Solvent Replacement for HCFC-225 for Cleaning Oxygen Propulsion System and Test Components

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Oxygen Standardization Coordinating Group
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Photo: NASA/SSC

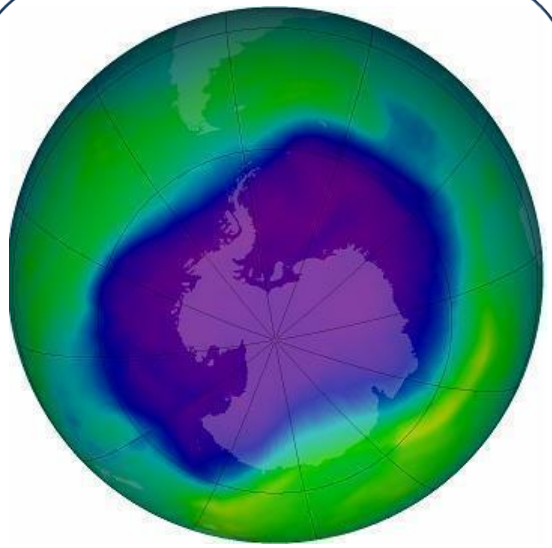
Driver: Ozone Depleting Substances (ODS) Phase-out of Critical Cleaning Solvents

1987-90: US ratified the Montreal Protocol on Substances that Deplete the Ozone Layer; Clean Air Act Amendments Title VI established phase-out requirements

- *US and global phase-out of Class I ODS including chlorofluorocarbon-113 (**Freon 113**), the primary oxygen-compatible solvent used for cleaning NASA propulsion systems and breathing oxygen systems.*
- *NASA qualified and adopted hydrochlorofluorocarbon (HCFC)-225 (Asahiklin **AK-225**) to replace CFC-113 for cleaning of propulsion oxygen systems.*

January 1, 2015: Title VI of the U.S. Clean Air Act banned manufacture/import of Class II ODS including HCFC-225

- *Large scale components for launch vehicle test stands still require an oxygen-compatible cleaning solvent.*
- *U.S. Air Force uses HCFC-225 for field cleaning of aviator's breathing oxygen system components.*
- *A replacement is required for HCFC-225.*



Source:
NASA's Ozone Hole Watch website
https://ozonewatch.gsfc.nasa.gov

Critical Cleaning for Oxygen Systems

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

HCFC-225 Use at NASA

- **The single isomer form, HCFC-225cb (AK-225G), is preferred over the more toxic HCFC-225ca/cb form.**
- **NASA Propulsion Test* uses > 8000 lbs/year AK-225G.**
  - **Large scale components are cleaned with AK-225G by flushing, vapor degreasing, or hand wiping.**
  - **Water-based cleaners are used for smaller components but these are flushed and verified clean with AK-225G.**
  - **NASA users recapture, distill, and re-use AK-225G where feasible.**
- ***Many users in NASA and the aerospace industry still rely on stockpiled CFC-113.***

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

DOD Stakeholders Contacted

- **Air Force:**
  - Wright-Patterson AFB
    (Mr. Michael Sanders, Ms. Mary Wyderski, Ms. Conchita Allen)
  - Tinker AFB (Mr. Chris Kissick)
  - Hill AFB (Dr. Jane Johnson)
- **NAVSEA:**
  - Portsmouth Naval Shipyard (Mr. Tim Dunn)
  - Naval Surface Warfare Center Caderock Division (NSWCCD)
    (Mr. Alexander Goloub, Mr. Peter McGraw, Mr. Peter Mullenhard)
- **NAVAIR:**
  - Naval Aviation Deport FRC Southeast, JAX
    (Ms. Ernestine Lawson, Ms. Kamin Downey)
- **No Army users** (per Wayne Ziegler/ARL)

HCFC-225 Use by DOD

- **US Air Force uses AK-225G for depot cleaning of aviators breathing oxygen systems**
  - **Parts are cleaned by flushing or hand wiping**
  - **In 2002, USAF qualified DuPont Ikon® P (perfluorobutyl iodide) for use where HCFC-225 is banned.**
    - AFRL-ML-WP-TR-2003-4040, *The Wipe Solvent Program,* February 2003.
    - Ikon® P discontinued by DuPont. The replacement, Capstone ® 4-I, is very expensive, requires 6-12 month lead time, not marketed as a cleaning solvent, not pure PFBI.
- **NAVSEA approved HCFC-225 for use with oxygen systems but uses stockpiled CFC-113.**
    - MIL-STD-1330D *Precision Cleaning and testing of Shipboard Oxygen, Helium, Helium-Oxygen, Nitrogen, and Hydrogen Systems*

