HCFC-225 Solvent Replacement Project - Cleaning and Verifying MSFC/SSC Propulsion Oxygen Systems

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Photo: NASA/SSC

HCFC-225 Solvent Replacement Project

- **Following prohibition of CFC-113, NASA propulsion test facilities used Asahiklin AK-225G (HCFC-225cb) solvent to clean and verify the cleanliness of propulsion oxygen system components.**
- **HCFC-225cb is a Class II Ozone Depleting Substance (ODS).**
- **Effective January 1, 2015, Title VI of the U.S. Clean Air Act banned manufacture/import and use of non-recycled HCFC-225ca or HCFC-225cb except for material in inventory before that date.***
- **The NASA Rocket Propulsion Test (RPT) Program funded a multi-center project to identify a replacement for AK-225G.**
  - **Marshall Space Flight Center, Huntsville, Alabama – Project leader**
  - **Stennis Space Center, Mississippi**
  - **Johnson Space Center's White Sands Test Facility, Las Cruces, New Mexico**
- **Target: Replace AK-225G prior to depletion of MSFC/SSC stock.**

*Reference 40 CFR 82.15(4)(i and ii) http://www.ecfr.gov/cgi-bin/text idx?SID=5132d3ccdc8ddce918c36d27f2297e68&node=se40.18.82_115&rgn=div8

Acknowledgements

This was a two year NASA multi-center effort:

- **Marshall Space Flight Center (MSFC)**
  - Materials & Processes Laboratory, Environmental Effects Contamination Team
  - Space Systems, Mechanical Fabrication Branch Precision Cleaning Lab
  - M&P Chemistry Lab and Combustion Research Facility
  - Propulsion Test and Valve and Component Shops
- **Stennis Space Center (SSC)**
  - Gas & Materials Science Laboratory
  - Component Processing Facility
  - NESC-SSC Chief Engineer
- **Johnson Space Center's White Sands Test Facility (WSTF)**
  - Oxygen Compatibility Test Team
- **NASA Engineering & Safety Center (NESC) Independent Assessment Team**
  - NESC-MSFC Chief Engineer
  - NESC-Langley Research Center Materials Laboratory
  - Gas & Materials Science Laboratory Lead Scientist, SSC

Acknowledgements

The following solvent suppliers contributed test solvent and technical support:

- Honeywell (Solstice™ Performance Fluid)
- 3M (L-14780 Developmental Solvent)
- DuPont Vertrel® Specialty Products (Vertrel® MCA)
- DuPont Chemicals and Fluoroproducts (Capstone® 4-I)
- Solvay Fluorides LLC (Solkane® 365mfc and Solvokane®)
- AGC Chemicals Americas (AE3000 and AE3000AT)*

Trademarks:

***Samples not received in time to support test schedule.**

Project Summary

- **A joint test plan was written, referencing the solvent selection criteria in ASTM G127 *Standard Guide for the Selection of Cleaning Agents for Oxygen Systems.***

  Materials Compatibility – Cleaning Effectiveness – Oxygen Compatibility

- **An exhaustive market search was performed for potential candidates.**
  - **Screening criteria included health/safety; environmental/regulatory; expected performance; business considerations.**
  - **All potentially viable candidates were halogenated solvents.**
  - **No bio-based cleaners met the screening criteria.**
- **All testing is complete.**
- **One solvent was recommended for implementation.**
- **One alternate solvent was identified as a potential back-up.**
- **The Final Report is complete and will be issued as an unrestricted NASA Technical Publication.**

The Solvent Selection Challenge

Safety, Health, and Environmental Requirements

Environmental

- ODP - ozone depleting potential
- VOC - volatile organic compound
- HAP - hazardous air pollutant
- GWP - global warming potential

Restrictions are expected to increase with time

Safety and Health

- Human Toxicity (exposure limits)
- Flammability (human safety)

Performance Requirements and Cost Considerations

- **Materials Compatibility**
  - Metals – corrosion
  - Nonmetals – swelling, cracking, leaching
- **Cleaning effectiveness**
  - Greases, oils, fingerprints, Krytox, etc.
  - Effective cleaner in the use condition (cold, flush, minimal agitation)
  - Solvent drying/removal
  - NVR verification process compatibility
- **Oxygen compatibility**
- **Cost Considerations**
  - Purchase cost and loss rate
  - Capital equipment
  - Transportation and Storage
  - Solvent stability/recyclability/disposal

Note: This project focused on use of AK-225G where water-based cleaning agents were not suitable.

