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

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ABSTRACT

Since the 1990's, when the Class I Ozone Depleting Substance (ODS) chlorofluorocarbon-113 (CFC-113) was banned, NASA's rocket propulsion test facilities at Marshall Space Flight Center (MSFC) and Stennis Space Center (SSC) have relied upon hydrochlorofluorocarbon-225 (HCFC-225) to safely clean and verify the cleanliness of large scale propulsion oxygen systems. Effective January 1, 2015, the production, import, export, and new use of HCFC-225, a Class II ODS, was prohibited by the Clean Air Act. In 2012 through 2014, leveraging resources from both the NASA Rocket Propulsion Test Program and the Defense Logistics Agency - Aviation Hazardous Minimization and Green Products Branch, test labs at MSFC, SSC, and Johnson Space Center's White Sands Test Facility (WSTF) collaborated to seek out, test, and qualify a replacement for HCFC-225 that is both an effective cleaner and safe for use with oxygen systems. Candidate solvents were selected and a test plan was developed following the guidelines of ASTM G127, Standard Guide for the Selection of Cleaning Agents for Oxygen Systems. Solvents were evaluated for materials compatibility, oxygen compatibility, cleaning effectiveness, and suitability for use in cleanliness verification and field cleaning operations. Two solvents were determined to be acceptable for cleaning oxygen systems and one was chosen for implementation at NASA's rocket propulsion test facilities. The test program and results are summarized. This project also demonstrated the benefits of cross-agency collaboration in a time of limited resources.

INTRODUCTION

Liquid and gaseous oxygen (LOX/GOX) systems used in bipropellant propulsion systems require a high level of cleanliness. Systems to be wetted by gaseous or liquid oxygen, and systems providing pressurization and/or purge (P&P) gases to these systems, must be clean, particularly of hydrocarbons and large (> 800 μ) particles [1], to avoid the potential hazard of a reaction and subsequent fire or explosion. Solvents used to clean and verify the cleanliness of oxygen systems and supporting test hardware must be compatible with the materials of construction of these systems and effective at removing expected contaminants to the level required. When complete removal of residual cleaning solvent from the component or system cannot be verified with a high level of confidence, the solvent must also be minimally reactive with LOX/GOX at the system use conditions.

Historically, chlorofluorcarbon-113 (CFC-113, Chemical Abstracts Service [CAS] number 76-13-1) solvent was used for these applications. When CFC-113, a Class I ODS was banned in the 1990's, hydrochlorofluorocarbon-225[1] (HCFC-225ca/cb [a dual isomer form], CAS 422-56-0 and CAS 507-55-1),

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[1] Manufactured by Asahi Glass Company, Ltd., Tokyo, Japan; supplied in North America by AGC Chemicals Americas, Exton, PA, under the product name Asahiklin AK-225. AK-225 is a blend of two isomers, 3,3-Dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca) (Chemical Abstract Service [CAS] Registry Number 422-56-0), and 1,3-Dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb) (CAS Number 507-55-1). References to HCFC-225 in this document refer to any form of this chemical, as the ca or cb isomer or a blend of both isomers. AK-225 refers specifically to the Asahiklin ca/cb isomer blend.

a Class II ODS, was selected by the Space Shuttle Program (SSP) to replace CFC-113 for final cleaning and verification of oxygen systems hardware where a suitable non-ODS replacement could not be found.[2] Beginning in 1999, SSP moved from HCFC-225ca/cb to the single isomer HCFC-225cb[3] (CAS 507-55-1), a less toxic product. [3] At that time, MSFC implemented HCFC-225cb for cleaning propulsion test hardware. In 2002, SSC adopted HCFC-225cb to perform final rinsing and verification of nonvolatile residue (NVR) cleanliness for oxygen test system hardware that could be cleaned by water-based processes. When referenced in this document, HCFC-225 refers to both HCFC-225ca/cb and HCFC-225cb.

An Inter-Center NASA test plan was developed for evaluating solvents to be used for cleaning of propulsion oxygen systems and associated P&P systems, ground support equipment, and test systems at MSFC and SSC, and for sampling of these systems for verification of cleanliness. In this test program, Asahiklin AK-225G (>99% HCFC-225cb) was used as the baseline solvent for comparison of cleaning efficiency and materials compatibility. The goal was to identify a single replacement solvent that meets or exceeds the performance of AK-225G in all rocket propulsion oxygen system applications at MSFC and SSC.

BACKGROUND AND TEST PLAN DEVELOPMENT

NASA USE OF HYDROCHLOROFLUOROCARBON-225

Prior to initiation of this project, the NASA Principal Center for Risk Analysis and Communication (RRAC) polled the NASA Centers to identify users of HCFC-225 (as HCFC-225cb or as older stock of HCFC-225ca/cb) within the 2009-2011 time frame, as well as users of stockpiled CFC-113. Three NASA locations: MSFC, MSFC-Michoud Assembly Facility (MAF), and SSC reported a high level of usage of HCFC-225 during this three year period, ranging from 3600 to 18,000+ kilograms (kg) (8000 to 40,000+ pounds [lb]). MAF is a manufacturing facility in New Orleans, LA, managed by MSFC. HCFC-225 was used at these facilities primarily for precision cleaning and verification of cleanliness of launch vehicle propulsion oxygen systems hardware, ground support equipment (GSE), and associated test systems. HCFC-225 was used at MAF for processing of Space Shuttle External Tank hardware until the retirement of the SSP in 2011. Future need is anticipated for a replacement for HCFC-225 at MAF for processing of oxygen system components for the next NASA launch vehicle, the Space Launch System (SLS).

Two other NASA locations, Goddard Space Flight Center (GSFC) and JSC-WSTF reported low levels of HCFC-225 usage, less than 23 kg (50 lb) in this time period, primarily for laboratory operations. COLLABORATION WITH THE DEPARTMENT OF DEFENSE ON HCFC-225 REPLACEMENT

During the time frame that this project was being formulated, via communications with the U.S. DOD/NASA Joint Service Solvent Substitution (JS3) Working Group, it was determined that NASA and DOD users shared a common interest in replacement of HCFC-225 for cleaning oxygen systems. The Defense Logistics Agency (DLA) – Hazardous Minimization and Green Products Branch funded a two year project for MSFC to identify and test two candidate solvents for replacement of HCFC-225.[4]

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[2] HCFC-225 was authorized for use on the Space Shuttle External Tank by Change Order 60, dated April 15, 1996, to SE-S-0073 *Space Shuttle Fluid Procurement and Use Control Specification*, Revision F [2]; HCFC-225 was later authorized for use on the Space Shuttle Orbiter by Change Order 63, dated February 10, 1997.

[3] Manufactured by Asahi Glass Company, Ltd., Tokyo, Japan; supplied in North America by AGC Chemicals Americas, Exton, PA, under the product name Asahiklin AK-225G. AK-225G contains only the less toxic isomer (>99%) 1,3-Dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb) (CAS Number 507-55-1). AK-225 and AK-225G were approved for use on the SSP for cleaning and verification of propulsion oxygen systems. Purchase of AK-225 by NASA was discontinued when the less toxic form, AK-225G, was determined to be an acceptable alternative.
[4] Military Interdepartmental Purchase Request (MIPR) SC04001200481, *Solvent Replacement for HCFC-225 for Cleaning Oxygen System Components,* final report delivered August 26, 2014.

The candidate solvents tested in the DLA study were Honeywell Solstice™ Performance Fluid (PF) and 3M L-14780 developmental solvent. These solvents were compared to two baseline solvents, AK-225G and DuPont™ Capstone® 4-I[5]. Capstone 4-I, a chemical intermediate composed primarily of perfluorobutyl iodide (PFBI), was provided by DuPont as a substitute for DuPont Ikon® Solvent P, a PFBI cleaning solvent approved by the U.S. Air Force (USAF) as a replacement for HCFC-225 for hand wipe cleaning of components for aviator's breathing oxygen systems where HCFC-225 is prohibited or unavailable. Ikon Solvent P cleaning solvent was discontinued by DuPont.

The tests performed for the DLA study were based on those reported in AFRL-ML-WP-TR-2003-4040, *The Wipe Solvent Program,* the test program used to qualify Ikon Solvent P for USAF applications. [4] The test methods used in the DLA study for NVR background, materials compatibility, and cleaning effectiveness were different than those used for this project and a smaller set of materials and contaminants were tested. Oxygen compatibility tests for the DLA study were performed at the MSFC Materials Combustion Research Facility. The tests for the DLA study were complimentary and provided very useful input to the test program reported here.

The schedule for the DLA study overlapped the schedule for this test program, with an earlier required completion date. Data obtained during the performance of the DLA study was used to supplement and inform the down-selection process during the course of this project.

TEST PLAN DEVELOPMENT

The test plan was developed jointly by a team of Materials and Processes (M&P) engineers, laboratory personnel, and end users from MSFC, SSC, and JSC-WSTF, and reviewed by the NASA Engineering and Safety Center (NESC). The solvent selection criteria described in ASTM G 127, *Standard Guide for the Selection of Cleaning Agents for Oxygen Systems*, were referenced for the development of this test plan. [5] The materials and contaminants specified in this plan were selected by an engineering team from MSFC and SSC using ASTM G 127 and ASTM MNL36 *Safe Use of Oxygen and Oxygen Systems* as a guide; considering historical and current propulsion system designs; and with input from users at MSFC and SSC propulsion test facilities and cleaning facilities regarding cleaning challenges with LOX/GOX systems encountered at their locations. [6] Test reports from the 1990's and 2000's to qualify HCFC-225 as a replacement for CFC-113 were also reviewed to capture previous test methods where applicable. [7 – 11][6]

The test procedures, metals and nonmetals to be tested for compatibility, and contaminants to be tested to compare cleaning effectiveness of the solvent candidates were detailed in the test plan. The test program was managed by the MSFC M&P Laboratory Environmental Effects Branch Contamination Control Team and, at the request of the RPT Program Manager, monitored by NESC representatives from MSFC and SSC. Test responsibilities were assigned to laboratories at MSFC, SSC, and JSC-WSTF based on the availability of laboratory facilities and expertise as follows:

A. NVR background in neat cleaning solvents by gravimetric and Fourier Transform Infrared (FTIR) methods: SSC and MSFC

B. Metals compatibility: SSC

C. Nonmetals compatibility: MSFC

D. Quick screen solvency: SSC

E. NVR removal efficiency: MSFC

F. Oxygen compatibility: JSC-WSTF

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[5] Earlier trade names used by DuPont for their family of PFBI-based products were Zonyl® and Ikon®. Capstone® 4-I is marketed by DuPont only as a chemical intermediate. DuPont does not currently offer a product based on PFBI as a cleaning solvent.
[6] In addition to the published references, NASA Materials and Processes Technical Information System (MAPTIS) reports for material codes 01229 (AK-225) and 04619 (AK-225G) were also reviewed.

G. Component level cleaning tests (field cleaning): MSFC and SSC

TEST SEQUENCE AND DOWN-SELECTION MILESTONES

Tests were scheduled to provide data to support Technical Interchange Meetings (TIM) to narrow the list of candidates prior to the expenditure of funds on costly and time consuming tests. At these TIMs the engineering team reviewed the data gathered to date and selected the most promising candidates to proceed to the next phase of tests. Measurement of the NVR background of each cleaning solvent was performed prior to use, therefore this test was repeated several times during the course of the project when new lots of material were received from the supplier. The test sequence and down selection milestones were as follows:

Test Phase 1: NVR background of neat solvent and quick screen solvency tests.

First Down-Selection: Select three solvents to proceed to phase 2.

Test Phase 2: Metals compatibility, nonmetals compatibility tests, and initial oxygen compatibility tests.

Second Down-Selection: Select two solvents to proceed to phase 3.

Test Phase 3: NVR removal efficiency and oxygen compatibility tests.

Final Down-Selection: Select one solvent to proceed to phase 4. If considered a viable alternative, then the solvent not selected was retained as a backup if any insurmountable issues arose during the final test phase.

Test Phase 4: Component level cleaning tests (field cleaning) and assessment of implementation requirements.