Replacement Solvent Considerations

Safety, Health, and Environmental Hazards

Environmental

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

Restrictions are expected to increase with time

Safety and Health

Toxicity (exposure limits)
Flammability (human safety)

Performance Requirements and Cost Considerations

Materials compatibility
- Metals – corrosion
- Nonmetals – swelling, cracking, leaching

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

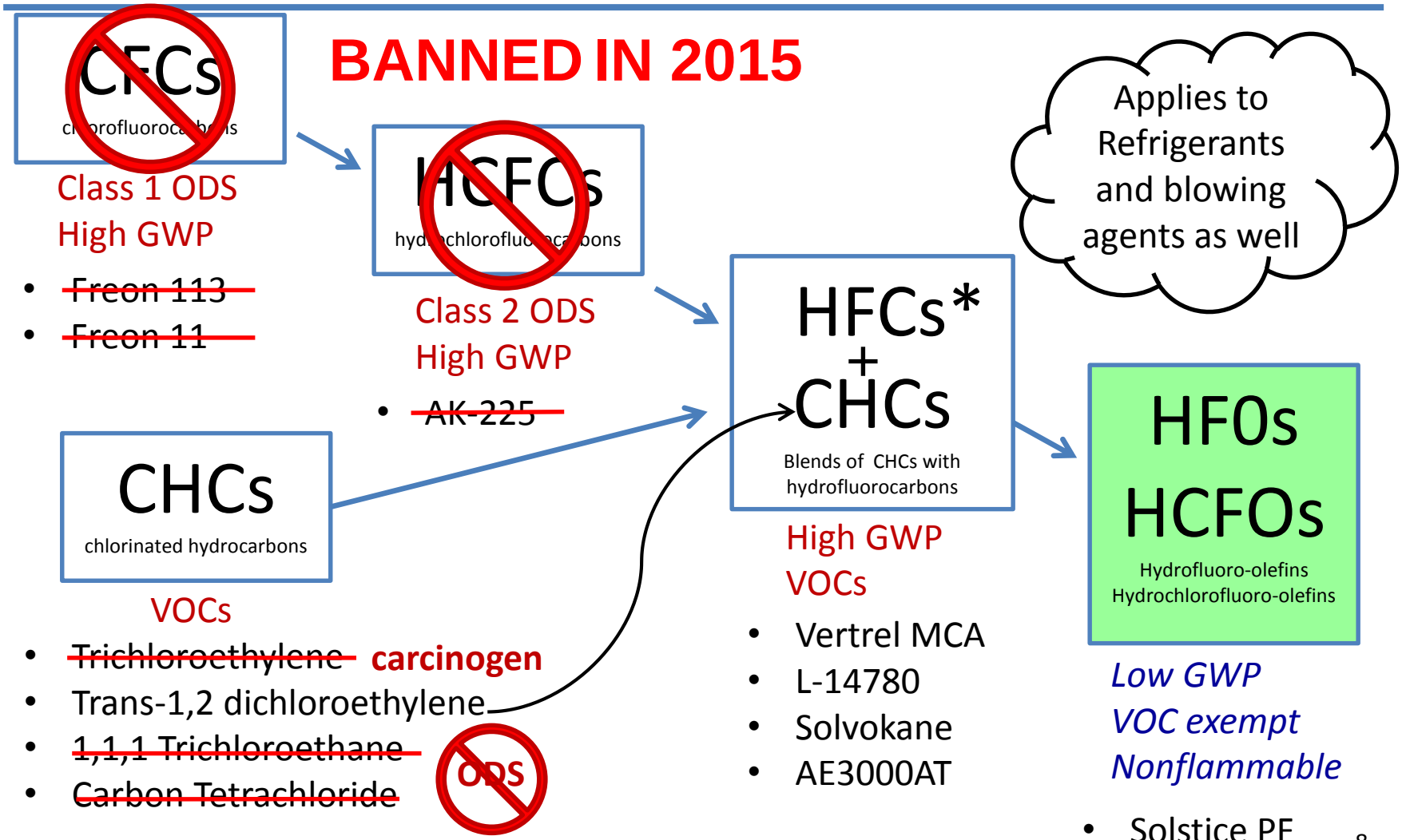
Oxygen compatibility/flammability
- Safe for use in oxygen systems