Solvent Blends - Observations

- **The best non-ODS/non-Hazardous Air Pollutant (HAP) pure solvents for removing hydrocarbons are very flammable.**
  - Ethyl acetate, cyclohexane, trans-1,2 dichloroethylene, petroleum-based solvents…
- **Many solvent blends are now marketed to replace CFCs/HCFCs.**
  - Fluorinated solvents are blended with tDCE to suppress the flammability of tDCE while retaining hydrocarbon-cleaning power.
  - Alcohols are added to enhance removal of particulate and ionic contaminants (i.e. flux). Not essential for cleaning oxygen systems.
  - Azeotropic (constant boiling) blends are preferred for vapor degreasing to maintain stable proportions over the life of the blend. Stability of proportions is important for predictability of flammability characteristics but little is understood about the stability of these blends when used under other conditions than constant boiling.
  - Azeotropes with tDCE will have boiling points below 48^{o}C (118^{o}F).
- **Chlorinated solvents including tDCE require stabilizer additives to prevent breakdown and corrosive acid formation.**
  - Stabilizer packages usually contain two or more additives and are considered proprietary. Different suppliers use different stabilizers, some are patented.
  - Although stabilizers are < 1% of the solvent formula they can affect reactivity in oxygen and can leave NVR residues sufficient to affect precision cleaning.

Observations on Solvent Screening for Cleaning Oxygen Systems

- **Prior to selecting solvent candidates to replace AK-225G, oxygen compatibility test records of other solvents were researched**
  - NASA Materials and Processes Technical Information System (MAPTIS).
  - Publications from five NASA-sponsored Aerospace Environmental Technology Conferences 1995-2003.
  - Other literature sources.
- **Conclusions:**
  - Solvent blends containing any form of alcohol performed poorly in oxygen compatibility tests.
  - Solvents that exhibited no flash point in air but did exhibit Upper Explosion Limit/Lower Explosion Limit (UEL/LEL) appeared to perform poorly in oxygen compatibility tests but this was not consistent.
  - Solvent blends with a higher percentage of tDCE performed poorly in oxygen compatibility tests. Insufficient data to establish a threshold and likely depends on the co-solvent and stabilizer additives. tDCE >50% is unlikely to perform well in oxygen compatibility tests.

Solvent Candidates

Single Component	Kb	AEL-8hr	Concerns
AGC Chemicals 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,-trifluoropropene	25	800 ppm	Boiling point of 19°C (66°F)
DuPont™ Capstone® 4-I (chemical intermediary) 85%+ Perfluorobutyl iodide	No data	375 ppm	Not compatible with Aluminum? Expensive, short supply
Solvay Solkane® 365mfc (HFC-365mfc) 1,1,1,3,3 Pentafluorobutane	14	1000 ppm	Low Kb may not clean well, Unusual flammability characteristics
Azeotropic Blends with trans-1,2 Dichloroethylene (tDCE)	(tDCE = 117)	(tDCE = 200 ppm)	Pure tDCE is flammable. Flash point in air = 2.2°C (36°F). NOT LOX compatible.
AGC Chemicals AE3000AT (new) 45% tDCE / 55% AE3000	32	200 ppm / 50 ppm	Expected to clean well, may not pass LOX test
3M L-14780 developmental solvent 22% tDCE /78% (HFE-347mcc3) methyl perfluoropropyl ether (3M HFE-7000)	Similar to MCA	200 ppm / 250 ppm	Boiling point of 28-30°C (82-86°F) – Performed well in past tests (1990's)
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 (Vertrel XF)	20	200 ppm	Cleans well but borderline LOX compatible on past tests. Low AIT at high GOX pressure.
Solvay Solvokane® (new) 30% tDCE/ 70% (HFC-365mfc) 1,1,1,3,3 Pentafluorobutane	25	200 ppm / 1000 ppm	Boiling point of 36°C (97°F), individual components are flammable

Kb = Kauri-Butanol value per ASTM D1133; AEL-8hr = 8 hour Airborne Exposure Limit

Test Approach

PHASE ONE:

- Nonvolatile Residue of Neat Solvents (MSFC/SSC) – Gravimetric and FTIR
- Quick Screen Solvency with Saturation and Odor Studies (SSC)
- First Down-Selection Sept 2013 - Selected 3 Candidates (MSFC/SSC/WSTF)

PHASE TWO:

- Metals Compatibility (SSC)
- Nonmetals Compatibility (MSFC)
- Initial Oxygen Compatibility Tests (WSTF)
- Second Down-Selection Feb 2014 - Selected 2 Candidates (MSFC/SSC/WSTF)
- NASA Engineering and Safety Center- Independent Assessment

PHASE THREE:

- Extended Oxygen Compatibility Tests and Assessments (MSFC/WSTF/IAT)
- Cleaning Effectiveness/Nonvolatile Residue Removal Efficiency (MSFC)
- On-Site Vendor Demonstrations (MSFC/SSC)
- Final Down-Selection Oct 2014 (MSFC/SSC/WSTF)

PHASE FOUR:

- Component Level Cleaning and Implementation Assessments (MSFC/SSC)

Materials Tested

- Materials to be tested with the solvent candidates were selected by a MSFC/SSC engineering team with input from:
  - Materials lists from ASTM MNL36 *Safe Use of Oxygen and Oxygen Systems* and ASTM G127
  - Historic and current propulsion system designs
  - Users from MSFC/SSC propulsion test facilities and cleaning facilities.
  - Test reports from 1990's-2000's to qualify HCFC-225 to replace CFC-113.

