro-1-butene	2 Reactions/10 Impacts	***Failed***
1-chloro-2,2,2-trifluoroethyl difluoromethyl ether	0 Reactions/20 Impacts	***Passed***
2-chloro-1,1,2-trifluoroethyl difluoromethyl ether	0 Reactions/20 Impacts	***Passed***
25% 4-bromo-3-chloro-3,4,4-trifluoro-1-butene 75% 1-chloro-2,2,2-trifluoroethyl difluoromethyl ether	1 Reaction/60 Impacts	***Passed***
50% 4-bromo-3-chloro-3,4,4-trifluoro-1-butene 50% 1-chloro-2,2,2-trifluoroethyl difluoromethyl ether	0 Reactions/20 Impacts	***Passed***
1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113)		***Passed***
1-iodononafluorobutane (Ikon P) (Taken From Reference 4)	2 Reactions/17 Impacts	***Failed***
1,3-dichloro-1,1,2,2,3-pentafluoropropane (AK-225)		***Passed***

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Flammability Tests

- *ASTM D93, "Standard Test Method for Flash Point by Pensky-Martens Closed Tester"*
- *Performed By Mainstream*
- *No Flash Points Observed For Candidate Solvents or Baseline Solvents*

Atmospheric Impact

- *Some Information Found In Open Literature*
- *Compounds With Unknown Information Tested By Dr. Vladimir Orkin of NIST*
  - *Measured Reactivity Toward Hydroxyl Radicals (Atmospheric Lifetime)*
  - *Measure UV Absorption Cross Section (ODP and GWP)*

Atmospheric Properties

Compound	ODP	GWP	Atmospheric Lifetime
1-chloro-2,2,2-trifluoroethyl difluoromethyl ether	0.004-0.03	200	2-5.9 yrs.
2-chloro-1,1,2-trifluoroethyl difluoromethyl ether	0.004-0.04	330	2.4-8.2 yrs.
4-bromo-3-chloro-3,4,4-trifluoro-1-butene	0.00014-0.012	< 10	4.2 days
methyl 2,2,2-trifluoroethyl-1-trifluoromethyl ether	0	13 - 43	65 days
CFC-113	0.9	5000	85 yrs.
Ikon-P	< 0.0025	< 2	2 days
AK-225	0.02-0.03	170-530	6.6 yrs.

Toxicity Characteristics

- *Ames Test For Mutagenicity*
- *Acute Skin Irritation (Rabbit)*
- *Acute Oral Toxicity (Rat)*
- *Tests Performed By ST&T Consultants*
  - *Performed per Good Laboratory Practice (GLP)*

Toxicity Properties

Compound	LD50	Ames	Dermal Irritation Index
1-chloro-2,2,2-trifluoroethyl difluoromethyl ether	8.1 g/kg	negative	0.2
2-chloro-1,1,2-trifluoroethyl difluoromethyl ether	13.0 g/kg	negative	0.08
4-bromo-3-chloro-3,4,4-trifluoro-1-butene	> 40 g/kg	negative	2.13
methyl 2,2,2-trifluoroethyl-1-trifluoromethyl ether	> 40 g/kg	negative	0.25
1-bromo-2-(trifluoromethyl)-3,3,3-trifluoropropene	0.1 g/kg	negative	1.33
CFC-113	43 g/kg	negative	mild irritant
Ikon-P	no data	negative	mild irritant
AK-225	> 5 g/kg	negative	no data

Dermal Irritation Index

3.0-4.9 = potential for severe irritation
2.0-2.9 = potential for moderate irritation
1.0-1.9 = potential for mild irritation
0.1-0.9 = potential for slight irritation
<0.1 = no irritation potential

Recommend Solvent Replacement

- *Ranking Scheme Developed Based On Properties Studied*
  - *Cost Included in Ranking*
- *Mixture of 25% 4-bromo-3-chloro-3,4,4-trifluoro-1-butene and 75% 1-chloro-2,2,2-trifluoroethyl difluoromethyl ether Recommended*