Initial results from the LOX Mechanical Impact tests performed at JSC-WSTF were found to be significantly different from those performed at MSFC for the DLA study following the same ASTM test method. As a result, an Independent Assessment Team (IAT) sponsored by the NESC was formed to investigate the test variables and conditions that could affect the results when testing the reactivity of liquids in LOX and to establish a modified test protocol for a subsequent set of tests that would provide a reliable reactivity ranking of the candidate solvents. Additional oxygen compatibility tests beyond the scope of the initial test plan were performed at MSFC and JSC-WSTF to support this independent assessment and provide final input for an oxygen compatibility analysis. Final LOX Mechanical Impact threshold ignition tests were performed at JSC-WSTF using the detailed test parameters recommended by the IAT. Heat of Combustion tests in accordance with ASTM D 4809, *Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method),* were also performed on the final two solvents and AK-225G to provide comparative data to support the final oxygen compatibility analysis. [12]

SELECTION OF SOLVENT CANDIDATES

IDENTIFICATION OF PROMISING SOLVENT CANDIDATES

During the initial phase of the DLA study, the critical performance parameters were identified and a thorough survey of the cleaning solvent industry was performed to identify promising candidates for cleaning oxygen systems. This survey included a review of publications from the efforts to replace CFC-113 and qualify HCFC-225 in the 1990's and 2000's, analysis of all cleaning solvent data recorded in the NASA Materials and Processes Technical Information System (MAPTIS) Material Selection Database, an extensive internet search, and evaluation of alternatives to ODS solvents approved under the U.S. Environmental Protection Agency (EPA) Significant New Alternatives Policy (SNAP). Solvent manufacturers and major blenders were contacted to identify new solvents that were in the developmental phase, but could be made available for test. A summary of this search was presented at

the 2012 International Workshop on Environment and Alternative Energy; 4-7 Dec. 2012; Greenbelt, MD; United States. [13]

SOLVENT SELECTION CRITERIA

The solvent selection criteria fell into two general categories: Safety, Health and Environmental (SHE) characteristics, and technical performance parameters. Subordinate to the SHE criteria and the technical performance requirements, business issues influencing cost and availability were also considered.

Safety, Health and Environmental Characteristics

Solvents that were classified by the EPA as a Class I or Class II Ozone Depleting Substance or contained a constituent classified as a Hazardous Air Pollutant (HAP) [14] were not accepted as test candidates. In addition, chemicals classified as human carcinogens were not accepted for consideration.

Solvents that meet NASA criteria for oxygen compatibility are expected to be inherently safer for personnel from a flammability perspective. The toxicity of solvent candidates was evaluated based on Acceptable Exposure Limits (AEL), 8-hour Time Weighted Average (TWA) or equivalent, as reported in the solvent Safety Data Sheet. Solvents with the highest AEL were the most preferred. Solvents with an AEL lower than 200 parts per million (ppm) were anticipated to require facility modifications or additional personal protective equipment for safe use.

Solvents were preferred that were lower in Volatile Organic Compound (VOC) content or VOC exempt as listed in the U.S. Federal Register [15] and published EPA determinations; and lower in 100-Year Global Warming Potential (GWP) as published in assessment reports by the Intergovernmental Panel on Climate Change (IPCC). [16] Solvents were also preferred based on expected ease of recapture, re-purification, and re-use.

Although spacecraft systems and launch support equipment are exempt from the requirements for federal procurement of bio-based cleaning agents [17], bio-based products as defined by the United States Department of Agriculture (USDA) Bio-Preferred Program were considered during the search for candidate solvents. No bio-based products met the screening criteria for test candidates.

Technical Performance Criteria

Technical performance criteria included materials compatibility, cleaning effectiveness, and oxygen compatibility. Boiling point was also considered because solvents with high boiling points (above 65°C [150°F]) can be difficult to dry and solvents with boiling points lower than common ambient temperatures may require pressurized storage and may evaporate too quickly for practical use.

Materials compatibility was evaluated based on vendor information and published literature. Solvents must not be corrosive to metals used in the construction of oxygen system hardware and existing test systems. Aqueous cleaning products, known to be corrosive to many metals when inadequately rinsed and dried, were not considered as candidates to replace HCFC-225 due to the difficulty of cleaning large scale propulsion test systems in the field without corrosion risks.

HCFC-225 and other halogenated solvents are known to be incompatible with some nonmetals. Current practice at MSFC and SSC is to remove most seals and other nonmetallic materials from oxygen system components prior to cleaning with halogenated solvents. Better compatibility with nonmetals used in oxygen system is preferred but was not an initial selection criterion.

The solvent used to clean oxygen systems must be capable of removing contaminants that pose a safety hazard to oxygen systems. This includes particulate, and hydrocarbon-based hydraulic fluids, oils, and greases. (References [1], [5] (section 6), and [6] (chapter 9).) Silicone oils are also of concern, but are generally prohibited around NASA propulsion system hardware and thus were not included in the

test program. Solvents are preferred that can also remove halogenated greases which are commonly used with oxygen systems due to their low reactivity. The solvent must be capable of removing NVR to below 1 mg/0.1 m^2 [7], the pass/fail criterion for most NASA LOX/GOX propulsion system components, when cleaning is performed by ambient temperature flush. Due to the large scale of launch vehicle components and test systems, cleaning methods that rely on mechanical action (e.g. ultrasonic agitation) and/or high temperatures are not practical in many cases. Ambient temperature flush was identified by the test team as the most challenging cleaning process for solvent performance at MSFC and SSC.

Kauri-butanol (Kb) value as reported by the vendor, determined in accordance with ASTM D 1133 *Standard Test Method for Kauri-Butanol Value of Hydrocarbon Solvents*, was used to estimate the cleaning power of the solvent. [19] High Kb values indicate relatively strong solvency. While Kb value is a limited measure of solvent performance, a review of past test data showed that solvents with Kb < 20 performed poorly at removing the soils of concern for oxygen systems. When a Kb value was not available, cleaning performance was estimated based on vendor literature and other published data.

Wetting Index has been used to estimate the ability of a cleaning agent to enter small orifices and lift particulate from surfaces. Solvents with a higher wetting index are expected to perform better at removal of particulate. The Wetting Index is calculated as:

Wetting Index = (1000 x density) / (surface tension x viscosity)

Solvents were preferred that had both a high Kb value and a high wetting index.

Flammable cleaning agents inadvertently remaining within an oxygen system pose a significant fire hazard. When a flammable solvent is used with an oxygen system component, extreme care must be taken to assure that the component is thoroughly dried and all solvent is removed. Precautions such as bake-out and vacuum drying are often impractical, and inspection of large test systems to assure complete solvent removal may be difficult. Due to the potential consequences of a fire, solvents used for final cleaning and verification of NASA propulsion test systems must demonstrate very low reactivity in oxygen. Solvents that reported a flash point in air on the SDS were considered unacceptable. Solvents with no lower or upper explosion limit as reported on the SDS and solvents that demonstrated favorable performance on previous NASA oxygen compatibility tests were preferred as test candidates.

Many fluorinated solvents with low Kb value are blended with trans-1,2 dichloroethylene (tDCE), alcohols, or other solvents to boost cleaning power. Nonflammable fluorinated constituents suppress the flammability of tDCE and alcohols. To assure that the performance properties will remain stable over time, only true azeotropic blends were considered as candidates. Historical solvent flammability data in MAPTIS showed that all blends containing alcohol (e.g., methanol, ethanol, isopropanol, etc.) failed the ambient LOX Mechanical Impact Ignition test. Therefore, solvents containing any alcohol were excluded. Also, MAPTIS data showed that solvent blends higher in tDCE content tended to fail LOX Mechanical Impact. While insufficient data was available to establish a tDCE threshold, blends containing more than 50% tDCE were considered highly unlikely to be compatible with LOX/GOX and were eliminated from the candidate list.

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[7] NASA specifications historically stated requirements for NVR in mg/ft^2. In later revisions, these units were changed to mg/0.1 m^2 with the footnote: "For the purpose of this specification 0.1 square meter = 1 square foot." [18]

Should more than one solvent be found to perform acceptably, cost and availability could determine the final selection. Expected cost and availability were considered during the initial evaluation, but were secondary to the SHE and technical performance criteria.

SOLVENTS SELECTED AS TEST CANDIDATES

The solvents selected for this test program were:

- AGC Chemicals Americas (distributor for Asahi Glass Company, Japan): Asahiklin AE3000 (new product) (1,1,2,2-tetrafluoroethyl-2,2,2-trifluoroethyl ether [hydrofluoroether (HFE)-347pc-f2] [CAS 406-78-0]).

- AGC Chemicals Americas (distributor for Asahi Glass Company, Japan): Asahiklin AE3000AT (new product) (45% trans-1,2 dichloroethylene [CAS no. 156-60-5]/ 55% 1,1,2,2- tetrafluoroethyl-2,2,2-trifluoroethyl ether [HFE-347pc-f2] [CAS 406-78-0] azeotrope).

- E. I. du Pont de Nemours and Company: Capstone 4-I, chemical intermediate (perfluorobutyl iodide [CAS no. 423-39-2], with other constituents).

- 3M: L-14780 Developmental Solvent[8] (22% trans-1,2 dichloroethylene [CAS no. 156-60-5]/ 78% methyl perfluoropropyl ether [HFE-347mcc3] [CAS no. 375-03-1] azeotrope).

- Solvay Fluorides, LLC: Solkane® 365 mfc (new product) (1,1,1,3,3 pentafluorobutane [CAS no. 406-58-6]).

- Solvay Fluorides LLC: Solvokane® (new product) (30% trans-dichloroethylene [CAS no. 156-60-5]/ 70% HFC-365 mfc 1,1,1,3,3 Pentafluorobutane [CAS no. 406-58-6] azeotrope).

- Honeywell: Solstice Performance Fluid (PF) (new product) (trans-1-chloro-3,3,3,-trifluoropropene [HCFO-1233zd(E)] [CAS no. 102687-65-0]).

- E. I. du Pont de Nemours and Company: Vertrel® MCA (38% trans-dichloroethylene [CAS no. 156-60-5]/ 62% 1,1,1,2,2,3,4,5,5,5-Decafluoropentane azeotrope [HFC-43-10mee] [CAS No. 138495-42-8]). This solvent contains a different stabilizer than some Vertrel MCA formulations previously tested by NASA.

The selection criteria for these solvents are shown in table 1.

Solvent samples were provided by the suppliers for this test program. AGC Chemicals Americas was unable to obtain test samples of AE3000 and AE3000AT from Japan in time to meet the schedule requirements. The SHE characteristics and expected performance of AE3000 and AE3000AT were less favorable than the other test candidates so this is not considered a significant omission. L-14780 and Vertrel MCA had been previously tested as replacements for CFC-113. L-14780 had performed well in previous NASA oxygen compatibility tests.[9] Vertrel MCA did not fully pass previous NASA oxygen compatibility tests [7], but was used for more than 10 years at NASA's Kennedy Space Center as the first step in a two-step cleaning process. Vertrel MCA was used to clean the hardware, followed by a rinse with an oxygen-compatible solvent with lower cleaning efficiency. This two-step process was identified as a fallback option for MSFC and SSC if no solvent was found to be acceptable as a replacement for

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[8] 3M does not currently market this blend of solvents. "L-14780 Development Solvent" is the 3M designation for the azeotropic blend of two commercially available products, 3M Novec™ 7000 (methyl perfluoropropyl ether) and trans-1,2 dichloroethylene. This product also contains stabilizer chemicals in concentrations below 1%.
[9] Test Report 97-31610, JSC-WSTF.

HCFC-225 in a single step process. None of the other solvent candidates had been previously tested by NASA for cleaning of propulsion oxygen systems.

Asahiklin AK-225G was used as the baseline solvent for this test program. At MSFC and SSC AK-225G solvent was supplied to the test labs from the production facilities. This solvent was drawn from production stock and verified to meet the NVR requirements of ≤ 2 ppm. It may have been recycled and distilled prior to delivery for test.

Table 1. Solvents Candidates Selected for Test.

Single Component	Kb ≥ 20	Expected to pass LOX test	Boiling Point > 38°C(100°F)	AEL 8 hour ≥ 200	Safe with Metals	VOC Exempt	100 Year GWP [1]
AE3000	NO	YES	YES	NO	YES	YES [2]	MID
Solstice PF	YES	YES	NO	YES	YES	YES [2]	LOW
Capstone 4-I	YES [3]	YES [4]	YES	YES	(5)	Unknown	Unknown
Solkane 365 mfc	NO	Unknown	YES	YES	YES	YES	MID
Azeotrope							
AE3000AT	YES	Unknown	YES	NO	YES	NO [6]	MID
L-14780	YES [3]	YES [4]	NO	YES	YES	NO [6]	MID
Vertrel MCA	YES	Unknown	YES	YES	YES	NO [6]	HIGH
Solvokane	YES	Unknown	NO	YES	YES	NO [6]	MID

Notes
(1) For any component in the solvent: HIGH is > 1000; MID is 10 – 1000; LOW is < 10.
(2) When solvent candidate selection was made, the request for VOC exemption for this solvent was in progress.
   EPA approval of VOC exemption has since been received.
(3) No Kb data available, but previous industry test data showed good cleaning performance.
(4) Historical LOX mechanical impact test data showed this material to be LOX compatible.
(5) A Boeing internal test report in support of the Space Shuttle Program indicated that this solvent might not be
   compatible with aluminum.
(6) This solvent blend contains trans-1,2 dichloroethylene which is not VOC exempt.

