HCFC 225G Replacement for Precision Cleaning of NASA's Propulsion Systems and Components

Presented By
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HCFC 225 Replacement Project

- Following the production phase out of CFC-113 (a class I ozone depleting substance) in Jan 1, 1996, NASA qualified and used Asahiklin AK-225G (HCFC-225cb) to clean and verify the cleanliness of propulsion (fuel and oxygen) components and systems.
- HCFC-225cb (AK225G) is a Class II ODS and was developed as a transitional substitute for CFC-113.
- In accordance with the Montreal Protocol and Title VI of the U.S. Clean Air Act, the manufacture/import and use of non-recycled HCFC 225 was banned on Jan 1, 2015 – does not apply to solvent in inventory.
- The NASA Rocket Propulsion Test (RPT) Program funded a multi-center project to identify a replacement for AK-225G.
  - Marshall Space Flight Center (MSFC), Huntsville, Alabama
    - MSFC M&P, Environmental Affects Branch managed this project.
  - Stennis Space Center (SSC), SSC, Mississippi
  - Johnson Space Center's White Sands Test Facility (WSTF), Las Cruces, New Mexico
- Objective: Find and implement a replacement solvent for AK225G prior to the depletion of MSFC & SSC stockpile.

Precision Cleaning for Oxygen Propulsion Systems

- Rocket propulsion systems have their own unique cleaning challenges.
  - Cleaning requirements for LOX/GOX systems used in propulsion systems are stringent.
    - LOX flows > 900 lb /second and at > 6000 psig requires a high level of cleanliness.
    - 400 A NVR (Hydrocarbon) limit of 1mg / 1ft ^{2} and no particulates > 400µ.
  - Insufficient cleanliness can result in the ignition of contaminants or the hardware by a variety of mechanisms (NVR, particle impact/ mechanical impact, etc.)
  - Solvents used to clean and verify the cleanliness of propulsion systems must be compatible with the materials used in these systems, have low reactivity in oxygen and effective at removing the contaminants to the level required.
- For industry, cleaning is a critical part of the manufacturing processes to ensure proper functioning of materials and equipment.
  - Can affect product performance and life cycles.
  - Fire and explosion hazards exist in oxygen systems for other government and industry sectors (military, medical, aviation, metals refining, gas manufacturing, chemical processing, etc.).

Test Plan

- This solvent replacement project was a two plus year effort.
- NASA Test Labs at Marshall Space Flight Center (MSFC), Stennis Space Center (SSC) and White Sands Test Facility (WSTF) collaborated to find, test and qualify a solvent replacement for HCFC 225G that is an effective cleaner and safe for use with oxygen systems.
  - A Multi Center Test Plan was Developed
  - ASTM G 127, “Standard Guide for the Selection of Cleaning Agents for Oxygen Systems”
  - ASTM MNL36, Safe Use of Oxygen and Oxygen Systems”
  - NASA Engineering Safety Center (NESC) reps. from MSFC and SSC monitored this project.
  - Independent Assessment Team (NESC Chief Eng. from MSFC and Lead from SSC Gas & Material Science Lab) investigated LOX Impact test discrepancies.

ASTM documents referenced for development of the test plan

Test Plan

- An exhaustive literature and market search were performed for potential candidate solvents.
  - 40 solvents were evaluated based on vendor data.
  - Solvents with low Kb (< 20), a measure of solvency were not considered as viable candidates [1]
  - 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 propulsion hardware and facility systems. Aqueous cleaning is more process sensitive (time, flow, temperature, rinsing, etc.), requires longer drying times, and cannot recycle - higher costs.
    - Trapped moisture can freeze and adversely affect the operation of hardware.
  - Hydrocarbon solvents used for removing hydrocarbon residues are flammable and were not considered as candidates.
    - Ethyl acetate, alcohols, cyclohexane, trans-1,2 dichloroethylene, petroleum-based solvents…etc.
  - Bio based solvents clean well, but have elevated NVR levels.