Solvent Volatility
- Must capture effluent to test for NVR

Business Considerations
- Solvent stability/recyclability/disposal
- Availability
- Cost per pound; Equipment modification costs

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

The Evolution of Cleaning Solvents



*Poor cleaners for hydrocarbon soils

Ground Rules for Solvent Candidates

The replacement solvent cannot be:

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

The replacement solvent must be:

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

The Search for Replacement Candidates

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

Initial Solvent Search Conclusions

- **No bio-based cleaners are potential candidates**
  - **All are flammable, high boiling point, and/or leave residues**
  - **Good industrial solvents, not suitable for precision cleaning**
- **The most effective non-ODS solvents for hydrocarbons are flammable, not candidates**
  - **Ethyl acetate, cyclohexane, trans-1,2 dichloroethylene (tDCE), nPB**
  - **Nonflammable solvents are all halogenated**
- **Most new nonflammable degreasing solvents are azeotropes of halogenated solvents with tDCE**
  - **tDCE added to improve solvency**
  - **NASA data indicates tDCE > 35-40% unlikely to pass LOX impact test**
  - **Azeotropes with low tDCE% have low boiling points**

Solvent Candidates

Single Component	Kb	AEL-8hr	Concerns
AGC Chemicals AE3000 (HFE-347pc-f2) 1,1,2,2-tetrafluoro-1-(2,2,2-trifluoroethoxy)-ethane	13	50 ppm	Low Kb may not clean well, toxicity
Honeywell Solstice PF (1233zd(E)) Trans-1-chloro-3,3,3,-trifluoropropene	25	800 ppm	Boiling point of 19°C (66°F)
DuPont Capstone 4-I (chemical intermediary) 85%+ Perfluorobutyl Iodide (PFBI)	No data	375 ppm	Not compatible with Aluminum? Expensive, short supply
Solvay Solkane 365mfc (HFC-365mfc) 1,1,1,3,3 Pentafluorobutane	14	1000 ppm	Low Kb may not clean well, unusual flammability characteristics
Azeotropic Blends with trans-1,2 Dichloroethylene (tDCE)	(tDCE = 117)	(tDCE = 200 ppm)	Pure tDCE is flammable.
AGC Chemicals AE3000AT 45% tDCE / 55% AE3000	32	200 ppm / 50 ppm	Expected to clean well, may not pass LOX test
3M L-14780 developmental solvent 22% tDCE /78% (HFE-347mcc3) methyl perfluoropropyl ether (3M HFE-7000)	Similar to MCA	200 ppm / 250 ppm	Boiling point of 28-30°C (82-86°F)
DuPont Vertrel MCA (new stabilizer) 38% tDCE/ 62% (HFC-43-10mee) 1,1,1,2,2,3,4,5,5,5-Decafluoropentane (Vertrel XF)	20	200 ppm	Cleans well but borderline LOX compatible on past tests. Low AIT at high GOX pressure.
Solvay Solvokane 30% tDCE/ 70% (HFC-365mfc) 1,1,1,3,3 Pentafluorobutane	25	200 ppm / 1000 ppm	Boiling point of 36°C (97°F), individual components are flammable.

Kb = Kauri-Butanol value, a measure of hydrocarbon cleaning power, per ASTM D1133
AEL-8hr = 8 hour Airborne Exposure Limit, a measure of human toxicity

Test Plan Summary

- **Nonvolatile residue in solvents as received**
- **Compatibility with 13 metals**
  - Liquid* and vapor phase immersion of metal specimens in each solvent at boiling.
    - *Similar to ASTM F 483-09, *Standard Practice for Total Immersion Corrosion Test for Aircraft Maintenance Chemicals*
  - Specimens inspected and weighed at 24 hours and 168 hours
- **Compatibility with 9 nonmetals**
  - Three specimens of each nonmetal were immersed in a fisher-porter tube filled with solvent and boiled for 15 minutes.
  - Similar to ASTM F 483-09, but much shorter duration.
  - After immersion, specimens were suspended in a desiccator for 30 minutes
  - Specimens were weighed, measured, and elastomers tested for hardness before and after exposure, and repeated until weight stabilized.
- **Cleaning Effectiveness with 9 Contaminants**
  - Simulates an NVR verification sampling procedure.
  - Assesses the ability of a solvent to remove NVR contaminants by ambient temperature flush.
- **Oxygen Compatibility**
  - Autogenous Ignition Temperature in GOX
  - LOX Mechanical Impact Ignition