NONVOLATILE RESIDUE BACKGROUND IN NEAT CLEANING SOLVENTS

NONVOLATILE RESIDUE BACKGROUND OF TEST SOLVENTS

NVR residues was tested at both SSC and MSFC on receipt of a new lot of material. The AK-225G that was supplied by MSFC and SSC production facilities and the Solstice PF were very low in NVR. The other solvents except Capstone 4-I were moderately low in NVR and varied between labs and between gravimetric and FTIR test methods. These were considered acceptable for further testing, but would require purification to meet the requirements for use as an NVR verification solvent. The differences in NVR results between labs and between test methods were noted for future investigation to determine whether these differences were due to lot-to-lot variability, solvent stability, NVR type, or other factors. The Capstone 4-I was the highest in NVR background. During these tests it was necessary to filter a large quantity of particulate from the Capstone 4-I. It was also noted that the Capstone 4-I had a very strong, objectionable odor.

COMPATIBILITY WITH FOURIER TRANSFOMR INFRARED ANALYSIS OF NONVOLATILE RESIDUE

A calibrated FTIR method is used at MSFC and SSC propulsion test facilities for measurement of NVR in AK-225G for initial verification of solvent purity and for measurement of NVR in the solvent rinsed

from a cleaned part to verify cleanliness. Ideally, the solvent rinse sample would be injected directly into the infrared (IR) liquid cell to measure NVR. CFC-113 was used this way. AK-225G, however, produces IR peaks in the same wavelength range as the hydrocarbon contaminants being measured. When measuring the NVR in AK-225G, the residue is dried and then reconstituted in tetrachloroethylene for FTIR analysis. None of the solvent candidates were compatible with direct measurement in the IR cell. Furthermore, the L-14780 appeared in some tests to leave a trace constituent in the residue that may interfere with the FTIR analysis. This residue was suspected to be a stabilizer component of the L-14780, an issue identified for further investigation.

QUICK SCREEN SOLVENCY

As a quick way to evaluate the cleaning power of the candidate solvents, each candidate was challenged with a mixed batch of contaminants representative of cleaning challenges for propulsion oxygen system components. The contaminant mix was prepared by dissolving 0.5240 g of equal parts of the following contaminants in 100 ml of AK-225G:

 a. 0.1023g of Mineral oil – pharmaceutical grade – mixed aliphatic

 b. 0.1018g of MIL-PRF-83282 – ester based hydraulic fluid [20]

 c. 0.1025g of Di-2-ethylhexylsebacate (gauge calibration oil), MONOPLEX® DOS

 d. 0.1112g of WD-40® (medium-heavy hydrocarbons)

 e. 0.1062g of Krytox® GPL103 (fluorocarbon lubricant for oxygen systems)

Aluminum weighing pans were doped with the contaminant mix, dried, weighed, and then cleaned by flushing with 100 ml of the test solvent in three steps, 30 ml, 30 ml, and then 40 ml. The solvent flush was collected in a clean beaker that was then dried and weighed to determine NVR removed. Each solvent was tested ten times and the results were averaged. The NVR cleaning efficiency (%) is reported as:

Percent Cleaning Efficiency = (mg of NVR removed / mg of NVR applied) x 100

The average cleaning efficiency results are shown in figure 1.

Figure 1. Solvent Screening Test Results for Cleaning Efficiency
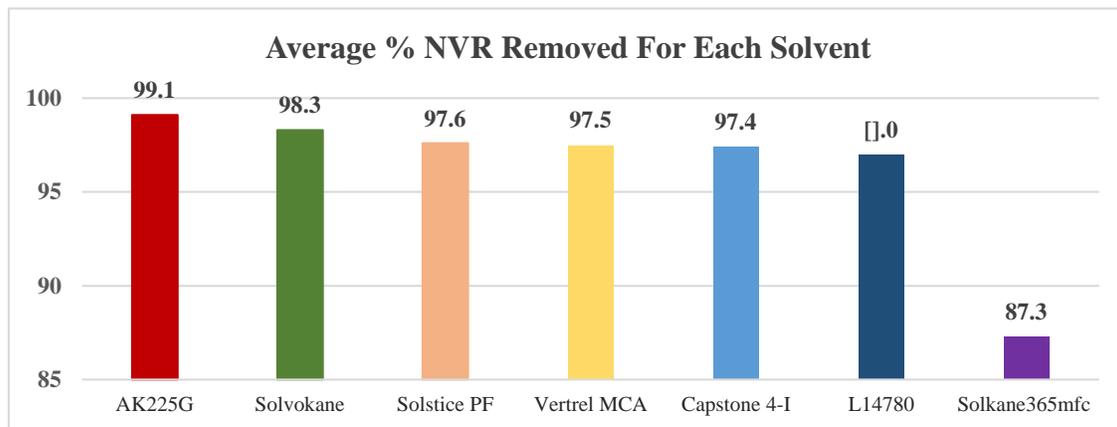
OBSERVATIONS ON MISCIBILITY AND SATURATION

During the quick look screening tests at SSC and cleaning efficiency tests performed at MSFC for the DLA study, it was noted that some contaminants in high doses tended to separate from several

candidate solvents. The substance solubility (e.g., hydraulic fluid) in a solvent can be measured as the saturation concentration or by the substance miscibility with the solvent. The miscibility of various contaminants in the candidate solvents was investigated further during the quick look screening tests. It was noted that Solstice PF and AK-225G showed a significantly higher saturation capacity than the other test candidates for the contaminants tested. The contaminants tested were:

a. MIL-PRF-83282 hydraulic fluid [20]
b. RP1 petroleum-based rocket propellant
c. Heavy weight (85-140W) petroleum-based gear oil

OBSERVATIONS ON ODOR

During the quick look screening tests, the SSC laboratory chemists were asked to provide general user feedback on the candidate solvents. The solvents were scored on a scale of 1-10 on odor strength, 1 being most favorable. AK-225G, Solstice PF, and L-14780 scored 5 or below. Solkane 365 mfc scored a 9 and Capstone 4-I, Vertrel MCA, and Solvokane scored a 10. Only the odor of the Capstone 4-I was considered to be highly objectionable.

FIRST DOWN-SELECTION

At the September 2013 TIM at SSC, the initial down-selection was performed to narrow the test set to three candidates. Data from NVR background tests and the Quick Screen Solvency test were reviewed and initial observations were shared regarding solvent odor, contaminant saturation capacity, and evaporative characteristics. Data obtained to date from the parallel DLA study on Solstice PF, L-14780, and Capstone 4-I was also shared.   This data included cleaning effectiveness tests, metals corrosion tests at ambient temperature, and initial LOX Mechanical Impact and AIT tests. MSFC reported that these three solvents performed well in the cleaning tests and the oxygen compatibility tests, but that Capstone 4-I was highly contaminated with particulate, was corrosive to the metals tested, and appeared to be unstable, rapidly changing color during test activities.

Solstice PF, Solvokane, and L-14780 were selected for further testing. All three solvents performed well in the quick screening solvency test and demonstrated other favorable characteristics. The cleaning performance of Solkane 365 mfc was significantly lower than the other candidates and it was determined that this solvent would not be acceptable for removing hydrocarbon contaminants to the low levels required for oxygen systems. It was also decided at this point that sufficient data was already available on Vertrel MCA to support future consideration as a fallback option should the three solvents selected for further testing fail to meet performance requirements.

Solstice PF demonstrated good cleaning efficiency (>97%), and had the most favorable SHE profile. Based on MSFC oxygen compatibility test data from the DLA study, it was expected to pass oxygen compatibility tests to be performed at JSC-WSTF. It was also observed during initial handling of Solstice PF that despite the low boiling point of 19°C (66°F) the solvent did not rapidly boil away and could be used for cleaning processes similarly to AK-225G and other higher boiling point solvents.

L-14780 demonstrated good cleaning efficiency (>97%). Based on historical test data from JSC-WSTF and MSFC oxygen compatibility test data from the DLA study, it was expected to again pass the oxygen compatibility tests to be performed at JSC-WSTF. The environmental data on this material was not as favorable as Solstice PF, but was more favorable than other candidates that were higher in VOC content and GWP.

Solvokane demonstrated good cleaning efficiency (>98%). Although the Solkane 365 mfc component is relatively high in GWP, it was the least toxic constituent of the azeotropes evaluated. No data was available at this point on oxygen compatibility.

METALS COMPATIBILITY

The corrosiveness of Solstice PF, L-14780, and Solvokane on metals was evaluated under conditions of total immersion in accordance with ASTM F 483-09, *Standard Practice for Total Immersion Corrosion Test for Aircraft Maintenance Chemicals* and in solvent vapor for comparison. [21] AK-225G was also included in this test set for comparison.

Six test coupons of each metal were weighed and suspended, three immersed in boiling solvent and three in the vapor region above the solvent, within a high pressure borosilicate tube. One coupon of each metal was weighed and retained as a control. See figures 2 and 3. The solvent was maintained at the boiling point using a constant temperature water bath. Test coupons were exposed for 24 hours, removed for inspection and weighing, and returned to the solvent for an additional 144 hours.

Figure 2. Metal coupons suspended in a High Pressure Rated Glass Tube

Figure 3. Coupons immersed in solvent and suspended in the vapor zone.

Thirteen ferrous and non-ferrous alloys were tested:

a. 304L stainless steel

b. A-286 PH stainless steel

c. 17-4 PH stainless steel

d. 440C stainless steel

e. 4140 low alloy carbon steel

f. Tin-Bronze

g. Brass – Admiralty brass CDA 443 (Copper Development Association)

h. Cobalt-Chromium-Nickel alloy - Elgiloy® (Elgiloy® Specialty Metals)

i. 2219-T6 aluminum

j. 6061-T6 aluminum

k. 2195-T8 aluminum-lithium (plate stock)

l.   Inconel™ 718 nickel alloy (Specialty Metals Corp.)

m. Monel™ 400 nickel alloy (Specialty Metals Corp.)

No visual change was observed in any of the metal coupons immediately after exposure and no significant weight changes were observed. However, four weeks after completion of solvent exposure, discoloration consistent with corrosion product was observed on the three specimens of 4140 low alloy carbon steel that had been immersed in the L-14780. This test was repeated later in the program and corrosion of 4140 carbon steel exposed to L-14780 was confirmed. The relationship between this observed corrosion and the individual components in L-14780 including the stabilizers has not been determined.

NONMETALS COMPATIBILITY

The compatibility of the solvent with nonmetals was evaluated under conditions of total immersion at the boil temperature of the solvent. This test method was similar to the ASTM F 483-09 test for metals compatibility [21], but exposure duration was much shorter. Exposure to the baseline AK-225G solvent was included in the test matrix for comparison. AK-225G is not compatible with several nonmetallic materials used in oxygen systems and no halogenated cleaning solvent is expected to be compatible with all nonmetals.

Three test specimens of each nonmetal, formed as O-rings or gaskets with a hole for hanging, were dried in a desiccator for 24 hours, weighed, measured for outer diameter (OD) in two directions, and immersed in boiling solvent within a high pressure borosilicate tube for 15 minutes. See figure 4. Elastomers were measured for hardness in accordance with ASTM D 2240 *Standard Test Method for Rubber Property – Durometer Hardness* Type A (Shore A durometer) at the point of maximum thickness prior to immersion. [22] One specimen of each material was weighed and retained as a control. The solvent was maintained at the boiling point using a constant temperature water bath. After immersion, the specimens were removed to the desiccator for 30 minutes and then weighed, measured, and inspected for evidence of deterioration. Specimens exhibiting a change in weight or linear swell of greater than 1% from the initial readings were returned to the desiccator for 24 hours and then re-measured. Specimens continuing to exhibit a change in weight or linear swell of greater than 1% from the initial readings were returned to the desiccator for an additional six days (seven days after immersion, total) and then re-measured.

Figure 4. O-rings suspended in solvent, ready for insertion into a heated water bath.

