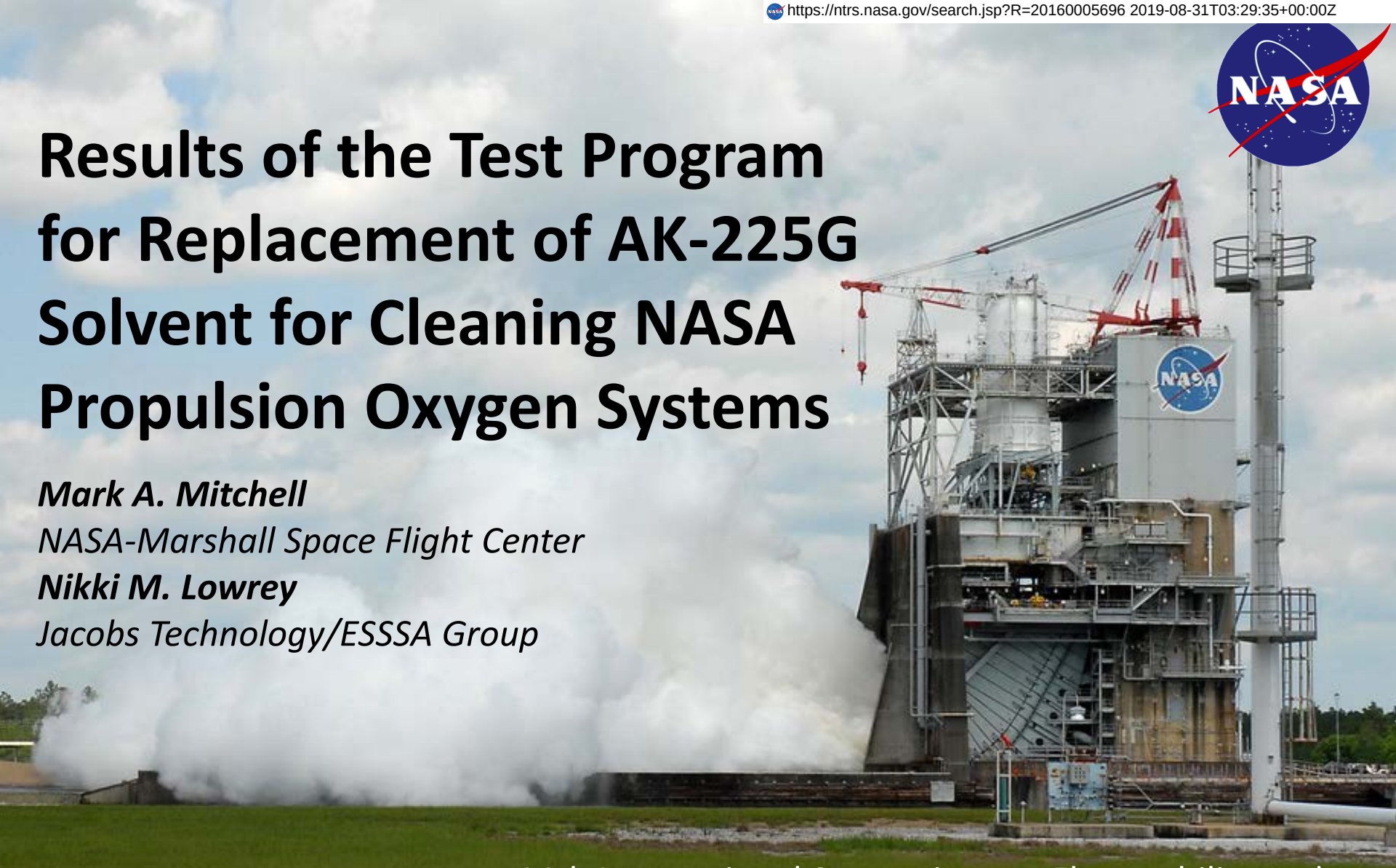
Results of the Test Program for Replacement of AK-225G Solvent for Cleaning NASA Propulsion Oxygen Systems

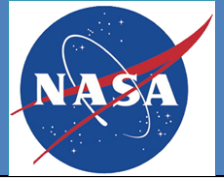
Mark A. Mitchell
NASA-Marshall Space Flight Center
Nikki M. Lowrey
Jacobs Technology/ESSSA Group



14th International Symposium on Flammability and Sensitivity of Materials in Oxygen Enriched Atmospheres
San Antonio, Texas, April 13-15, 2016

Photo: NASA/SSC

AK-225G 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.