Materials Tested

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

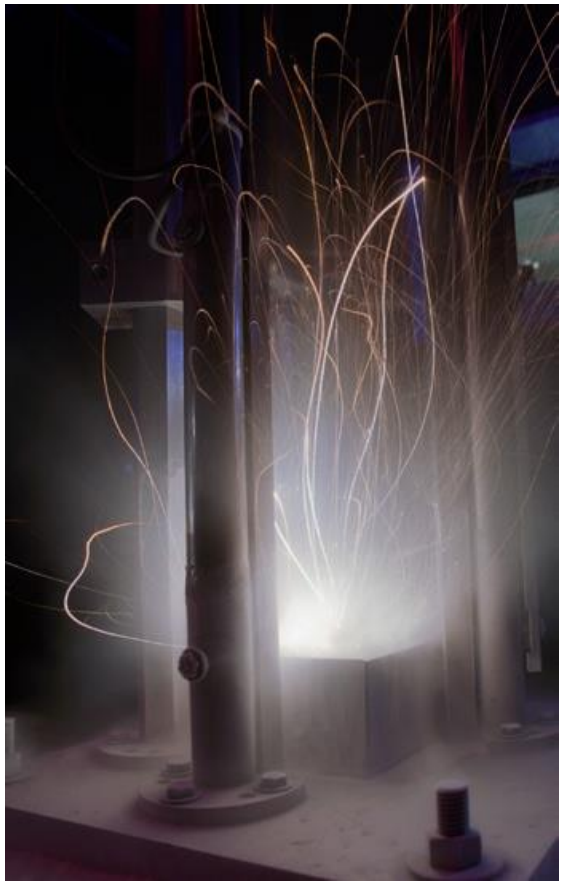
METALS
- Carbon Steel (4140)
- Stainless Steels (17-4PH, A286, 304 & 440C)
- Nickel Alloys (Monel® 400, Inconel® 718)
- Co Cr Ni Alloy (Elgiloy®)
- Tin Bronze
- Brass (Naval Brass)
- Aluminum (6061 -T6, 2195 -T8 & 2219 -T6)

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

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

Oxygen Compatibility Tests

- **For unrestricted use in liquid or gaseous oxygen systems, materials must be shown to be compatible at a range of expected use temperatures and pressures.**
- **Defining the limiting temperatures and pressures for cleaning solvents can be difficult so the approach is conservative.**
- **The solvent that is the most ignition resistant is preferred.**
- **Tests were performed in the MSFC Combustion Research Facility and JSC-WSTF.**



Reaction in liquid oxygen caused by a metal pin striking a sample immersed in oxygen.

Oxygen Compatibility Conclusions

- All candidate solvents are “flammable” (as well as AK-225G).
  - These solvents rank well compared to other “good”, commonly used nonmetallic materials.
- Solvent high volatility increases O_2 compatibility as they possess a low kindling chain potential due to their likelihood to evaporate prior to transferring energy to other system materials.
- Solstice™ PF and L-14780 as tested are determined to be an acceptable flammability risk for cleaning of NASA propulsion oxygen systems; safe for use with reasonable efforts to assure adequate removal prior to introduction of oxygen to the system.
  - Questions remain regarding flammability of L-14780 stabilizer residue and off-nominal blend ratio.

Conclusions

- **Honeywell Solstice™ PF selected to replace AK-225G for cleaning and NVR verification of NASA propulsion oxygen system hardware.**
  - **3M L-14780 is a potential alternate but requires resolution of excess NVR from stabilizers and unknowns regarding oxygen compatibility of potential variations in the blend.**
- **Volatile liquids are difficult to test for oxygen compatibility, require more controls during test.**
- **If stabilizer additives are required, they can affect NVR results (even in very low quantities) and must be controlled for oxygen cleaning.**
- **Both of these solvents are expected to be capable of cleaning metal components used in oxygen systems to meet the cleanliness requirements of those systems.**
- **The candidate solvents performed comparably to AK-225G in materials compatibility tests; results should be similar in comparable use situations.**
- **Capstone® 4-I is not an acceptable substitute for AK-225G or Ikon® P.**
  - **Metal corrosion and stability were unacceptable.**