Nine nonmetals, including three elastomers, were tested:

Elastomers:

a. FKM poly(hexafluoropropylene-co-vinylidene fluoride) elastomer, FKM Compound V0747-75 (Parker Hannafin) [equivalent to Viton A (DuPont)]

b. FFKM poly(tetrafluoropropylene-co-perfluoromethylvinyl ether) elastomer, Kalrez® (DuPont)

c. NBR poly(acrylonitrile-co-butadiene) rubber (Buna N) – Mil-G-21569B Class I [23]

Non-elastomers:

d. PTFE Polytetrafluoroethylene – Algoflon® E2 (Solvay Solexis)

e. FEP fluorinated ethylene-propylene copolymer – FEP Teflon® (DuPont)

f. Polychlorotrifluoroethylene (PCTFE) – Kel-F® 81 (3M)

g. Aromatic polyimide – Vespel® SP21 (DuPont)

h. PEEK polyether ether ketone – Ketron® PEEK (Quadrant Engineering Plastic Products)

i. PTFE with silica fiber – Gylon® style 3502 for oxygen service (Garlock)

Weight gain and linear swell recorded for each nonmetal with each of the four solvents, AK-225G, Solstice PF, L-14780, and Solvokane, are shown in tables 2 through 5, using the following colors for visual comparison of the relative compatibility of these materials:

- Red = Post Test Gain >10% or Gain after 7 days > 5% or weight loss > 5%
- Yellow = Post Test Gain >5% or Gain after 7 days > 3% or weight loss > 2%
- Green = Post Test Gain < 5% and Gain after 7 days < 3% and weight loss < 2%

The three candidate solvents performed equal to or better than AK-225G in these nonmetal compatibility tests. Current cleaning protocols at MSFC and SSC that require removal of incompatible nonmetallic components prior to cleaning with AK-225G will be acceptable when using any of the three alternate candidates. Although a red, yellow, or green cell is an indication of the degree of incompatibility, the decision whether or not to expose each of these nonmetals to a particular solvent should be determined by the user of that nonmetal.

Table 2. AK-225G Test Results for Solvent Compatibility with Nonmetals

Material	% Weight Gain			% Linear Swell		
	Post Test	After 24 hours	After 7 days	Post Test	After 24 hours	After 7 days
FKM (V0747-75) (Note 1)	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 Algoflon	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 2)	-	-

Note 1: Test for FKM (VO747-75) compatibility with AK-225G was performed twice.
Note 2: Linear swell measurements for Gylon not valid. The process to cut Gylon from sheet results in an irregular outer edge.

Table 3. Solstice PF Test Results for Solvent Compatibility with Nonmetals

Material	% Weight Gain			% Linear Swell		
	Post Test	After 24 hours	After 7 days	Post Test	After 24 hours	After 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 Algoflon	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)	-	-

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

Table 4. L14780 Test Results for Solvent Compatibility with Nonmetals

Material	% Weight Gain			% Linear Swell		
	Post Test	After 24 hours	After 7 days	Post Test	After 24 hours	After 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 Algoflon	0.1	-	-	0.0	-	-
FEP Teflon	0.3	-	-	-0.2	-	-
PCTFE (Kel-F)	0.0	-	-	-0.1	-	-
Vespel 21	0.1	-	-	0.0	-	-
PEEK	0.1	-	-	0.2	-	-
Gylon	0.1	-	-	(Note 1)	-	-

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

Table 5: Solvokane Test Results for Solvent Compatibility with Nonmetals

Material	% Weight Gain			% Linear Swell		
	Post Test	After 24 hours	After 7 days	Post Test	After 24 hours	After 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 Algoflon	0.1	-	-	1.1	-	-
FEP Teflon	0.1	-	-	-0.4	-	-
PCTFE (Kel-F)	0.0	-	-	0.2	-	-
Vespel 21	0.3	-	-	-0.1	-	-
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

The test methods specified in the test plan for oxygen compatibility were selected to parallel tests performed in the past by NASA for replacement of ODS solvents for cleaning oxygen systems. Two tests

were performed to evaluate the ignition sensitivity in LOX/GOX. These tests had been performed at MSFC for the DLA study.

AMBIENT LOX MECHANICAL IMPACT TEST METHOD

Each solvent was tested in accordance with ASTM G86-98a (Reapproved 2011), *Standard 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. [24] This test is referred to as the LOX Mechanical Impact test. This test method is specified in NASA-STD-6001 *Flammability, Offgassing, and Compatibility Requirements and Test Procedures,* as Test 13A. [25]

Solvent was transferred to a small sample cup (referred to as the "grease cup") to obtain a sample thickness (depth) of 1.27 ± 0.13mm (0.050 ± 0.005 in.). The solvent in the grease cup was frozen on a chill bar (JSC-WSTF) or cold box (MSFC) using liquid nitrogen (LN2). The grease cup with solid solvent was placed into a one-piece sample cup and the cup was filled with LOX. This LOX-filled sample cup containing the grease cup with frozen solvent was then placed into the base of the pre-chilled impact tester, the striker pin was placed, and the impact was performed in accordance with ASTM G86-98a. The pass criteria, as in previous NASA tests, was no reactions in 20 impacts or not more than 1 reaction in 60 impacts. Specimens that did not pass at 98J (72 ft-lb) impact force were tested at progressively lower impact energies until no reactions were observed.

AUTOGENOUS IGNITION TEMPERATURE (AIT) TEST METHOD

Each solvent was tested in accordance with ASTM G72-09, *Standard Test Method for Autogenous Ignition Temperature of Liquids and Solids in a High Pressure Oxygen-Enriched Environment*, modified for testing of volatile liquids. [26] Tests were performed at 0.34 MPa (50 psia) and 13.8 MPa (2000 psia) based on previous solvent tests performed by NASA in a joint program with the U.S. Naval Sea Systems Command [7] and for the USAF. [27]

ASTM G72-09 does not contain specific instructions for handling of volatile liquids to assure that sufficient material is present to obtain valid data after purging of the test chamber with oxygen. Previous AIT test reports for solvents from the 1990's did not specify how the sample was handled to prevent excessive loss. During AIT tests performed by MSFC for the DLA study, the solvent and sample tubes were chilled with an ice bath to reduce loss prior to test. For these tests of Solstice PF, the sample tubes were filled with 0.50 g of solvent rather than 0.20 +/- 0.03 g as specified in ASTM G72-09 to assure that sufficient solvent would be present in liquid form after purging of the test chamber with oxygen to achieve an oxygen concentration >99%. During development of the test plan JSC-WSTF recommended elimination of the purging step rather than use of a larger sample size.

During the performance of the initial AIT tests at JSC-WSTF, due to the failure of several of the solvent samples to react up to the temperature threshold limit (TL) of the test apparatus (427°C [800°F]), concerns were raised that the test results may not be valid. JSC-WSTF performed several additional tests to investigate the effects of greater fuel quantity (sample weight), greater pressures than 0.34 MPa (50 psia) for the low pressure test, sample temperature, and test chamber purging.

As a result of these investigations, NASA proposed changes to ASTM G72-09 to improve repeatability when testing volatile liquids. This proposal was submitted to ASTM committee G04 on Compatibility and Sensitivity of Materials in Oxygen-Enriched Atmospheres, the governing committee for this standard. The recommended changes were:

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

b. 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.

c. 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.

d. Note: A non-ignition at maximum temperature when testing at lower pressures (<6.9 MPa [<1000 psia]) 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 10.3 MPa (1500 psia) or higher and increased sample mass (suggested 1.0 g) is recommended to confirm an unreactive material.

OXYGEN COMPATIBILITY TESTS PERFORMED PRIOR TO THE SECOND DOWN-SELECTION

Test results on Solstice PF, L-14780, and Solvokane for LOX Mechanical Impact performed by MSFC for the DLA study indicated that Solvokane was significantly more reactive than Solstice PF or L-14780. AIT tests for Solvokane were not completed at MSFC prior to the TIM for the second down-selection. Data to date on materials compatibility and cleaning effectiveness were very similar for the three remaining solvent candidates therefore additional oxygen test data was required as a discriminator. The oxygen compatibility tests specified in the test plan to be performed at JSC-WSTF were expedited to provide additional information prior to the second down-selection milestone.

OXYGEN COMPATIBILITY TESTS PERFORMED AT JSC-WSTF

The oxygen compatibility tests performed by JSC-WSTF prior to the second down-selection included LOX mechanical impact at ambient pressure and at elevated pressure with threshold determination; and AIT tests using the modified test parameters described above.

None of the three solvents tested for LOX Mechanical Impact at JSC-WSTF, Solstice, L-14780, and Solvokane, passed the screening criteria at 98 J (72 ft-lb) impact energy. Each solvent was tested at lower impact energies to determine ignition threshold. In addition, JSC-WSTF tested each solvent for LOX Mechanical Impact at 98 J (72 ft-lb) impact energy in variable pressure accordance with ASTM G 86-98a (NASA-STD-6001 Test 13B). The results of the LOX Mechanical Impact tests performed at JSC-WSTF, and performed by MSFC for the DLA study, prior to the second down-selection are shown in table 6.

Table 6. Comparison of LOX Mechanical Impact Ignition Test Results

Solvent	JSC-WSTF			MSFC (DLA Study)	
	Ambient LOX Impact at 98 J (72 ft-lb)	LOX Impact Threshold for 0/20 Reactions (Note 1)	Pressure Threshold for No Reactions at 98 J (72 ft-lb)	Ambient LOX Impact at 98 J (72 ft-lb)	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 (54.6 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.

The significant discrepancy in reaction thresholds observed in the ambient LOX Mechanical Impact tests at JSC-WSTF and MSFC was unexpected. While it was apparent that Solvokane was the most reactive, this data did not provide confidence to distinguish between the reactivity of Solstice PF and L-14780. An IAT sponsored by the NESC was formed to investigate the test variables and conditions that could affect the test results when testing the reactivity of liquids in LOX and to establish a modified test protocol for a subsequent set of tests that would provide a reliable reactivity ranking of the candidate solvents.

AIT test results obtained at MSFC for the DLA study were available for L-14780 and Solstice PF prior to the first down-selection. AIT results from MSFC and JSC-WSTF, when a reaction was observed below the TL of the apparatus, are compared in table 7 (shown in °F for comparison to historic test data). At JSC-WSTF, the sample size was 1000 mg. At MSFC, the sample size for Solstice PF was 500 mg; for L-14780 it was 200 to 230 mg.

Table 7. Comparison of AIT Test Results at JSC-WSTF and MSFC

| | Low Pressure (Note 1) | | | | 13.8 MPa (2000 psia) | | | |
| | JSC-WSTF | | MSFC (DLA study) | | JSC-WSTF | | MSFC (DLA Study) | |
	Avg °F	Std Dev	Avg °F	Std Dev	Avg °F	Std Dev	Avg °F	Std Dev
AK-225G	528 @ 0.48 MPa (70 psia)	5			446	-		
AK-225 (Note 2)	TL	-			TL	-		
L-14780	454 @ 1.4 MPa (200 psia)	-	300 (Note 3)	1	322	15	TL	-
Solstice PF	464	16	510	9	360	5	411	34
Solvokane	496	22	-	-	305	3	-	-

Note1: Low Pressure AIT test was performed at 0.34 MPa (50 psia) unless otherwise noted. At JSC-WSTF, if TL was observed the test was repeated at a higher pressure.

Note 2: Historic data for AK-225. [7] [27]

Note 3: Two of three tests showed unusual low energy reactions. The third test was a TL.

The AIT acceptance criteria stated in the test plan were based on criteria used in past solvent evaluations for use with oxygen systems. [27]

Category A - AIT > 400 °F – Acceptable for use in oxygen systems.
Category B - AIT 250 °F to 400 °F – May be used with caution in oxygen systems.
Category C - AIT < 250 °F – Not recommended for use in oxygen systems.

When a reaction was observed with the larger sample size, all three solvent candidates met the AIT criteria to be acceptable for use at lower pressures and acceptable for use with caution at higher pressures.

Historic AIT test data for AK-225 (the dual isomer form), assumed to have been performed with the standard sample size of approx. 200 mg, showed no reactions up to the TL of the test apparatus. A repeat of this test for AK-225G with a larger sample size showed that although no reaction was observed at 0.34 MPa (50 psia) to the TL, reactions were observed at 0.48 MPa (70 psia) and 13.8 MPa (2000 psia) indicating that AK-225G is more reactive than previously thought.

SECOND DOWN-SELECTION

DATA REVIEWED FOR THE SECOND DOWN-SELECTION

At the February 2014 TIM at JSC-WSTF, the project team reconvened to narrow the test set to two candidates. The data reviewed at this TIM included the test results for quick screen solvency, metals compatibility, nonmetals compatibility, and the results for the oxygen compatibility tests completed to date. Test results for metals and nonmetals compatibility available to date from the DLA study were also reviewed. The DLA tests for materials compatibility had been performed by ambient immersion for longer time periods (21 days for metals, and 30 days for nonmetals) on a smaller set of materials. The DLA tests for nonmetals, which included exposure up to 90 days, were not complete at the time of this TIM. Solvokane was not tested for metals compatibility in the DLA study. The DLA test results for materials compatibility were shown to correlate well with the test results shown in this report.

In addition to the test data obtained to date, the project team also reviewed the environmental and health data for the solvent candidates. This included status updates on VOC exemption and SNAP approval for Solstice PF.

SOLVENTS SELECTED FOR FURTHER TESTING

The objective for the February 2014 TIM was to down-select the solvent candidates from three to two. Solstice PF and L-14780 were selected to proceed to the next phase of testing for the following reasons:

1. All three solvents performed equal to or better than AK-225G for nonmetals compatibility. All of the metals compatibility tests were determined to be acceptable although corrosion of 4140 carbon steel after exposure to L-14780 was noted for further investigation. Low alloy carbon steel is unusual in the construction of oxygen systems, but is used in associated test apparatus.