METALS

- Carbon Steel (4140)
- Stainless Steels (17-4PH, A286, 304 & 440C)
- Nickel Alloys (Monel® 400, Inconel® 718)
- Co Cr Ni Alloy (Elgiloy®)
- Tin Bronze
- Brass (Naval Brass)
- Aluminum (6061 -T6, 2195 -T8 & 2219 -T6)

NONMETALS

- FKM V0747-75 (like Viton® A)
- FFKM (Kalrez®)
- Buna-N
- PTFE Algoflon® E2
- FEP Teflon®
- Kel-F® 81 PCTFE
- Vespel® SP-21
- Ketron® PEEK
- Gylon® 3502

CONTAMINANTS

- Mineral Oil
- WD-40®
- MIL-PRF-83282 (synthetic hydraulic fluid)
- Di-2-ethylhexylsebacate (gauge calibration oil)
- Krytox® GPL103 (lubricant)
- Mobil™ DTE-25 (machine hydraulic fluid)
- Simulated fingerprint (ASTM D4265)
- Krytox® 240AC & Christo-lube® (grease)
- Big Red Grease (crane grease)

Quick Screen Solvency Test

SSC Gas & Materials Science Lab

Seven Solvents Tested

- AK-225G
- Solstice™ PF
- L-14780
- Capstone® 4-I
- Solkane®
- Solvokane®
- Vertrel® MCA

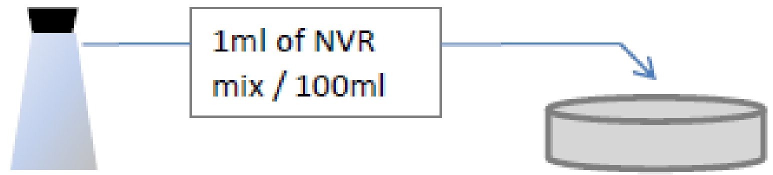
Mixed Contaminant – Equal Parts:

- Mineral Oil
- WD-40®
- MIL-PRF-83282 Hydraulic Fluid
- Di-2-ethylhexylsebacate (gauge calibration oil)
- Krytox® GPL103 (fluorocarbon lubricant for oxygen systems)

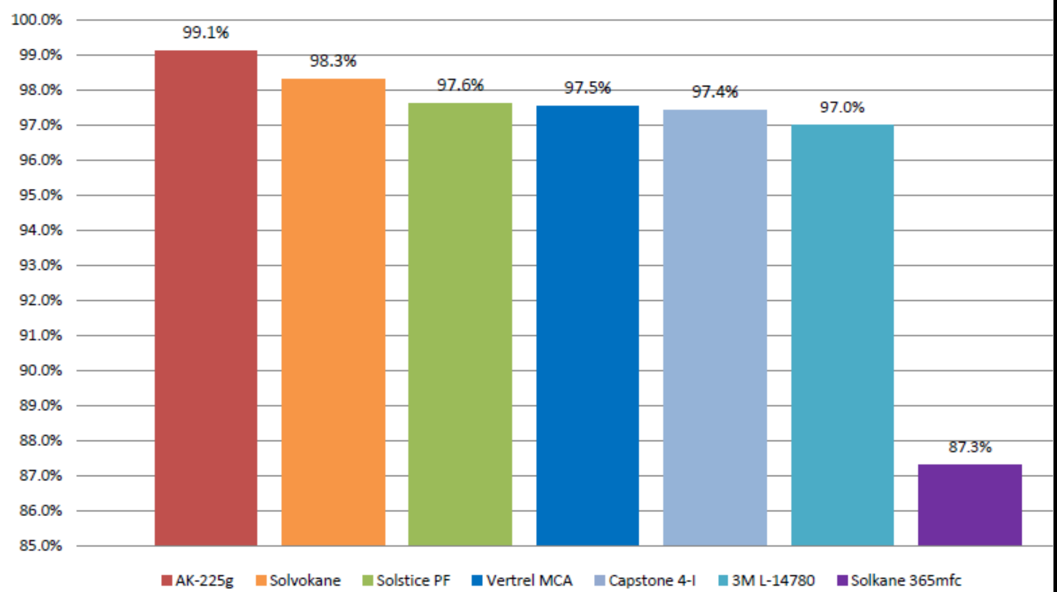
0.5240 g mixed in 100 ml AK-225G as a carrier solvent

Odor Observations:

- Only Capstone® 4-I odor was highly objectionable



A standard quantity of mixed contaminant is applied to a dish, dried, and weighed. The dish is flushed three times with the test solvent. The dish is re-weighed and % removal is calculated. Repeated 10X each solvent.



FIRST DOWN SELECTION

- Solstice™ PF, L-14780, and Solvokane® were selected for further testing.
  - Performed well in solvency tests; no user objections to odor.
  - Favorable health and/or environmental characteristics.
- Solkane® performed poorly in the quick look solvency tests.
- Capstone® 4-I was found to be highly contaminated with particulate and unstable, rapidly changing color during test activities, and corrosive. Needs a stabilizer.
  - Tests at MSFC for a non-NASA customer showed that Capstone® 4-I rapidly corroded stainless steel, aluminum, and nickel alloys.
  - DuPont™ indicated that there was insufficient business case to develop a stabilizer for Capstone® 4-I to support use as a cleaning solvent.
- Vertrel® MCA data in NASA records was considered sufficient at this point.