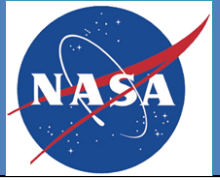
Target: Find replacement for AK-225G and implement prior to depletion of MSFC/SSC stock.

Participants

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 (IAT)**
  - 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:

***The Dupont Performance Chemicals segment is now The Chemours Company**

****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.**
- **Tests were performed at MSFC, SSC, and WSTF.**
- **One solvent was recommended for implementation.**
- **One alternate solvent was identified as a potential back-up.**
- **The final report was published April 2015.**

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 Candidates

Single Component	Kb	AEL-8hr	Concerns
AGC Chemicals AE3000 (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 (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 (PFBI)	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.
AGC Chemicals AE3000AT 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)
DuPont Vertrel MCA (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 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, a measure of hydrocarbon cleaning power, per ASTM D1133
AEL-8hr = 8 hour Airborne Exposure Limit, a measure of human toxicity

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

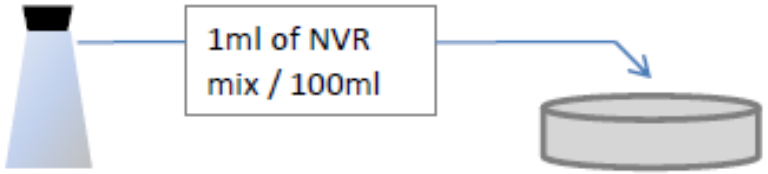
CONTAMINANTS
- Mineral Oil
- WD-40®
- MIL-PRF-83282 (synthetic hydraulic fluid)
- Di-2-ethylhexylsebacate (gauge calibration oil)
- Krytox® GPL103 (lubricant)
- Mobil ® DTE-25 (machine hydraulic fluid)
- Simulated fingerprint (ASTM D4265)
- Krytox® 240AC & Christo-lube® (grease)
- Big Red Grease (crane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



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.

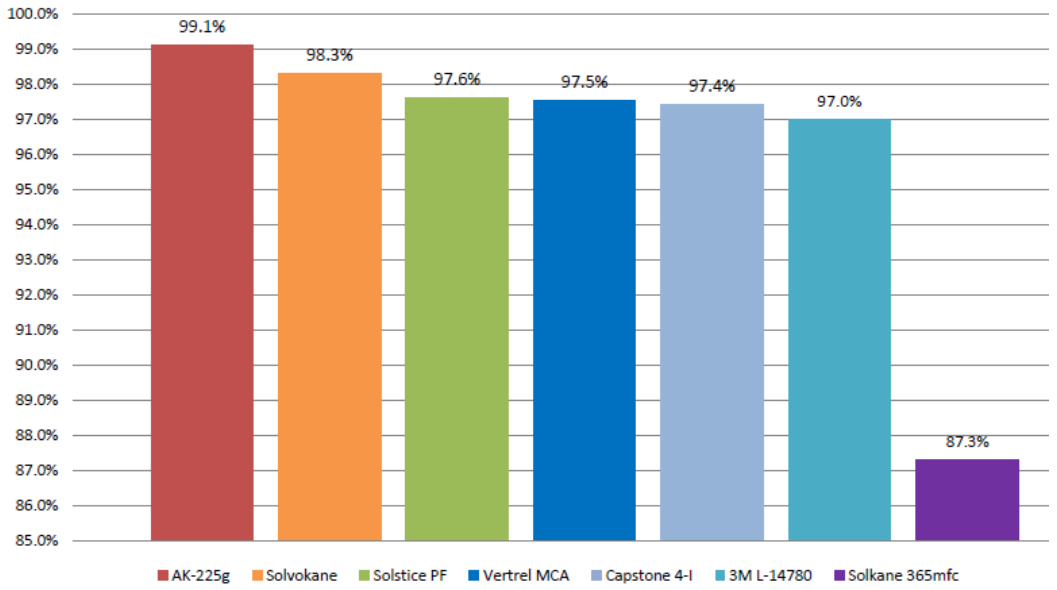
Mixed Contaminant – Equal Parts:

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

Mixed in AK-225G as a carrier solvent

Odor Observations:

- Only Capstone 4-I odor was highly objectionable



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.**
  - **Tests at MSFC for a non-NASA customer showed that Capstone 4-I rapidly corroded stainless steel, aluminum, and nickel alloys.**
- **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)

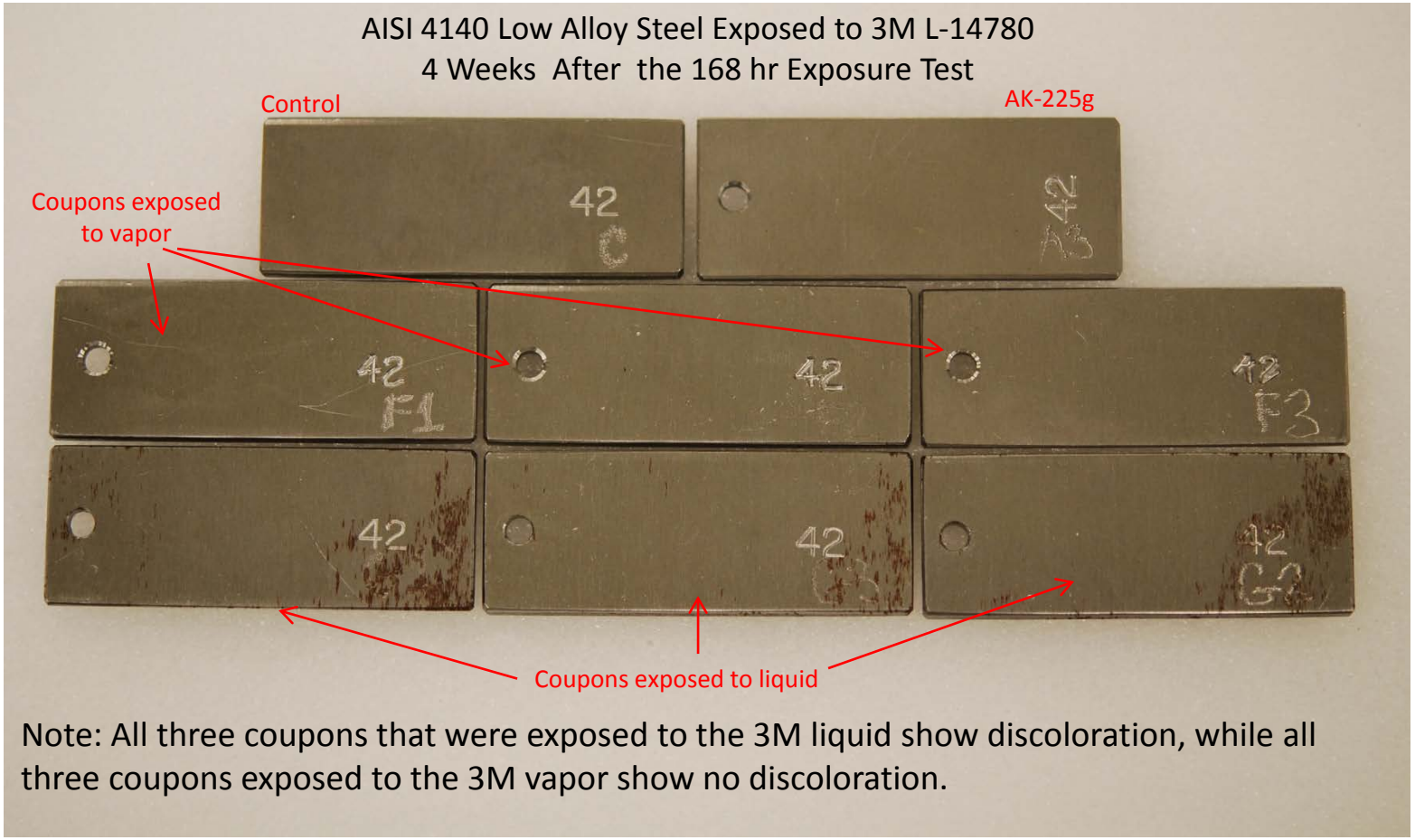
Coupons set in High Pressure Rated Glass Tube.