2. Solstice PF was preferred based on environmental and health criteria. L-14780 was preferred over Solvokane based on environmental criteria, but Solvokane was preferred over L-14780 based on toxicity.

3. Oxygen Compatibility: Solvokane was significantly more reactive in LOX than Solstice PF or L-14780. The AIT data did not reveal a clear distinction between the three solvents. Also discussed during this TIM was the flammability and reactivity of the two primary components in Solvokane: Solkane 36 5mfc and tDCE. Both of these components are stated on their SDS to be flammable in air. Based on the LOX Mechanical Impact test data and the SDS data, the project team concluded that use of Solvokane with oxygen systems was contraindicated. This was the deciding factor in the down-selection.

NONVOLATILE RESIDUE REMOVAL EFFICIENCY

The purpose of the nonvolatile residue removal efficiency test was to assess the ability of a solvent to remove specific contaminants by ambient temperature flush. This test method was designed to mimic the NVR verification sampling process used at MSFC and SSC for oxygen systems hardware. Stainless steel test panels were fabricated for this test based on the test panel used in ASTM E 1235-08 *Standard test Method for Gravimetric Determination of Nonvolatile Residue (NVR) in Environmentally Controlled Areas for Spacecraft,* [28] but with ¼ the surface area to yield a 152 mm x 152 mm (6 in x 6 in) flat, lipped surface. Individual contaminants were applied to the test panel to achieve a target contamination level of approximately 40 mg/0.1 m^2. The contaminant was air dried and then baked for two hours at 55 $^\circ$C (130 $^\circ$F). Under a fume hood, the contaminated panel was mounted on a stand and gently flushed first with 200 ml of the test solvent and then with 200 ml of AK-225G. Each solvent flush was captured in a clean beaker. The test configuration is shown in figure 5. The captured solvent was analyzed for NVR content by drying and gravimetric analysis. These tests were performed for Solstice PF, L-14780, and AK-225G. AK-225G was included for comparison. Each solvent/contaminant combination

was tested three times. If the results did not agree within 10%, then the test was repeated.   The contaminant removal efficiency for the test solvent was calculated as:

$$\frac{(m_T - m_{TB})}{(m_T - m_{TB}) + (m_{AK} - m_{AKB})} \times 100 = \% \text{ NVR removed},$$

where:

m_T = mass of contaminant removed by the test solvent
m_{TB} = mass of the background NVR in the test solvent blank
m_{AK} = mass of the contaminant removed by the second rinse with HCFC-225cb
m_{AKB} = mass of the background NVR in the HCFC-225cb solvent blank

Figure 5. Configuration to flush a test panel for the NVR removal efficiency test.

The NVR contaminants used to challenge the candidate solvents were:

a. Mineral oil – CAS 8042-47-5 (representative of RP-1 fuel, petroleum-based hydraulic oils, and most petroleum-based motor oils and tube bending oils).

b. Petroleum-based machine tool hydraulic fluid, ISO grade 46 – Mobil DTE™ 25 (Exxon Mobil Corp.).

c. Synthetic hydraulic fluid, MIL-PRF-83282, fire resistant, synthetic hydrocarbon base - Brayco Micronic® 882 (Castrol Industrial North America).

d. Di-2-ethylhexyl sebacate (gauge calibration oil) - MONOPLEX DOS (The C. P. Hall Co.)

e. Fingerprint simulated by synthetic sebum, modified Spangler soil per ASTM D 4265-98 (R 2007), *Standard Guide for Evaluating Stain Removal Performance in Home Laundering*, section A2.16.2 (Scientific Services S/D, Inc., Sparrow Bush , NY). [29]

f. Fluorocarbon grease - Krytox 240AC (DuPont™Chemical Solutions).

g. Heavy paraffinic grease (crane grease), U-101 Big Red Grease (Universal, Inc.)

h. WD-40 aerosol (medium-heavy aliphatic hydrocarbons) (WD-40 Company).

i. Christo-lube® MCG 111 (Lubrication Technology, Inc.) fluorocarbon grease was added to the test set after the release of the test plan when it was determined that Christo-lube was commonly used as a substitute for Krytox 240AC at MSFC and SSC.

Charts comparing the removal efficiency of the candidate solvents versus AK-225G for each solvent are shown in figures 6 through 14. Cleaning efficiencies over 100% are due to the tolerance of the analytical balance and subtraction of solvent NVR background. The cleaning efficiencies of the candidate solvents were determined to be similar to the cleaning efficiencies of AK-225G and therefore suitable for cleaning NASA propulsion oxygen systems.

Figure 6. Mineral Oil Removal Efficiency.
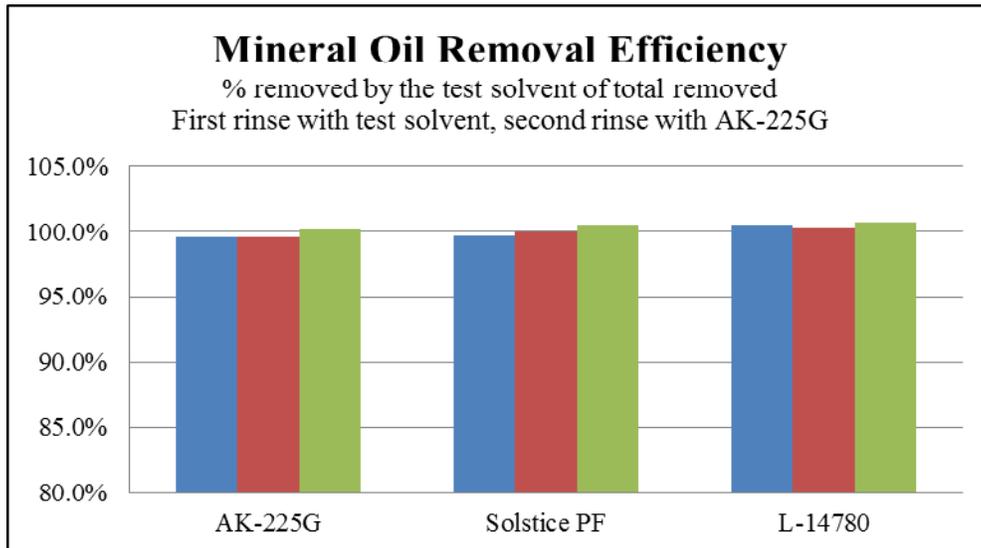
Figure 7. Mobil DTE25 Hydraulic Oil Removal Efficiency.
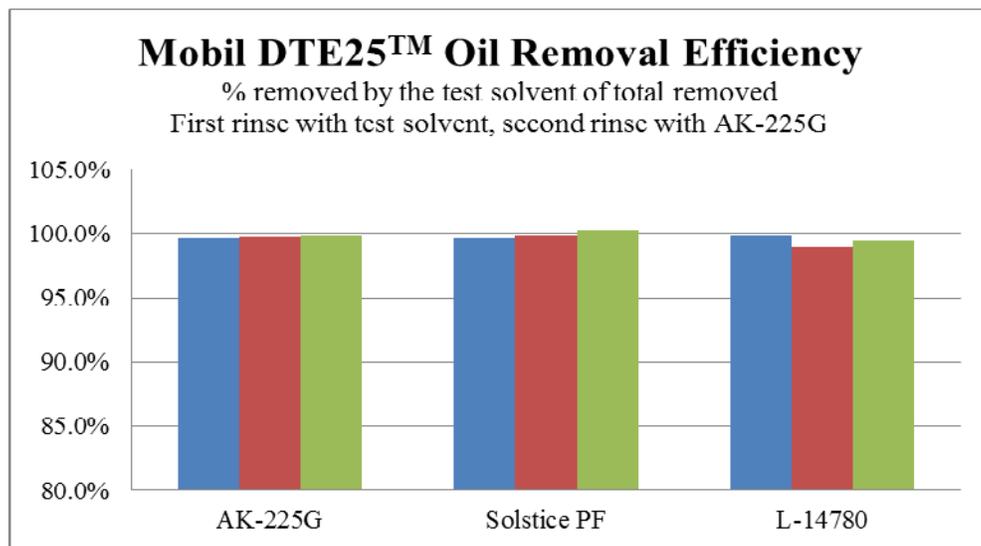
Figure 8. MIL-PRF-83282 Hydraulic Fluid Removal Efficiency.
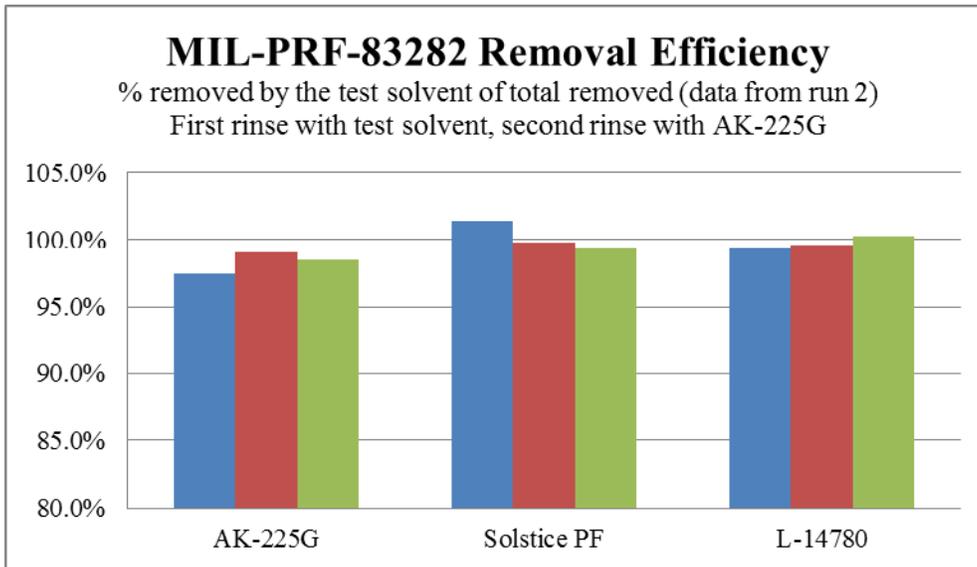
Note: Data from Run 2. Test was repeated due to inconsistency of total contaminant recovered per plate due to spilled solvent during the tests of L-14780 and inadequate percentage of target contaminant mass collected.

Figure 9. Di-2-ethylhexyl Sebacate Removal Efficiency.
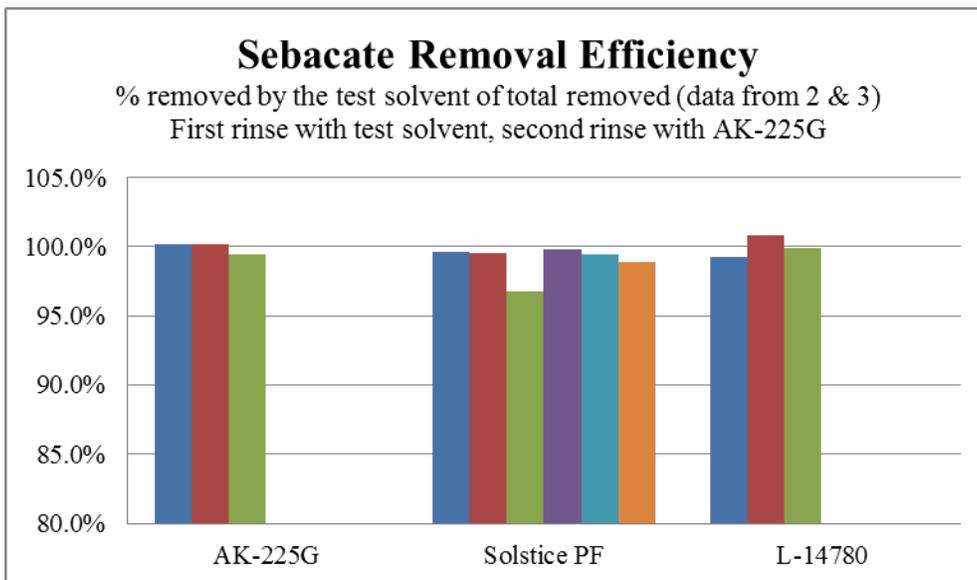
Note: Data from Runs 2 and 3. Test was repeated due to inconsistency of total contaminant recovered per plate in Run 1. Three added tests were added for Solstice PF (Run 3) to confirm performance.