Metals Compatibility

SSC Gas & Materials Science Lab

Liquid and Vapor phase immersion of metal specimens in each solvent at boiling.

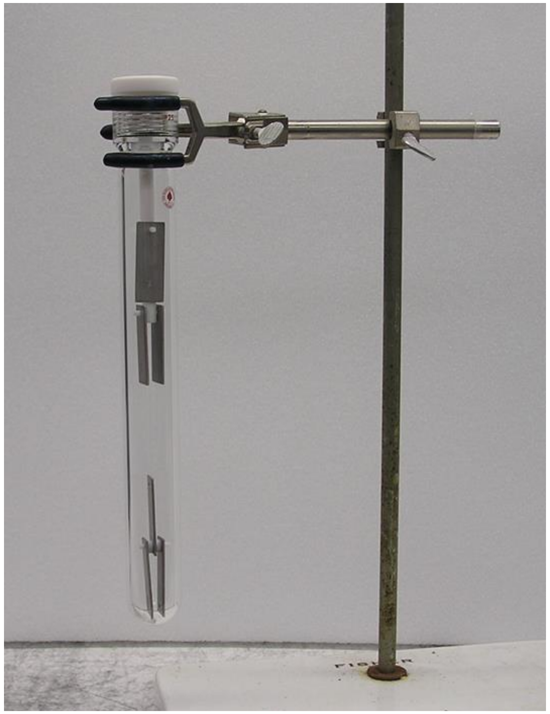
Specimens inspected and weighed at 24 hours and 168 hours

Four Solvents

- AK-225G
- Solstice™ PF
- 3M L-14780
- Solvokane®

Thirteen Metals

- Carbon Steel (4140)
- Stainless Steels (17-4PH, A286, 304 & 440C)
- Nickel Alloys (Monel® 400 & Inconel® 718)
- Co Cr Ni Alloy (Elgiloy®)
- Tin Bronze
- Brass (Naval Brass)
- Aluminum (6061 -T6, 2195 -T8 & 2219 -T6)



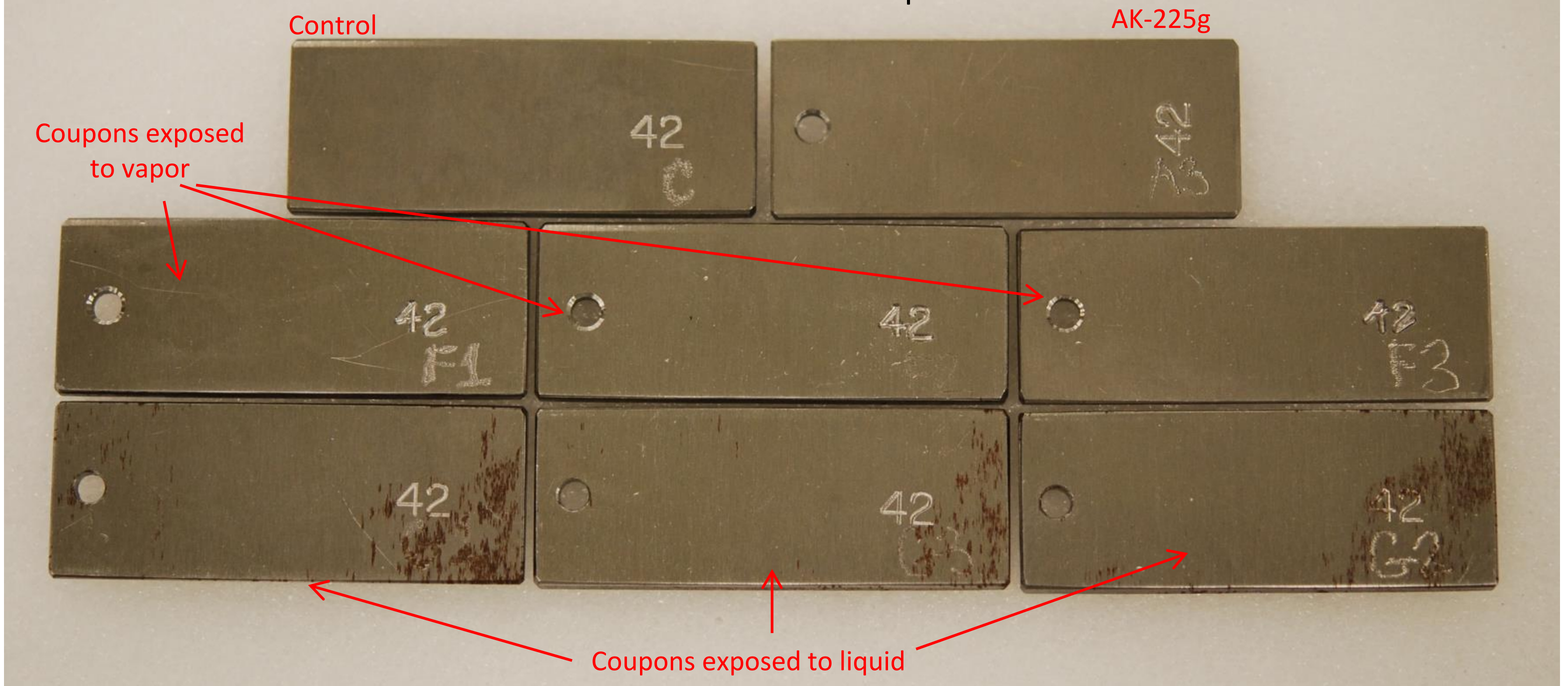
Coupons set in High Pressure Rated Glass Tube.