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.

*ASTM F 483-09, *Standard Practice for Total Immersion Corrosion Test for Aircraft Maintenance Chemicals*

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.**



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.

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

*Test method similar to ASTM F 483-09, but much shorter duration.

Nonmetals Compatibility Results

Solvents performed equal or better than AK-225G

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	-	-

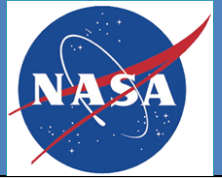
L-14780	% Weight Gain			% Linear Swell		
Material	Post Test	24 hours	7 days	Post Test	24 hours	7 days
FKM (V0747-75)	5.9	3.6	2.6	1.8	1.0	0.7
FFKM (Kalrez)	6.0	3.6	2.5	2.9	1.9	1.4
NBR (Buna-N)	6.3	1.7	-0.3	2.0	0.6	0.4
PTFE Teflon	0.1	-	-	0.0	-	-
FEP Teflon	0.3	-	-	-0.2	-	-
PCTFE (Kel-F)	0.0	-	-	-0.1	-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

Initial Oxygen Compatibility Tests

AK-225G, Solstice PF, L-14780, and Solvokane



- **LOX Mechanical Impact**
  - ASTM G86-98a (R2011), *Test Method for Determining Ignition Sensitivity of Materials to Mechanical Impact in Ambient Liquid Oxygen and Pressurized Liquid and Gaseous Oxygen Environments*, section 4.2, *Ambient LOX Impact Test*, at 98 J (72 ft-lb) impact energy.
  - Used a grease cup to contain frozen solvent.
  - Additional tests performed at lower impact energy and higher pressure.
- **Autogenous Ignition Temperature**
  - ASTM G72-09, *Test Method for Autogenous Ignition Temperature of Liquids and Solids in a High Pressure Oxygen-Enriched Environment*
  - Tests performed at 0.34 MPa (50 psia) and 13.8 MPa (2000 psia) for comparison to previous solvent tests.
  - 3M Novec® 7100 (HFE-7100) also tested as a control.
  - WSTF investigated variables to assure valid test of volatile liquids such as cleaning solvents.

SECOND DOWN SELECTION

- Solstice PF, L-14780, and Solvokane performed well for cleaning and materials compatibility.
  - L-14780 corrosion of carbon steel was noted for further investigation.
- Solvokane was most reactive in both LOX impact and AIT tests – eliminated as a candidate.
- Significant discrepancies were observed between MSFC and WSTF LOX Mechanical Impact data.
  - The NESC Independent Assessment Team was formed to investigate test variables.
  - Extended oxygen compatibility tests, including heat of combustion, and an Oxygen Compatibility Assessment were added to the test plan.

Nonvolatile Residue Removal Efficiency

- **Simulates an NVR verification sampling procedure.**
- **Assesses the ability of a solvent to remove NVR contaminants by ambient temperature flush.**

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).