Figure 10. Synthetic Sebum Removal Efficiency.
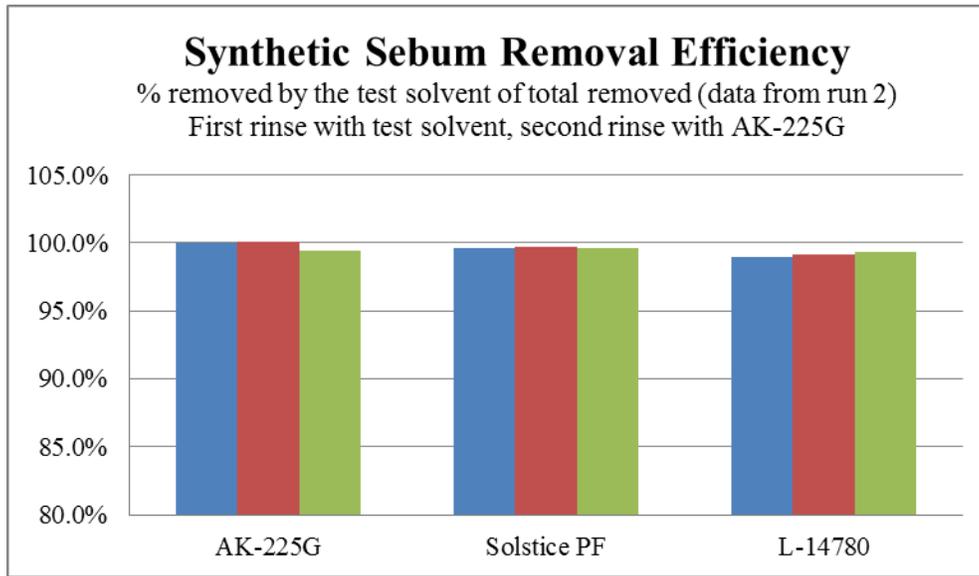
Synthetic Sebum Removal Efficiency
% removed by the test solvent of total removed (data from run 2)
First rinse with test solvent, second rinse with AK-225G

Note: Data from Run 2. Test was repeated due to inconsistency of total contaminant recovered per plate in Run 1.

Figure 11. Krytox Grease Removal Efficiency.

Krytox® Grease Removal Efficiency
% removed by the test solvent of total removed
First rinse with test solvent, second rinse with AK-225G
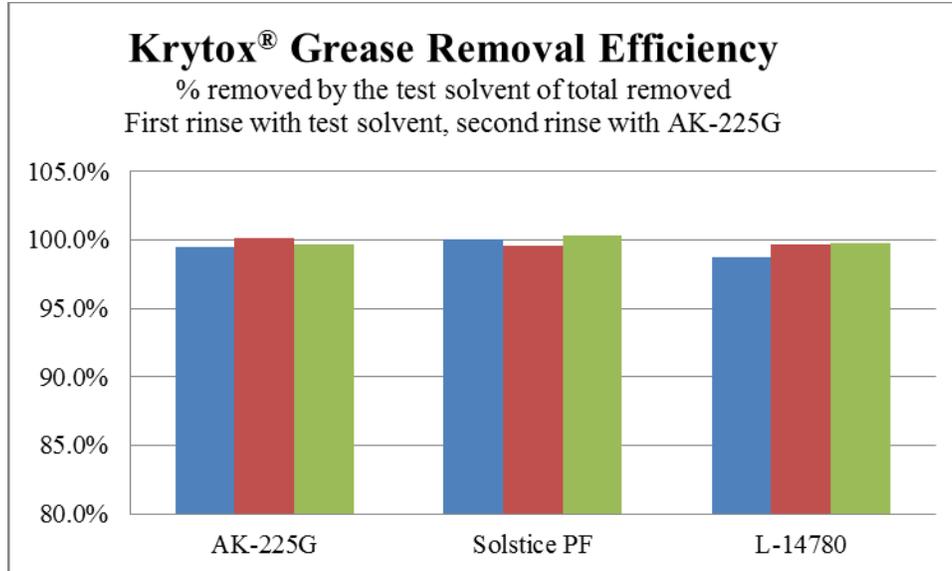
Figure 12. Crane Grease Removal Efficiency.
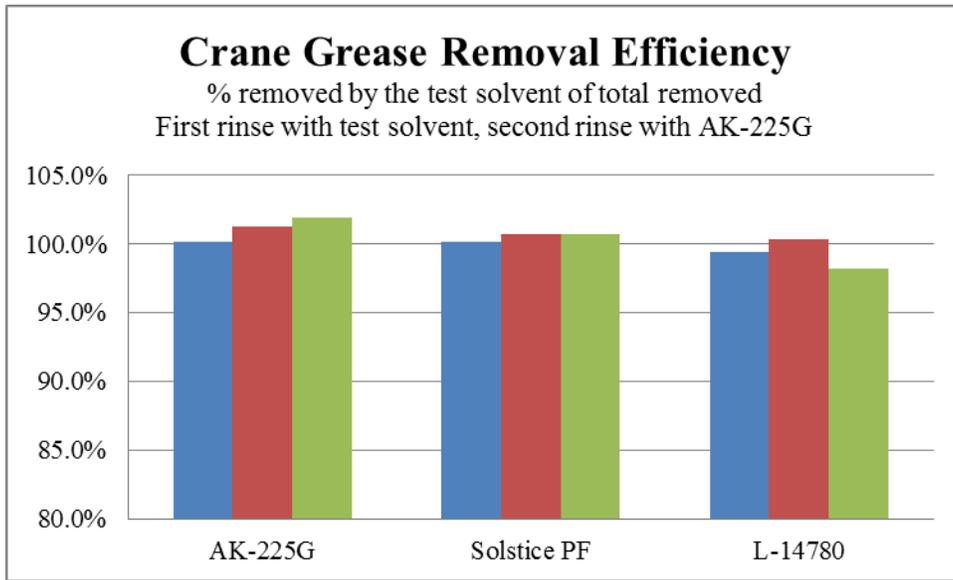
Figure 13. WD-40® Removal Efficiency.
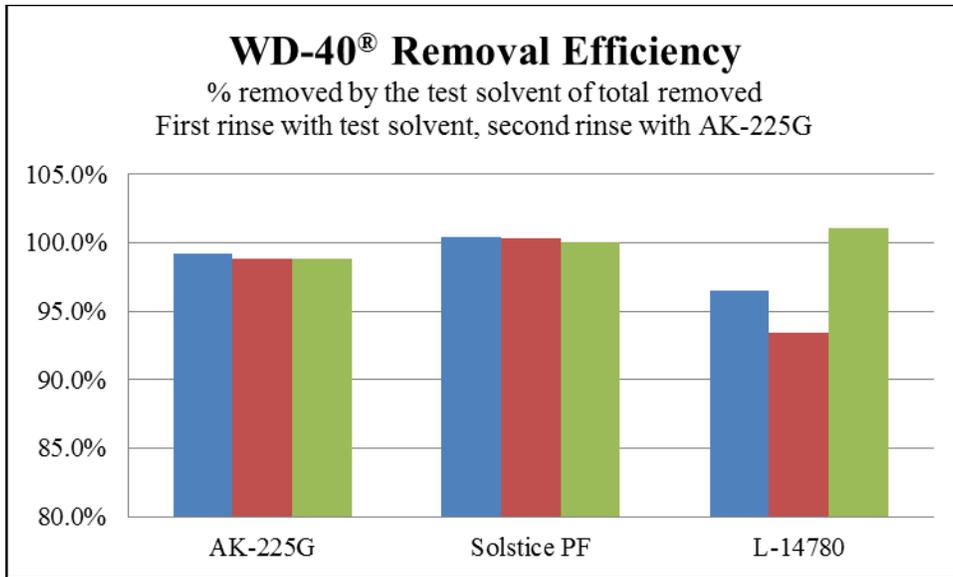
Note: WD-40 contains a high percentage of volatile components that evaporate during initial drying. Total contaminant recovered was < 30%. This creates a more variable result.

Figure 14. Christo-Lube Grease Removal Efficiency.
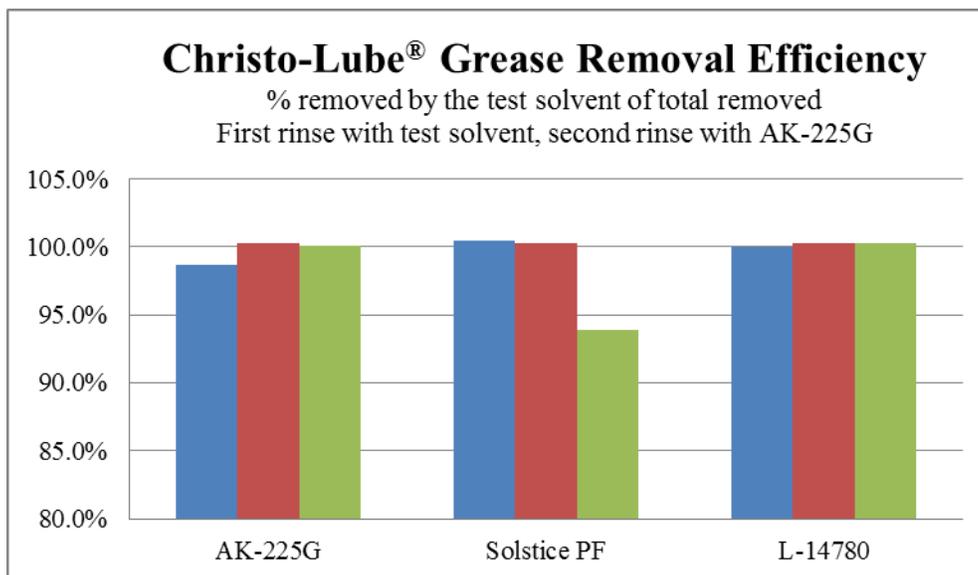
EXTENDED OXYGEN COMPATIBILITY TESTS AND ASSESSMENT

REFINEMENT OF LIQUID OXYGEN MECHANICAL IMPACT TEST FOR VOLATILE LIQUIDS

In response to the discrepant results between the ambient LOX Mechanical Impact ignition tests performed at MSFC and JSC-WSTF, tests were repeated at each site witnessed by representatives of the NESC IAT. A table was developed to identify the variables be tested at each location. (See table 8.) Engineers and technicians from each test facility traveled to the other facility with cleaned and packaged sample cups, disks, and striker pins to perform tests to explore this matrix of variables. On completion of the tests, the results were compared and the IAT recommended a set of modified test parameters to maximize repeatability and confidence in the data. Ambient LOX Mechanical Impact tests of Solstice PF and L-14780 were repeated at JSC-WSTF using the modified test parameters. A complete discussion of this investigation is captured in NASA technical publication 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.* [30]

The modified test parameters developed as a result of the independent assessment do not deviate from the ASTM G 86-98a test protocols, but are refinements determined to be necessary for repeatability when testing volatile liquids such as cleaning solvents using a grease cup. These refinements will be recommended to ASTM committee G04 for potential incorporation into the test method. The refined test parameters were:

a. Acceptance criteria: Reactions occurring when the striker pin impacts the test material alone are counted towards the acceptance criteria. Reactions resulting from non-uniform impacts on the edge of the grease cup, which may expose fresh aluminum or create point or line contact, are unreliable indicators of the reactivity of the material and are disregarded.

b. Use of rebound catcher: The rebound catcher, required for the high pressure mechanical impact test (NASA-STD-6001 Test 13B), is not required for Test 13A by ASTM G 86-98a. Use of the rebound catcher reduces uncontrolled variables such as a shift in position of the grease cup after the initial impact or partial vaporization of the test sample that may result in a reaction on a secondary impact after no reaction on the initial, controlled impact.

Table 8: Matrix of Variables Tested for the Independent Assessment

LOX Impact Threshold Testing	MSFC	JSC-WSTF
Insert disks	No inserts	Add Inserts
MSFC technician prepare samples		MSFC and JSC-WSTF Cleaning
JSC-WSTF technician prepare samples	JSC-WSTF and MSFC Cleaning	
11/16 inch sample cup	Use	Use
Cleaning	JSC-WSTF cleaning	MSFC cleaning
Common solvent filtration	Same solvent container and filters	
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.

c. Use the stainless steel insert disk under the grease cup within the sample cup: Use of the insert disk provides a more rigid impact surface and thus a more rigorous test. ASTM G 86-98a is unclear on when the insert disk is to be used.

d. Solvent sample preparation: Filter the solvent to remove any background particulate prior to test.

e. Humidity control: Prepare test samples in an area with relative humidity less than 60% for improved test sensitivity.

f. Grease cup dimensions: Use the original ASTM G 86-89 [31] grease cup dimensions for consistency. Conversion of ASTM G 86 from inch-pound to metric units created a slight disparity in grease cup dimensions from older stock to newly manufactured stock.

Due to the difficulty of placing and retaining the grease cup in the center of the sample cup that is then filled with LOX, the IAT recommended the development of a one piece grease cup/sample cup for future tests. This would reduce the number of false indications due to the striker pin impacting the edge of the grease cup.