Six coupons of each alloy were exposed to each solvent, three immersed and three in vapor, retained by Teflon spacers. After exposure, coupons were compared to an unexposed control coupon and a coupon exposed to AK-225G.

Metals Compatibility Results

- **No change observed in any alloy/solvent combination immediately after 24 hour and 168 hour exposure.**
- **Four weeks later, discoloration was observed on the 4140 low alloy steel exposed to the 3M L-14780. Test was repeated and confirmed.**

AISI 4140 Low Alloy Steel Exposed to 3M L-14780
4 Weeks After the 168 hr Exposure Test



Note: All three coupons that were exposed to the 3M liquid show discoloration, while all three coupons exposed to the 3M vapor show no discoloration. When the test was repeated, all coupons exposed to liquid and vapor showed discoloration.

Nonmetals Compatibility

MSFC M&P Contamination Lab

Three specimens of each nonmetal were immersed in a fisher-porter tube filled with solvent and boiled for 15 minutes.

- After immersion, specimens were suspended in a desiccator for 30 minutes
- Specimens were weighed, measured, and elastomers tested for hardness before and after exposure, and repeated until weight stabilized.

Four Solvents

- AK-225G
- Solstice™ PF
- 3M L-14780
- Solvokane®

Nine Nonmetals

- FKM V0747-75
- FFKM (Kalrez®)
- Buna-N
- PTFE Teflon
- FEP Teflon
- Kel-F® 81 PCTFE
- Vespel® SP-21
- Ketron® PEEK
- Gylon®

Nonmetals Compatibility Results

AK-225G	% Weight Gain			% Linear Swell		
Material	Post Test	24 hours	7 days	Post Test	24 hours	7 days
FKM (V0747-75) (tested 2X)	12.6	7.8	5.5	5.0	3.0	2.7
	16.0	9.4	6.7	4.9	3.6	3.7
FFKM (Kalrez)	14.5	7.7	5.0	4.0	2.7	1.7
NBR (Buna-N)	14.7	6.6	3.0	1.4	-1.5	-2.1
PTFE Teflon	0.2	-	-	1.1	0.4	-
FEP Teflon	0.5	-	-	-1.2	-0.5	-
PCTFE (Kel-F)	0.2	-	-	0.5	-	-
Vespel 21	0.0	-	-	-0.2	-	-
PEEK	0.0	-	-	0.9	-	-
Gylon	0.2	-	-	Note 1	-	-

SOLSTICE PF	% Weight Gain			% Linear Swell		
Material	Post Test	24 hours	7 days	Post Test	24 hours	7 days
FKM (V0747-75)	12.4	6.2	3.6	4.6	2.3	0.4
FFKM (Kalrez)	4.2	2.1	1.3	1.1	-0.4	1.8
NBR (Buna-N)	5.6	1.6	0.0	0.6	-0.5	-0.1
PTFE Teflon	0.2	-	-	0.5	-	-
FEP Teflon	0.3	-	-	-0.2	-	-
PCTFE (Kel-F)	0.1	-	-	0.7	-	-
Vespel 21	0.0	0.0	-	-0.4	0.1	-
PEEK	0.0	-	-	0.9	-	-
Gylon	0.0	-	-	Note 1	-	-

L-14780	% Weight Gain			% Linear Swell		
Material	Post Test	24 hours	7 days	Post Test	24 hours	7 days
FKM (V0747-75)	5.9	3.6	2.6	1.8	1.0	0.7
FFKM (Kalrez)	6.0	3.6	2.5	2.9	1.9	1.4
NBR (Buna-N)	6.3	1.7	-0.3	2.0	0.6	0.4
PTFE Teflon	0.1	-	-	0.0	-	-
FEP Teflon	0.3	-	-	-0.2	-	-
PCTFE (Kel-F)	0.0	-	-	-0.1	-	-
Vespel 21	0.1	-	-	0.0	-	-
Ketron PEEK	0.1	-	-	0.2	-	-
Gylon	0.1	-	-	Note 1	-	-

SOLVOKANE	% Weight Gain			% Linear Swell		
Material	Post Test	24 hours	7 days	Post Test	24 hours	7 days
FKM (V0747-75)	17.8	9.3	6.0	8.3	4.8	3.0
FFKM (Kalrez)	1.7	1.1	0.7	0.4	2.4	-1.0
NBR (Buna-N)	12.9	4.0	0.7	2.9	0.6	-0.3
PTFE Teflon	0.1	-	-	1.1	-	-
FEP Teflon	0.1	-	-	-0.4	-	-
PCTFE (Kel-F)	0.0	-	-	0.2	-	-
Vespel 21	0.3	-	-	-0.1	-	-
Ketron PEEK	0.1	-	-	-0.1	-	-
Gylon	0.0	-	-	Note 1	-	-

Note 1: Linear swell measurements for Gylon not valid. The process to cut Gylon from sheet results in an irregular outer edge.