Key Physical Properties

- *Measured At 25°C By Mainstream*
  - *Liquid Density*
  - *Liquid Viscosity*
  - *Surface Tension*
  - *Vapor Pressure*
  - *Boiling Range*
  - *Freezing Point*

Key Physical Props. At 25°C

Property	Value
Liquid Density	1.53 g/ml
Liquid Viscosity	0.554 cP
Surface Tension	17.1 dyne/cm
Vapor Pressure	264 mm Hg
Boiling Range	55-96°C
Freezing Point	< -127°C

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Cleaning An Oxidizer System

- *Air Force Oxidizer System Sent to Mainstream*
- *Procedure Based on NASA WSTF Cleaning Studies*
- *Contaminants:*
  - *Krytox GPL 224*
  - *83282 Hydraulic Oil*
  - *7808 Hydraulic Grease*
  - *81322 Hydrocarbon Grease*
  - *2 Solutions Prepared: 0.95 and 1.6 grams of Each Contaminant Dissolved in CFC-113*
  - *32 ml. of Solution Introduced to System*

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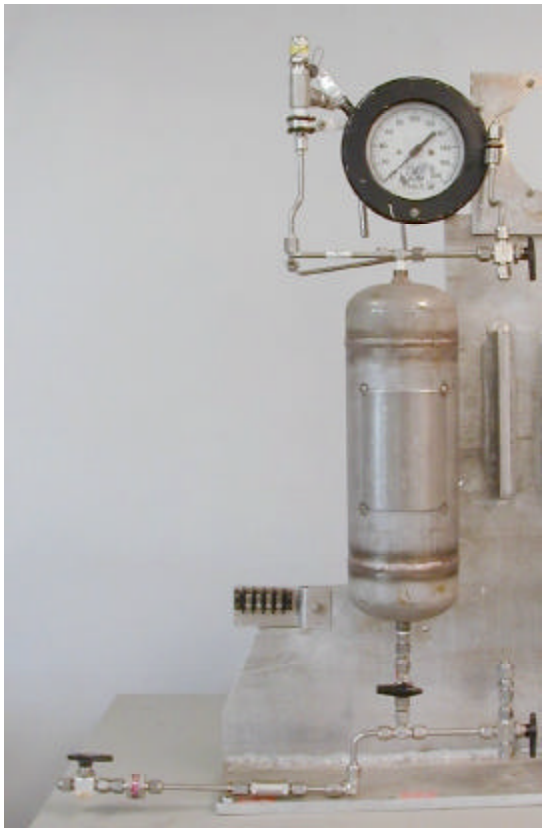
Photograph of System



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Cleaning Results

Contaminant Solution	**CFC-113 Results**	**Mainstream Solvent Blend Results**
Dilute (0.95 grams each contaminant)	80.3 % Removal	89.6 % Removal
Concentrated (1.56 grams each contaminant)	90.6 % Removal	74.0 % Removal

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Assess Manufacturability

- *Patent Application Filed With USPTO*
- *Mainstream's Estimated Delivery Price:*
  - *$185/gallon at 500 gallons per month*
- *Technology Spun-off Into HVAC&R Industry*
  - *Flushing Solvent*
  - *Leak Detector For Furnace Heat Exchangers*
  - *Sensitive Refrigerant Leak Detector*

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Conclusions

- *Replacement Solvent For CFC-113 For Cleaning Oxygen Systems Identified*
  - *Superior to CFC-113 in Coupon Solvency Tests*
  - *Similar to CFC-113 in Cleaning Oxygen Systems*
  - *Acceptable Toxicity and Atmospheric Properties*
  - *Non-Flammable and Oxygen Compatible*
  - *Affordable Cost*
  - *Spin-off Commercial Applications in HVAC&R Industry*

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