LOX Mechanical Impact tests of Solstice PF and L-14780 were repeated at JSC-WSTF in September 2014 using the modified test parameters. In these tests, both solvents met the screening criteria at 98 J (72 ft-lb). Solstice reacted once in 61 impacts at 98 J (72 ft-lb). L-14780 showed no reactions in 70 impacts at 98 J (72 ft-lb). These results were consistent with the original test results seen at MSFC therefore the tests were not repeated with the modified test parameters at MSFC.

HEAT OF COMBUSTION TESTS

To supplement the AIT and LOX Mechanical Impact data, Heat of Combustion (HOC) tests were performed at JSC-WSTF for Solstice PF, L-14780, and AK-225G. HOC tests were performed in accordance with ASTM D 4809, *Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method).* [12] HOC is a measure of the energy released per gram of material should an ignition occur. It is an indicator of the potential for the material, if ignited, to ignite an adjacent material within the oxygen system and thus propagate the kindling chain. HOC test results for these solvents, compared to some nonmetals commonly used within oxygen systems, are shown in table 9.

Table 9. Heat of Combustion for Solvents versus Common Nonmetals used in Oxygen Service.

Comparison Materials		Heat of Combustion (cal/g) at 3.45 MPa (500 psia) JSC-WSTF Test Data 2014 Guidance per ASTM G 63-99 Section 7.6.6: <2,500 cal/g Preferred 2,500 to 10,000 cal/g Use With Care >10,000 cal/g Poor
Common nonmetals used successfully in oxygen service	FluoroGreen E600	2400*
	PTFE	1700*
	PCTFE	2557*
Honeywell Solstice PF		2448
3M L-14780		1925
Asahi AK-225G		1153

* Published data. [6]

OXYGEN COMPATIBILITY ANALYSIS OF SOLVENTS

JSC-WSTF performed an analysis of the oxygen compatibility of Solstice PF and L-14780 versus AK-225G using the approach described in ASTM G 63 *Standard Guide for Evaluating Nonmetallic Materials for Oxygen Service* for performing an Oxygen Compatibility Assessment (OCA). [32] An OCA as defined in ASTM G 63-99 requires definition of the system within which the material will be used, including temperature, pressure, and configuration. The oxygen system within which a cleaning solvent might be entrapped due to a process escape is undefined, as is the quantity of solvent that might be entrapped. To evaluate the potential risk of using a solvent with known reactive properties for cleaning an oxygen system, engineering judgment is required to compare the properties of the solvent with those of other solvents and nonmetals that have been successfully used with oxygen systems in the past. This is the basis of the oxygen compatibility analysis performed by JSC-WSTF and reported in WSTF # 15-46483, NASA White Sands Test Facility Solvent Investigation Special Report, January 2014.

Solstice PF and L-14780 were found to be flammable in enriched oxygen environments, and plausible ignition mechanisms have been demonstrated. These test also showed AK-225G to be flammable in enriched oxygen environments. However, this does not preclude the safe use of these solvents in oxygen systems. A comparison of the HOC and AIT of Solstice PF and L-14780 versus AK-225G and other common oxygen system materials showed these materials to be "in family". Both solvent candidates were comparable to each other but poorer in oxygen compatibility compared to AK-225G.

The volatility of these two solvents provided a challenge in their evaluation; however, this characteristic will also aid in the safe use of the materials. Regardless of the ignition method, sufficient material is required for ignition, making for an unlikely scenario. In the event of ignition, testing has shown the energy released upon combustion is most likely insufficient to kindle to soft goods.

Based on this oxygen compatibility analysis, Solstice PF and L-14780 have been determined to be an acceptable flammability risk for cleaning and NVR verification of NASA propulsion oxygen systems and associated hardware. These solvents are safe for use with reasonable efforts to assure that the solvent is adequately removed prior to introduction of oxygen to the system. Because these solvents are somewhat more reactive than the historically used solvents, CFC-113 and HCFC-225/HCFC-225cb, additional precautions, such as the use of hydrocarbon detectors to verify solvent removal, are recommended.

ON-SITE VENDOR DEMONSTRATIONS

PURPOSE OF THE ON-SITE DEMONSTRATIONS

Both of the solvents selected as the final candidates to replace AK-225G have boiling points below 32°C (90°F) and therefore are expected to require some modifications to current procedures to prevent excessive loss. The suppliers of these solvents were invited to visit MSFC and SSC to demonstrate the use of their product to the end users and to answer questions. Honeywell and 3M accepted this invitation to provide a demonstration at both facilities. M&P engineers from MSFC witnessed these demonstrations at both facilities.

HONEYWELL DEMONSTRATIONS

The boiling point of Honeywell Solstice PF is 19 °C (66 °F), below the typical operating temperatures of cleanrooms and laboratories at MSFC and SSC, and below ambient temperatures in Huntsville, Alabama, and the Gulf Coast of Mississippi during a significant portion of the year. Propulsion test operations are performed year-around at both locations and component processing operations must frequently be performed without the benefit of air conditioning. Solstice PF must be shipped and stored in pressure vessels due to the low boiling point. The primary purpose of the Honeywell demonstrations was to alleviate concerns that the solvent would boil away too quickly for practical use, or require costly special handling methods.

Concerns were raised early in this project whether a solvent with a boiling point of 19 °C (66 °F) would be impractical for use during the summer months in south Mississippi. To alleviate these concerns, representatives of Honeywell visited SSC on September 18-19, 2013, to demonstrate Solstice PF to SSC engineers and technicians. A Honeywell chemist demonstrated the product at the SSC Component Processing Facility. This facility is an open air shop with large doors that uses localized filtration (such as clean tents) when required. The day of this demonstration was warm and the doors were open. The ambient temperature was 30°C (86°F) with 83% relative humidity.

On November 4-6, 2013, representatives of Honeywell visited MSFC to discuss the potential use of Solstice PF in the vapor degreaser currently used with AK-225G in the MSFC Test Laboratory's Valve and Components Lab. The boiling point of Solstice PF is much lower than AK-225G, therefore there was concern that Solstice PF would be ineffective as a vapor degreasing solvent. As a minimum, it was expected that major modifications to, or replacement of, this vapor degreaser would be required. To alleviate these concerns, Honeywell brought a vapor degreaser demonstration unit to MSFC to show how their product could perform in equipment adapted for that purpose. During this visit, representatives of Honeywell also demonstrated Solstice PF to MSFC engineers and technicians in field cleaning operations within MSFC propulsion test areas.

The feedback from the demonstrations of Solstice PF at SSC and MSFC was positive. Users at both facilities recommended proceeding with Solstice PF as a potential replacement candidate for AK-225G. The requirements to transport and store Solstice PF in pressure vessels were discussed during the demonstrations at SSC and MSFC. Users at both facilities considered these requirements to be only a minor inconvenience that could even potentially save storage and disposal costs with a cylinder exchange program. Technicians at MSFC liked the convenience of dispensing solvent directly from a small pressure vessel with a hose and nozzle rather than transferring and dispensing it from the pressurized canister sprayers currently used with AK-225G.

It was noted during the demonstration at MSFC that the Solstice PF Spray Cleaner product, which contains Solstice 1234ze as the propellant, is a different product that must be considered separately from the single component Solstice PF liquid. Unlike Solstice PF (1233zd(E), trans-1-chloro-3,3,3-trifluoropropene) which has no Upper Explosion Limit (UEL) or Lower Explosion Limit (LEL) in air, Solstice 1234ze (trans-1,3,3,3-Tetrafluoroprop-1-ene) exhibits flame limits in air at temperatures in excess of 28°C (82.4°F). Solstice 1234ze propellant dissolved in Solstice PF could alter the flammability of Solstice PF in oxygen. Therefore, Solstice PF Spray Cleaner should not be used as a substitute for Solstice PF for cleaning components for oxygen service without separate oxygen compatibility tests for

this product. When needed, Solstice PF should be pressurized with gaseous nitrogen (GN2). Solstice PF may also be pressurized by heating the vessel in which it is stored with a heating blanket.

3M DEMONSTRATIONS

The boiling point of L-14780 is 28-30°C (82-86°F), significantly lower than the boiling point of AK-225G and well within the range of ambient temperatures in Huntsville, Alabama, and the Gulf Coast of Mississippi during the summer months. Although this is higher than the boiling point of Solstice PF, L-14780 may also require modified procedures for shipping, storage, and use. Representatives from 3M were invited to demonstrate their product at MSFC and SSC to obtain user feedback prior to the final down-selection.

On August 20, 2014, representatives of 3M including a solvent chemist visited MSFC to discuss the potential use of L-14780 in the vapor degreaser currently used in the Valve and Components Lab, and to demonstrate the use of their product in manual cleaning applications to MSFC Test Laboratory engineers and technicians. They also answered questions from the users regarding solvent testing, distillation and handling.

During the 3M demonstration at MSFC, technicians in the Valve and Components Lab tried L-14780 with their NVR sampling and verification apparatus. During this trial, a residue was detected in the FTIR spectrometer that partially overlapped and interfered with the hydrocarbon peaks used to measure residual NVR contamination. This was the same concern noted earlier when testing the solvent for background NVR. The 3M chemist stated that this residue was probably one of the stabilizers. 3M agreed to supply samples of the stabilizers used in L-14780 for comparison to the residue detected in these tests.

Immediately after the demonstration at MSFC, the 3M representatives traveled to south Mississippi to demonstrate their product at SSC the following day. On August 21, 2014, the 3M representatives demonstrated their product at the SSC Component Processing Facility. A 3M chemist demonstrated use of L-14780 for cleaning of several components including complex tubing.

Requirements for packaging, transportation, and shipping of L-14780 were discussed during these meetings. 3M informed NASA that L-14780 may be shipped and stored in four liter/one gallon bottles or smaller but, due to its boiling point and vapor pressure, larger volumes of L-14780 require stronger containers than the lined carbon steel pails and drums used for AK-225G. L-14780 may be shipped and stored in stainless steel 55 gallon drums or 5 gallon pressure vessels. For large quantity users, a container exchange program could be arranged.

The feedback from the demonstrations of L-14780 at SSC and MSFC was mostly positive. Users at both facilities recommended proceeding with L-14780 as a potential replacement candidate for AK-225G. It was noted, however, that one of the solvent stabilizers apparently interfered with the hydrocarbon peaks measured during verification of NVR using FTIR. This would require MSFC and SSC labs to use a different quantitative method to verify NVR. It was also noted that use of a four-component solvent (L-14780 is an azeotrope of methyl perfluoropropyl ether and tDCE plus two stabilizer chemicals) would require more analytical monitoring for quality control during distillation and recycling than AK-225G, a one component solvent that does not require a stabilizer.

FINAL DOWN-SELECTION

DATA EVALUATED FOR THE FINAL DOWN-SELECTION

A TIM was convened at JSC-WSTF on October 21-22, 2014, to select the final replacement candidate for AK-225G. All of the data obtained to date was summarized and reviewed. The oxygen compatibility test data was discussed in detail and the oxygen compatibility analysis was presented by JSC-WSTF. A table of decision parameters was presented and the committee rated the final solvent

candidates on these parameters. The results of this assessment are shown in table 10. An X indicates the preferred solvent for that parameter.

Table 10. Decision Point Parameters for the Selection of a Replacement for AK-225G.

	Honeywell Solstice PF	3M L-14780	No Preference	Notes
SHE				
Environmental	X			Based on GWP and VOC comparison.
Health and Safety	X			Based on AEL comparison.
Technical/Performance				
Metals Compatibility			X	L-14780 corrosion on carbon steel after exposure and storage noted, but not considered a concern for selection
Nonmetal 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.				

FINAL SELECTION

The project team agreed that Solstice PF and L-14780 met the primary technical performance requirements, but with some questions remaining regarding L-14780:

a. The cleaning efficiency of both solvents was comparable to AK-225G for the contaminants of concern. Both solvents were capable of achieving the cleanliness requirements for MSFC and SSC propulsion oxygen systems hardware, GSE, and associated test systems.

b. Materials compatibility for both solvents was equal to or better than AK-225G, with the exception of L-14780 with 4140 low alloy carbon steel. Although used in test support apparatus, low alloy carbon steel is unusual in the construction of NASA propulsion oxygen systems, therefore the team concluded that this is not a barrier to use of L-14780 with systems that do not contain low alloy carbon steel. L-14780 should not be used to clean other systems containing low alloy carbon steels without further investigation and precautions to prevent corrosion.

c. Solstice PF and L-14780 as tested were judged to be acceptable for use with NASA propulsion oxygen systems, with reasonable efforts to assure that the solvent is adequately removed prior to introduction of oxygen to the system. Although both solvents were shown to be more reactive in oxygen than CFC-113 or HCFC-225/HCFC-225cb, their flammability characteristics were "in family" with other nonmetals that have been used safely within oxygen systems. Furthermore, the lower boiling points of these solvents contribute to faster drying and a reduction in the probability of solvent entrapment within an oxygen system component after cleaning.

d. Two concerns remained regarding the suitability of L-14780 for use in MSFC and SSC propulsion oxygen system applications:

1. A residue was detected in the test samples of L-14780 that interfered with the MSFC/SSC test method for verification of NVR by FTIR. In some samples tested gravimetrically, the residue exceeded the solvent residue limits required by MSFC and SSC specifications. If the residue was confirmed to be a stabilizer of L-14780 rather than a contaminant that could be removed by distillation without affecting the L-14780, then L-14780 as currently formulated may be unsuitable for use by MSFC and SSC. It was also recommended that the NVR residue attributed to the stabilizer should be tested for HOC to assure that this residue does not pose a greater flammability risk than other contaminants intended to be precluded by the 1 mg/0.1 m^2 NVR cleanliness limit for NASA propulsion oxygen systems.