Autogenous Ignition Temperature

- ASTM G72 Autogenous Ignition Temperature Tests
  - AK-225G, Solstice™ PF, L-14780, and Solvokane® tested.
  - 3M Novec® 7100 (HFE-7100) also tested as a control.
  - WSTF investigated variables to assure valid test of volatile liquids such as cleaning solvents
    - Increased sample weight up to 1.00 +/- 0.10 gram
    - Pre-chill of solvent sample to minimize loss
    - If no ignition at low test pressures, increase test pressure.
- Recommended wording for G72 section 8.2 submitted to ASTM G04 (Barry Newton, 10-22-2014) for testing of volatile liquids.
  - Includes increasing sample size and test pressure (for low pressure tests) when non-ignition occurs.

Work Item- G72 Recommended changes

Recommended Changes: Increased Sample Size, Sample chilling , Increased pressure if TL observed at low P ranges (<1000psi),

8.2 Weigh out a 0.20 +/- 0.03-g sample, either in liquid or solid form, into the sample holder.

TO:

8.2 Weigh out a sample into the sample holder.

8.2.1 Solid or non-volatile liquid sample weight should be 0.20 +/- 0.03-g

8.2.2 For volatile liquids such as cleaning solvents, a larger sample weight up to 1.00 +/- 0.10-g may be required to obtain a valid AIT result. It is good practice to pre-chill volatile liquids with boiling points near or below room temperature using an ice bath to prevent excessive loss of solvent prior to test. It is recommended a final weight be taken immediately before test to verify quantity present.

Note: A lab may choose to incrementally approach the sample size of 1g evaluating pressure spikes and system safety limits as sample size increments are increased.

Note: A non ignition at maximum temperature when testing at lower pressures (<1000psi) may indicate an insufficient oxidizer to fuel ratio. When testing at lower pressures, if obtaining a non-ignition at maximum temperature it is recommended that testing be performed at higher pressures until an AIT is obtained. If suspected, testing at the standard 1500psia or higher and increased sample mass (suggested 1.0g) is recommended to confirm an unreactive material.

Proposed wording developed by Susana Harper (NASA-JSC/WSTF), Fred Juarez (NASA-JSC/WSTF(Jacobs)), Jennifer McMillian (NASA-MSFC) and Nikki Lowrey (NASA-MSFC(Jacobs))

10-22-2014

Initial LOX Mechanical Impact Tests

- Solvokane® was most reactive (also in AIT tests) – eliminated as a candidate.
- Significant discrepancies observed between MSFC/WSTF data.
- NESC Independent Assessment Team formed to investigate test variables.

Solvent	JSC-WSTF			MSFC (External Study)	
	Test 13A Ambient LOX Impact at 98 J (72 ft-lb)	**Test 13A LOX Impact Threshold for 0/20 Reactions (Note 1)**	**Test 13B Pressure Threshold for No Reactions at 98 J (72 ft-lb)**	**Test 13A Ambient LOX Impact at 98 J (72 ft-lb)**	**Test 13A LOX Impact Threshold (Note 2)**
Solstice™ PF	**Fail**	20 J (15 ft-lb)	52 MPa (7500 psi)	**Pass** - 0/20	98 J (72 ft-lb)
L-14780	**Fail**	54 J (40 ft-lb)	52 MPa (7500 psi)	**Pass** – 0/20	98 J (72 ft-lb)
Solvokane®	**Fail**	< 14 J (10 ft-lb) (Note 3)	< 3.5 MPa (500 psi) (Note 3)	**Fail** – 2/6	74 J (55 ft-lb)

Notes:
(1) Energy Threshold Screening Method in accordance with ASTM G 86-98a.
(2) Determined by the Bruceton sensitivity test method.
(3) Lower limit of the test apparatus. Threshold could not be determined.

Nonvolatile Residue Removal Efficiency

This test simulates an NVR verification sampling procedure.

Individual contaminants were applied to a test panel and dried, flushed with the test solvent, and the effluent was dried and weighed. The panel was sampled again with AK-225G to measure nonvolatile residue not removed by the test solvent that was removed by AK-225G. NVR was measured gravimetrically. Each test was repeated 3 times. If results varied >10%, or the total contaminant weight recovered was significantly different than the contaminant weight applied, the test set was repeated.

Three Solvents

- AK-225G
- Solstice™ PF
- 3M L-14780

Test Panels:

Stainless steel.
Design based on ASTM E1235-08.
152 x 152 mm (¼ ft^2).