No claim is made regarding Solstice PF or 3M L-14780 for:
- **Safety/efficacy with materials or contaminants other than those tested**
- **Suitability with breathing oxygen systems (not evaluated)**
  - **MSFC proposal to DLA is in work to test Solstice™ PF for cleaning breathing air/oxygen systems and components**

Acknowledgements

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

*The Dupont Performance Chemicals segment is now The Chemours Company

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

- Trade names and trademarks are used in this presentation 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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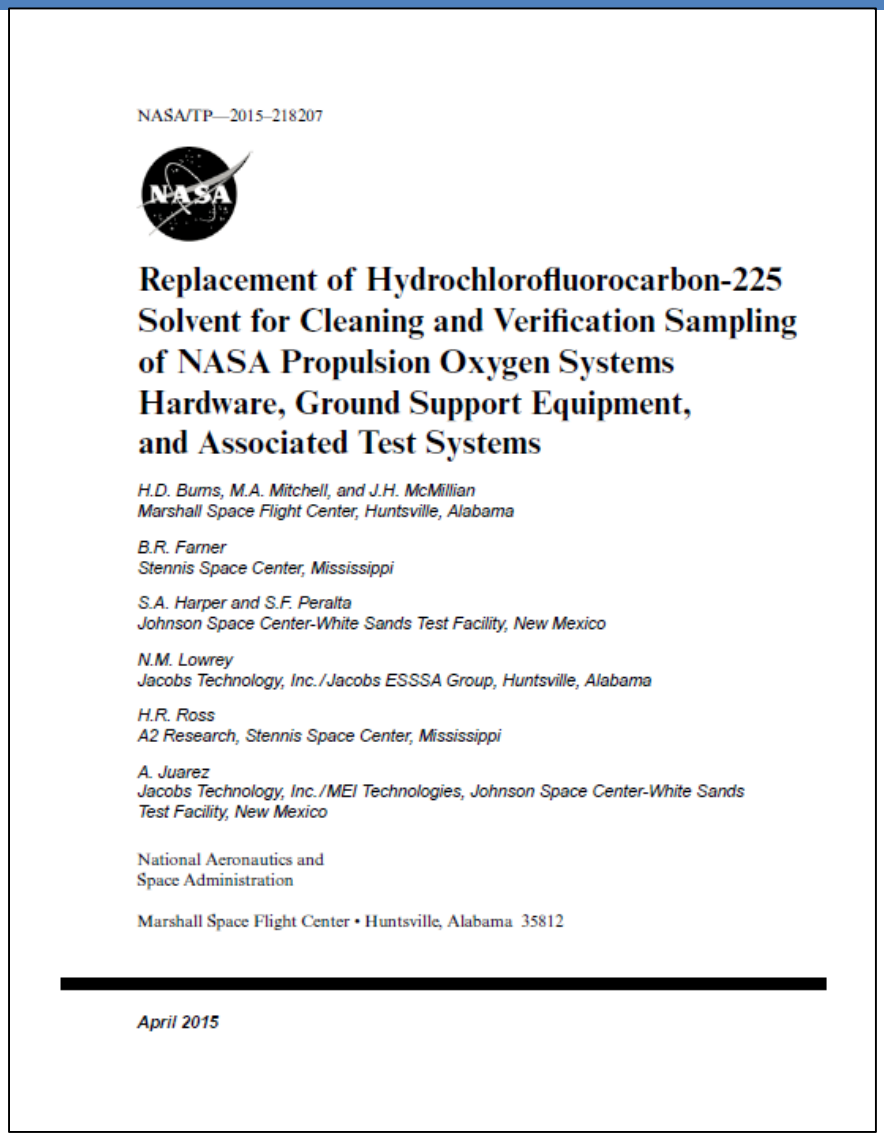
- Thanks to personnel at Marshall Space Flight Center (MSFC), Stennis Space Center (SSC), and Johnson Space Center-White Sands Test Facility (WSTF) for supporting this project.

Final Report



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

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

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

Thank You for Your Attention!

Any Questions?

Interested in Collaborating on Cleaning Processes?

Please contact:

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