2. It was noted that the L-14780 formula tested is an azeotrope only at the boiling point of the solvent. The boiling point of the HFE component is 34°C (93°F), significantly lower than the boiling point of tDCE, 48°C (118°F). If an escape of L-14780 were left within an oxygen system component stored at a temperature below the boiling point, it is possible that the HFE fraction could evaporate preferentially leaving a solvent enriched in tDCE. Whether this enriched blend would pass the NASA criteria for oxygen compatibility is unknown.

The technical performance concerns remaining for L-14780 could potentially be resolved with more testing and, if necessary, reformulation of the stabilizer. However, the greater certainty of performance of a single component material made Solstice PF the preferred candidate.

Solstice PF was clearly preferred over L-14780 for its lower toxicity and favorable environmental characteristics. Solstice PF has a higher AEL than AK-225G or L-14780. Solstice PF is also one of a new class olefin-based halogenated chemicals that breaks down rapidly in the atmosphere. It fully meets all currently identified environmental requirements and goals including very low GWP. Neither solvent had an objectionable odor. Both solvents were expected to be accepted by the end users.

As a single component solvent that does not require stabilizers, Solstice PF was preferred over the four component L-14780 azeotropic blend with stabilizers for implementation and business considerations. A single component material will require less analytical effort to monitor its chemical composition for quality assurance. Also, the performance of L-14780 is dependent on chemical stabilizers to prevent chemical breakdown of the tDCE component. These implementation issues are minor when purchasing and dispensing a cleaning solvent from small containers for one time use, but become significant when the solvent is used in a vapor degreaser for an extended time period and when repeatedly recovered, distilled, and reused.

Honeywell Solstice PF was selected as the preferred solvent to replace AK-225G at MSFC and SSC. 3M L-14780 was identified as a potential backup should Solstice PF become unavailable in the future or should unforeseen obstacles to implementation arise during the final assessment phase. The remaining technical performance concerns noted for L-14780 would need to be resolved. As noted previously, DuPont Vertrel MCA, used in a two-step cleaning process, was also identified as a backup. The final selection of Solstice PF was driven by SHE factors, by the remaining technical questions regarding use of L-14780, and for business considerations related to the cost and complexity of monitoring and maintaining a multiple-component material.

COMPONENT LEVEL CLEANING AND IMPLEMENTATION ASSESSMENTS

OBJECTIVES OF THE COMPONENT LEVEL CLEANING AND IMPLEMENTATION ASSESSMENTS

Investigations were performed at MSFC and SSC to assess the use of the new solvent in place of AK-225G in actual launch vehicle and engine test operations. The purpose of these investigations was to confirm that the solvent was suitable for use in field operations and to identify any potential issues with user acceptance. Necessary modifications to equipment and procedures were also noted during these activities to assess potential cost and schedule impacts of the transition from AK-225G to the new solvent. Personnel involved in these investigations were primarily the end users: engineers, test technicians, and laboratory personnel currently processing NASA propulsion oxygen system hardware. The objectives of the final component level cleaning and implementation assessments were to confirm the suitability of the replacement solvent in the intended final applications and to identify required modifications to equipment and procedures necessary to transition to the new solvent.

MSFC END USER EVALUATIONS

Solstice PF was provided to the MSFC Propulsion Test office for direct comparison to AK-225G in actual field cleaning tasks. Solvent field cleaning trials performed at a test stand included flanges, B-nuts, tubing, piping and instrumentation. The Propulsion Test technicians reported that they saw no difference in the cleaning performance or usage rate of Solstice PF versus AK-225G. Solstice PF was reported to seem colder and evaporate faster than AK-225G, but the faster evaporation was seen as a plus. Some icing from moisture condensation was observed on the aluminum foil on which parts were placed for cleaning, but not on the parts themselves.

Due to the age of the vapor degreasing system in the Valve and Component Lab now used with AK-225G, a request had already been submitted to the capital plan for a replacement. Discussions were held with a vapor degreaser supplier to identify the requirements for a system using Solstice PF and verify that a system could be supplied within the current cost estimate. No other new equipment or modifications were identified as necessary.

SSC END USER EVALUATIONS

To verify the performance of the solvent in a shop operation, the cleaning trials similar to those performed during the vendor demonstrations were repeated for Solstice PF and L-14780. Flex hose, rigid tubing, and fittings from the Component Processing Facility were contaminated, cleaned, and quantitatively analyzed to measure cleaning efficiency.

SSC identified a capital requirement for a new distillation system designed to purify and contain Solstice PF. Purchase of a second distillation system will support transition from AK-225G to Solstice PF without disruption of operations.

LABORATORY IMPLEMENTATION ASSESSMENTS

The MSFC M&P Contamination Lab performed three additional tests not described in the test plan. These tests were to:

a. Confirm the effectiveness of Solstice PF to remove particulate.
b. Confirm the capability of a real time hydrocarbon analyzer ("sniffer") to detect the presence of residual Solstice PF entrapped within hardware.
c. Evaluate the use of a Gas Chromatograph/Mass Spectrometer (GC/MS) for receiving inspection and determination of lot-to-lot consistency of Solstice PF.

The particulate removal test was designed to verify that rinsing with Solstice PF would meet the particulate requirements for propulsion system components. In accordance with MSFC-SPEC-164D, *Cleanliness of Components for Use in Oxygen, Fuel, and Pneumatic Systems, Specification for*, [1] oxygen systems and associated hardware must be verified free of particulate > 800 μ in longest dimension, and silting of fine particulate is prohibited. For fuel system hardware, the particulate size limit is 400 μ.

In particulate removal test 1, three clean stainless steel panels, one for each solvent to be tested, were heavily contaminated with Course Test Dust (reference ISO 12103-1, *Road Vehicles – Test Dust for Filter Evaluation – Part 1: Arizona Test Dust*, Type A4). [33] The test dust was brushed through a number 60 sieve, 250 μ (.01 in) pore size, onto panels wetted with distilled water. The panels were then air dried in a filtered flow bench. The contaminated panels were rinsed with AK-225G, Solstice PF, and L-14780 from a PTFE squeeze bottle. A visual inspection with white task lighting showed that the particulate was not removed. The solvent flush was repeated with a Sure Shot® sprayer (Milwaukee Sprayer Mfg. Co, Inc.) pressurized to 70 psi. This removed most, but not all, of the particulate. The remaining particulate was successfully removed with solvent moistened lint free wipers.

In particulate removal test 2, clean, dry stainless steel panels were lightly dusted with Course Test Dust using the Number 60 sieve and brush. For each of the three solvents, a flush from the PTFE squeeze bottle achieved visual cleanliness. The particulate removed from the panels was visible in the solvent captured from the flush when inspected with white light.

The conclusion of these particulate removal tests was that flushing of lightly contaminated surfaces is sufficient to meet the required particulate cleanliness levels, but heavily contaminated surfaces must be pre-cleaned prior to flushing or cleaned manually. This is the current standard procedure.

Trials were performed to evaluate the drying properties of Solstice PF and to confirm that a real-time sensor could be used to detect the presence of Solstice PF within a component that was not adequately dried. The sensor used for this test was a hand held Yellow Jacket AccuProbe UV Leak Detector, Model 69336, with solid electrolyte sensor. The sensor is used by holding a "sniffer" probe at an orifice of a tube or other component to detect trace vapor from solvent that was inadequately removed from the part. The system was set on "high sensitivity".

For each test, solvent was poured into a test article, the test article was capped (for tubes), and rocked or rotated to wet all interior surfaces. The tubes were stainless steel of various lengths and OD. The solvent was then poured out, the article was dried (or not) and the sniffer was used to detect residual solvent. These tests showed that:

a. The sniffer detected AK-225G, Solstice PF, and L-14780.

b. AK-225G and Solstice PF were removed to below the detection limit of the sniffer by low pressure purge for a sufficient length of time.

c. Ambient drying for two hours was insufficient to remove AK-225G from inside a pipe but was sufficient to remove Solstice PF.

d. Solstice PF appeared to dry more rapidly than AK-225G, consistent with the lower boiling point.

Three samples of Solstice PF from three lots were submitted to the MSFC Chemistry Laboratory for analysis by GC/MS to determine the constituents of the solvent and compare these lots for consistency. This was a first step toward determining a receiving inspection test for the solvent. The analysis showed that GC/MS could be used for receiving inspection and that all three lots contained >99% trans-1-chloro-3,3,3-trifluoropropene.

FOLLOW-UP INVESTIGATION OF L-14780 RESIDUE

During the demonstrations of L-14780 at MSFC and SSC, residue from L-14780 was detected during NVR verification by the FTIR method. The SSC Gas and Materials Science laboratory performed an evaluation of solvent residue from L-14780. A 200 ml sample of the solvent evaporated to dryness yielded 5.7 mg of residue, visible as dried droplets in the evaporating pan. This residue was analyzed by FTIR spectrometer. The FTIR results were compared to mineral oil and to a sample provided by 3M of one of the proprietary stabilizers used in L-14780. The residue from L-14780 matched the reference spectra of the stabilizer.

To be suitable for use as an NVR verification solvent for NASA rocket engine test facilities, solvents are required to have NVR background residue < 2 ppm weight/weight or <1 mg NVR/200 ml. For use as a cleaning solvent for propulsion systems, the MSFC purity requirement is ≤ 10 mg NVR per 500 ml of solvent. [1] The quantity of stabilizer detected in L-14780 exceeds both of these requirements. The solvent purity requirement may be achieved by distillation in-house to remove impurities. The stabilizer, however, is not an impurity, but is an essential component to inhibit the deterioration of the solvent. Discussion with a 3M chemist confirmed that the quantity of the stabilizer required by the 3M solvent specification exceeds these NASA purity requirements. This makes the current formulation of L-14780 unsuitable for use at MSFC or SSC.

Many different chemical formulas are used by solvent manufacturers to stabilize their products. It is possible that the azeotrope of methyl perfluoropropyl ether and tDCE could be reformulated by 3M with a different stabilizer formula to meet the MSFC and SSC requirements for NVR background residue. This would be considered a new product by NASA and require testing.

CONCLUSIONS

The following conclusions resulted from this Test Project:

Solstice PF is acceptable and preferred as the replacement for HCFC-225 solvent for cleaning and NVR verification sampling of NASA propulsion oxygen systems hardware, GSE, and associated test systems. Solstice PF is recommended for cleaning and NVR sampling in applications at NASA propulsion test facilities where AK-225G is currently used.

3M L-14780 as formulated does not meet the solvent purity requirements for cleaning and NVR verification of NASA propulsion oxygen systems hardware, GSE, and associated test systems, due to the required concentration of the stabilizer. This issue could potentially be resolved by reformulation of the stabilizer and testing of the reformulated product.

Solstice PF and L-14780 were shown to be flammable in enriched oxygen environments and more reactive than AK-225G. However, it was concluded that these products could be safely used with propulsion oxygen systems when reasonable precautions are in place to assure that the solvent is adequately removed prior to introduction of oxygen to the system. Uncertainties remain regarding the stability of the HFE/tDCE ratio of L-14780 when stored at a temperature lower than the boiling point of the azeotrope. This could potentially affect the flammability risk of solvent inadvertently left within an oxygen system component. Also, the relative flammability of a stabilizer residue versus other NVR contaminants has not been assessed. Due to these uncertainties, L-14780 is judged to be a higher risk than Solstice PF.

LIMITATIONS

No claim is made here regarding the safety or efficacy of Solstice PF or L-14780 with materials or contaminants other than those tested.

No claim is made here regarding the suitability of Solstice PF or L-14780 for use with breathing oxygen systems. Use of a halogenated cleaning solvent with breathing oxygen systems requires an appropriate toxicology assessment by the using organization. Evaluation of these solvents for suitability with breathing oxygen systems was beyond the scope of this project.

ACKNOWLEDGMENTS

TRADEMARKS

Trade names and trademarks are used in this report for identification only. This usage does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

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