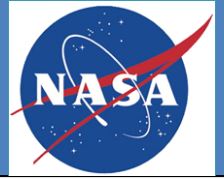
Nine Contaminants

- 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 (≈ 40 mg/0.1m^2)

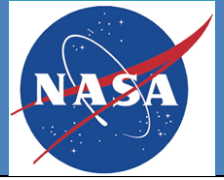
RESULTS: Cleaning efficiency of the candidate solvents was similar to AK-225G – effective at removing NVRs of concern.

Extended Oxygen Compatibility Tests



- **MSFC and WSTF protocols for the ASTM G86 LOX Mechanical Impact tests were analyzed. Modified test parameters were developed to improve repeatability with volatile solvents.**
  - **Both Solstice PF and L-14780 exhibited 98 J (72 ft-lb) energy threshold during modified G86 testing.**
- **Heat of Combustion test added 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)***
  - **AK-225G, Solstice PF and L-14780 were tested.**

Solvent Oxygen Compatibility History



- **Past Oxygen Compatibility Approach for Solvents**
  - **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.**
- **Oxygen Compatibility Assessment Approach**
  - **Approach described in ASTM G 63 *Standard Guide for Evaluating Nonmetallic Materials for Oxygen Service***
  - **Requires consideration of both ignition potential and propagation potential.**

Oxygen Compatibility Conclusions

- All candidate solvents are “flammable” (as well as AK-225G).
  - 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.

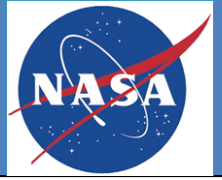
Phase 4 Implementation Assessments

- **Handling for NVR analysis comparable to AK-225G**
  - **Both solvents require reconstitution of NVR residue with perchloroethylene for FTIR analysis.**
  - **Evaporation rate not problematic for capture of NVR flush.**
- **Stabilizer interference detected in samples of L-14780**
  - **NVR background from stabilizer was too high for NVR verification sampling.**
- **End user acceptance of Solstice PF and L-14780.**
  - **Performed well in a variety of end user operations.**
  - **No objectionable odor.**
  - **Required changes to handling and transportation requirements due to low boiling points are manageable.**
    - **Solstice PF requires pressure vessels for transport & storage**
    - **L-14780 requires stainless steel drums.**

Regulatory and Health Comparison

Solvent	EPA Approved as Non-ODS	VOC	100 Year GWP	8 Hour Acceptable Exposure Limit
AK-225G (BASELINE)	Now banned ODS Class II	Exempt	160	400 ppm
Solstice PF	**Yes**	**Exempt** (Final rule 8/28/2013)	**Very Low** < 1	800 ppm
L-14780	**Yes**	**Not Exempt** (tDCE) (HFE portion is exempt)	**Low** HFE=370 tDCE = negligible	HFE: 250 ppm tDCE: 200 ppm