Nine Contaminants

- Mineral Oil
- WD-40®
- MIL-PRF-83282 hydraulic fluid
- Mobil DTE™-25 hydraulic fluid
- Di-2-ethylhexylsebacate
- Simulated fingerprint
- Krytox® 240AC grease
- Big Red crane grease - heavy paraffinic grease
- Christo-Lube® grease

Target initial contamination was ≈ 10 mg/panel (yields ≈ 40 mg/0.1m^2)

RESULTS: Cleaning efficiency of the candidate solvents was similar to AK-225G

LOX Impact Variable Test Matrix Developed by the IAT

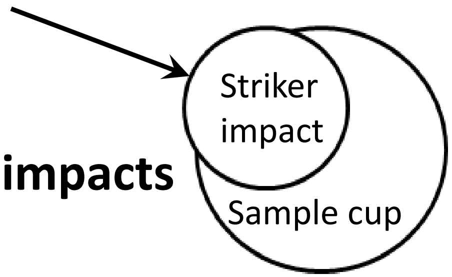
Test technicians from each facility traveled to the other facility to prepare test samples, using cleaned sample cups from the other facility. Witnessed by IAT.

LOX Impact Threshold Testing	MSFC	JSC-WSTF
Insert disks	No inserts	Add Inserts
MSFC technician prepare samples	Std MSFC method	MSFC & JSC-WSTF Cleaning
JSC-WSTF technician prepare samples	JSC-WSTF & MSFC Cleaning	Std JSC-WSTF method
11/16 inch diameter sample cup	Use	Use
Cleaning	JSC-WSTF cleaning	MSFC cleaning
Common solvent filtration	Same solvent container and filters at both	
Test with solvent from the same container	Std MSFC method	Std JSC-WSTF method
Humidity	Low	High
Rebound catcher	Use*	Use

*Test not performed due to shortage of specimen cups.

Modified Test Parameters Used for Final LOX Impact G86 Testing

- **Modified Test Parameters**
  - **Acceptance criteria- no non-uniform ignitions**
    - **Reduce uncontrolled test variables**
    - **Ignition suspect due to striker deformation of the cup**
  - **Use Rebound Catcher**
    - **Reduce uncontrolled test variables**
    - **Many of the ignitions occurred on secondary impacts**
  - **Use SS insert disks beneath grease cups**
    - **Worst case energy input**
  - **Preparation Humidity <60%**
    - **Increased test sensitivity**
  - **Use G86-89 original cup dimensions**
    - **Consistency**



- **Both Solstice™ PF and L-14780 exhibited 98 J (72 ft-lb) energy threshold during modified G86 testing.**

Oxygen Compatibility History for Solvents

- **Past Oxygen Compatibility Approach**
  - Solvents were found acceptable (non-ignitable) by
    - Autogenous Ignition Temperature (G72)
    - LOX Mechanical Impact (D2512/ G86)
  - Past approach was effective as some solvents such as AK-225G showed non-ignitions in past data.
  - All candidates (as well as past proven solvents) now known to be "flammable" in oxygen enriched environments.
  - New, more rigorous approach needed.
- **Present Oxygen Compatibility Approach**
  - NASA 6001
    - NASA TM-2007-213740 (Oxygen Compatibility Assessment)
    - ASTM G63 approach

Heat of Combustion

- **LOX Mechanical Impact and AIT measure ignition potential. ASTM G63 approach also requires data on propagation potential.**
  - **HOC test added to test plan to support comparison of energy release/ propagation potential.**
- **ASTM D4809 *Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method)***
  - **Gelatin capsules used to contain material for test. (see ASTM D240 *Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter)***
  - **AK-225G, Solstice™ PF, and L-14780 were tested.**

Oxygen Compatibility Ranking with Other Common Oxygen System Materials Using Heat of Combustion and Autogenous Ignition Testing

MORE COMPATIBLE

Material	HoC (Cal/g)
AK-225G	1153
TFE Teflon	1701
3M L-14780	1925
Fluorogreen	2402
Solstice PF	2448
Kel-F/Neoflon	2558
Viton A	3995
IPA	7165
Vespel SP-21	7603
Nylon 6/6	7905
Buna-N	9909
Polypropylene	11107

MORE COMPATIBLE

Material	AIT (ºC)
Fluorogreen	479
TFE Teflon	434
Kel-F/Neoflon	377
Vespel SP-21	321
AK-225G	230
Solstice PF	182
Nylon 6/6	178
Polypropylene	174
3M L-14780	161
Viton A	155
Buna-N	142

Common O_2 System Materials

Oxygen Compatibility Ranking Conclusions

- **All candidate solvents are "flammable" (as well as AK-225G).**
  - **2 top candidate solvents have equivalent performance for GOX and LOX Mechanical Impact. 98 J (72 ft-lb) energy threshold by modified G86.**
  - **2 top candidate solvents rank similarly for AIT/HOC.**
  - **These solvents rank well compared to other "good", commonly used nonmetallic materials.**
- **Solvent high volatility increases O_2 compatibility as they possess a low kindling chain potential due to their likelihood to evaporate prior to transferring energy to other system materials.**
- **Solstice™ PF and L-14780 as tested are determined to be an acceptable flammability risk for cleaning of NASA propulsion oxygen systems; safe for use with reasonable efforts to assure adequate removal prior to introduction of oxygen to the system.**
  - **Questions remain regarding flammability of L-14780 stabilizer residue and off-nominal blend ratio.**

Vendor Hands-On Demonstrations

Technical and business representatives from Honeywell and 3M provided product demonstrations to MSFC and SSC End Users

- Solvents demonstrated to engineers and technicians in use environments
- Answered questions about packaging, handling, distillation, QA, etc.

Hands-On Observations

- NVR sampling/analysis procedure comparable to AK-225G
  - Both solvents have issues for direct NVR measurement by FTIR; requires reconstitution of NVR residue with perchloroethylene.
  - Solvent handling for collecting, transporting, and filtering, and drying NVR samples was similar. Evaporation rate not problematic.
  - NVR filter paper material may need to be changed.
- Stabilizer interference detected in some samples of L-14780
  - NVR background from stabilizer too high for NVR verification sampling.
  - Stabilizer detected as NVR in FTIR scans.
- End user acceptance was comparable.
  - No objectionable odor.
  - Changes to handling and transportation requirements due to low boiling points seem to be manageable.
    - Solstice™ PF requires pressure vessels for transport & storage
    - L-14780 requires stainless steel drums.
  - MSFC technicians liked the Solstice™ PF small pressurized containers with nozzles for manual cleaning field operations.

Decision Point Factors

	Honeywell Solstice™ PF	3M L-14780	No Preference	Notes
SHE				
Environmental	x			Based on GWP and VOC comparison.
Health and Safety	x			Based on Acceptable Exposure Limit comparison.
Technical/Performance				
Metals Compatibility			x	L-14780 corrosion on carbon steel after exposure and storage noted, but not considered a concern for selection
Non-metal Compatibility			x	
Cleaning Effectiveness			x	
NVR Verification	x			L-14780 complicates NVR analysis with the FTIR method. Correction for interference peak is required. Residue detected in some tests.
Oxygen Compatibility			x	L-14780 - Analysis on the FTIR residue should be performed. Vendor commitment on stabilizer consistency required.
Implementation				
Hands On	x*			Operator preference.
Solvent Cost	x			Based on vendor feedback, not firm quotes.
Reclamation			x	
Facility Mods			x	Both require some facility mods to vapor degreaser and distillers for different boiling point, heat of vaporization, etc.
Equipment Needs		x		Solstice™ PF need for pressure vessels
Vendor Readiness	x			Solstice™ PF now manufactured in Louisiana
Solvent Maintenance Cost	x			L-14780 requires four component monitoring/ possible adjustments
Disposal Cost	x			Trans in L-14780 can go acidic requiring hazardous disposal.

* Slight preference.

Regulatory and Health Comparison

Solvent	Boiling Point	SNAP Approved as Non-ODS	VOC	100 Year GWP (IPCC AR5, 2013)	8 Hour Acceptable Exposure Limit
AK-225G (BASELINE)	56°C (134°F)	Now banned ODS Class II	Exempt	525	400 ppm
Solstice™ PF trans-1-chloro-3,3,3,-trifluoropropene (CAS 102687-65-0)	19°C (66°F) **[Note 1]**	**Yes**	**Exempt** (Final rule 8/28/2013)	**Very Low** < 1	800 ppm
L-14780 78% methyl perfluoropropyl ether / 22% trans-1,2 dichloroethylene CAS 375-03-1/156-60-5	28-30°C (82-86°F) **[Note 2]**	**Yes**	**Not Exempt** (tDCE) (HFE portion is exempt)	HFE=530 tDCE = negligible	HFE: 250 ppm tDCE: 200 ppm

Note 1: Requires shipment and storage in pressure vessels.
Note 2: Can be shipped/stored in 4 liter or 1 gallon glass bottles or stainless steel drums. Cannot be shipped in standard lined steel drums or pails.

Final Selection

- **Honeywell Solstice™ Performance Fluid (PF) - Primary**
  - Single component solvent. Performs very well. Lower boiling point than desired, but manageable. Also marketed as a liquid blowing agent (LBA). Now being produced at a plant near Baton Rouge, Louisiana.
- **3M L-14780 – Potential Alternate**
  - Azeotrope of methyl perfluoropropyl ether (78%) and trans-1,2 dichloroethylene (22%) plus stabilizer additives. Performs well, but there are concerns pertaining to excess NVR from some stabilizers and azeotropic stability at off-nominal temperatures. These concerns could potentially be resolved with reformulation/control of stabilizers and further testing.
- **No claim is made regarding Solstice™ PF or L-14780 for:**
  - **Suitability for use with breathing oxygen systems (not evaluated)**
  - **Safety/efficacy with materials or contaminants other than those tested.**

Lessons Learned

- **Publish a unified report containing all test protocols and process used for solvent selection – in case we need to do this again.**
- **Solvents (volatile liquids) are difficult to test for oxygen compatibility – more controls are required for repeatability.**
  - **Recommendations made to ASTM G04 committee for refinements to AIT (G72) and LOX Mechanical Impact (D2512/G86) for testing solvents.**
  - **Testing at only one lab would not have identified G86 issues.**
- **All solvents are reactive with oxygen under some conditions – the ASTM G63 / Oxygen Compatibility Assessment approach is useful to evaluate the risks of use.**
- **Stabilizer additives, although < 1% of the solvent, can affect NVR residues and must be considered and controlled for oxygen system cleaning applications.**

Any Questions?