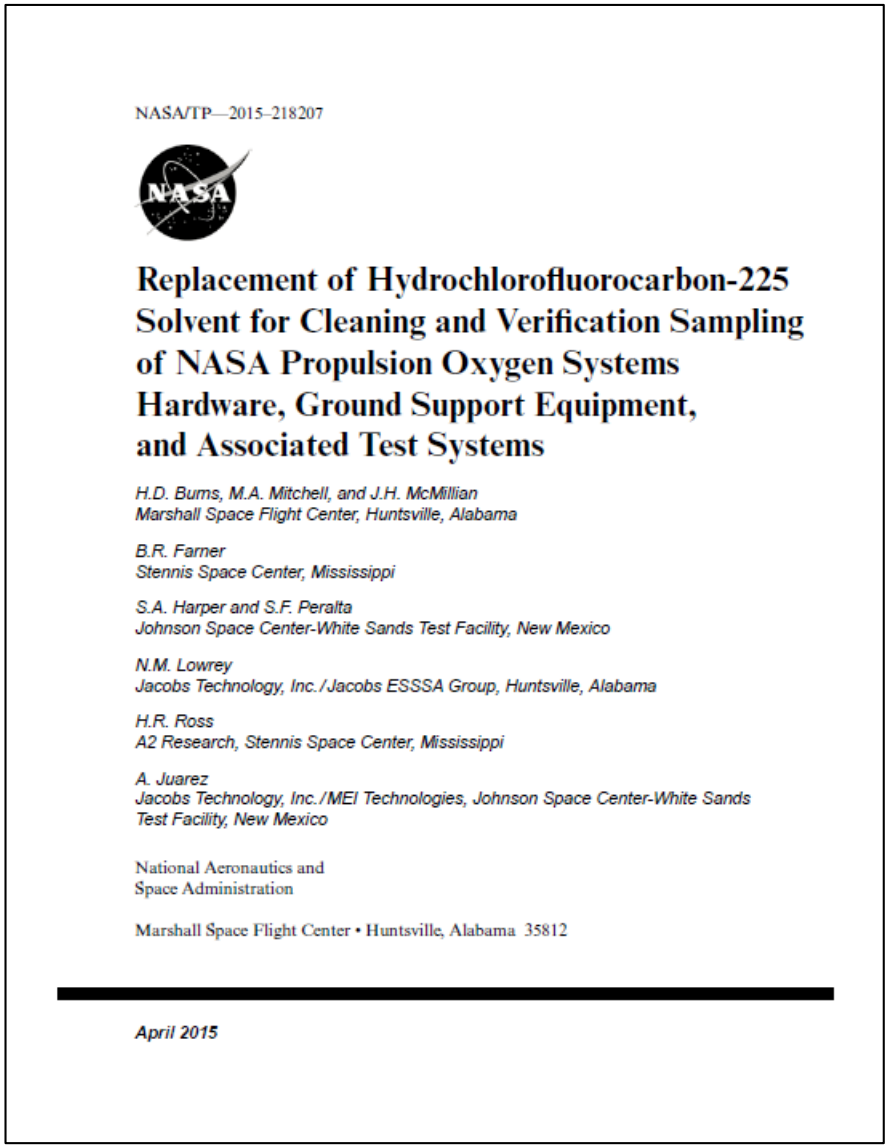
Conclusions and Lessons Learned



- **Honeywell Solstice PF selected to replace AK-225G for cleaning and NVR verification of NASA propulsion oxygen system hardware.**
  - **3M L-14780 is a potential alternate but requires resolution of excess NVR from stabilizers and unknowns regarding oxygen compatibility of potential variations in the blend.**
- **Volatile liquids are difficult to test for oxygen compatibility, require more controls during test.**
- **Stabilizer additives (< 1% of solvent) can affect NVR results, must be controlled for oxygen cleaning.**

No claim is made regarding Solstice PF or L-14780 for:
Suitability with breathing oxygen systems (not evaluated)
Safety/efficacy with materials or contaminants other than those tested

Final Report



NASA/TP—2015–218207

Replacement of Hydrochlorofluorocarbon-225 Solvent for Cleaning and Verification Sampling of NASA Propulsion Oxygen Systems Hardware, Ground Support Equipment, and Associated Test Systems

H.D. Burns, M.A. Mitchell, and J.H. McMillian
Marshall Space Flight Center, Huntsville, Alabama

B.R. Farner
Stennis Space Center, Mississippi

S.A. Harper and S.F. Peralta
Johnson Space Center-White Sands Test Facility, New Mexico

N.M. Lowrey
Jacobs Technology, Inc./Jacobs ESSSA Group, Huntsville, Alabama

H.R. Ross
A2 Research, Stennis Space Center, Mississippi

A. Juarez
Jacobs Technology, Inc./MEI Technologies, Johnson Space Center-White Sands Test Facility, New Mexico

National Aeronautics and
Space Administration

Marshall Space Flight Center • Huntsville, Alabama 35812

April 2015

The complete NASA Report, NASA/TP-2015-218207, is available at:

http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20150006941.pdf

Thank You for Your Attention!

Any Questions?

Interested in Collaborating on Cleaning Processes?

Please contact:

Mark Mitchell
NASA/MSFC/EM50
mark.a.mitchell@nasa.gov