[1] Kb = Kauri-Butanol value, a measure of hydrocarbon solvency per ASTM D1133

Test Plan

- Performance Requirements
  - Materials compatibility (metals and non metals)
  - Cleaning effectiveness for in use condition (cold flush, minimal agitation)
  - Oxygen compatibility
    - LOX Mechanical Impact, Auto Ignition Temp (AIT) and Heat of Combustion (HOC)
  - Safety and Health Hazards
    - Low toxicity (exposure limits)
    - Non flammable (human safety)
- Minimal Environmental Impacts
  - No Ozone Depleting Potential
  - Not Classified as an Hazardous Air Pollutant
  - Low Global Warming Potential (Future regulations w/ additional restrictions are expected in the near future)
  - Low VOC or VOC Exempt
  - SNAP Approval

Solvent Candidates

Single Component	Kb	AEL- 8hr	Concerns
AGC Chemicals AE3000 (new) (HFE-347pc-f2) **1,1,2,2-tetrafluoro-1-(2,2,2-trifluoroethoxy)-ethane**	**13**	**50 ppm**	**Low Kb may not clean well, toxicity**
Honeywell Solstice™ PF (new) (1233zd(E)) **Trans-1-chloro-3,3,3,-trifluoropropene**	**25**	**800 ppm**	**Boiling point of 19°C (66°F) GWP (100 yr) 1**
DuPont™ Capstone® 4-I (chemical intermediary) 85%+ Perfluorobutyl iodide	**No data**	**375 ppm**	**Not compatible with some metals. Photo reactive, expensive, short supply.**
Solvay Solkane® 365mfc (HFC-365mfc) **1,1,1,3,3 Pentafluorobutane**	**14**	**1000 ppm**	**Low Kb may not clean well, Unusual flammability characteristics**
Azeotropic Blends with trans-1,2 Dichloroethylene (tDCE)	(tDCE = 117)	(tDCE = 200 ppm)	Pure tDCE is flammable. Flash point in air = 2.2°C (36°F). NOT LOX compatible.
AGC Chemicals AE3000AT (new) **45% tDCE / 55% AE3000**	**32**	**200 ppm / 50 ppm**	**Expected to clean well, may not pass LOX impact test.**
3M L-14780 developmental solvent **22% tDCE /78% (HFE-347mcc3) methyl perfluoropropyl ether (3M HFE-7000)**	**Similar to MCA**	**200 ppm / 250 ppm**	**Boiling point of 28-30°C (82-86°F) – Performed well in past tests (1990's)**
DuPont™ Vertrel® MCA (re-eval with new stabilizer) 38% tDCE/ 62% (HFC-43-10mee or Vertrel XF) 1,1,1,2,2,3,4,5,5,5-Decafluoropentane	**20**	**200 ppm**	**Cleans well but borderline LOX compatible on past tests. Low AIT at high GOX pressure. XF has GWP (100 yr) 1640**
Solvay Solvokane® (new) 30% tDCE/ 70% (HFC-365mfc) 1,1,1,3,3 Pentafluorobutane	**25**	**200 ppm / 1000 ppm**	**Boiling point of 36°C (97°F), individual components are flammable. GWP (100 yr) 556.**

AEL-8 hr = 8 hour Acceptable Exposure Limit

Test Approach

PHASE 1:

- NVR Screening Testing for Solvent Cleaning Efficiency and Odor Studies (SSC)
- Nonvolatile Residue of Neat Solvents (MSFC/SSC) – Gravimetric and FTIR
- First Down-Selection Sept 2013 - Selected 3 Candidates (MSFC/SSC/WSTF)

PHASE 2:

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

PHASE 3:

- Extended Oxygen Compatibility Tests and Assessments (MSFC/WSTF/NESC IAT)
- LOX Impact Energy Threshold (ASTM G 86 retest using D2512-82)
- AIT (Ignition Resistance in GOX) & HOC (Energy Release / Propagation Damage Potential in GOX)
- Cleaning Effectiveness/Nonvolatile Residue Removal Efficiency (MSFC)
- Final Down-Selection Oct 2014 (MSFC/SSC/WSTF)

PHASE 4:

On Site Vendor Demonstrations and Component Level Cleaning

Performance ranking used to down select solvents

NVR Screening Test Results for Solvent Cleaning Efficiency

Avg. NVR Removal of Test Solvents

Contamination Level = 3.4 mg /5.31 in^2 $\approx$ 92 mg / ft^2

NVR Mix (Equal Parts)

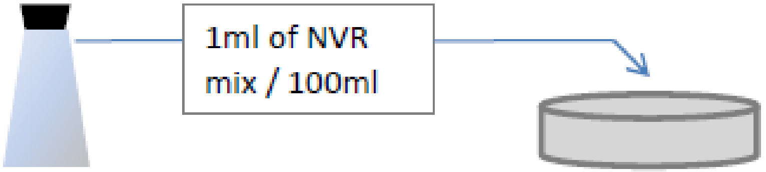
Mineral Oil – pharmaceutical grade – mixed aliphatic

MIL-PRF-8382 – ester based hydraulic fluid

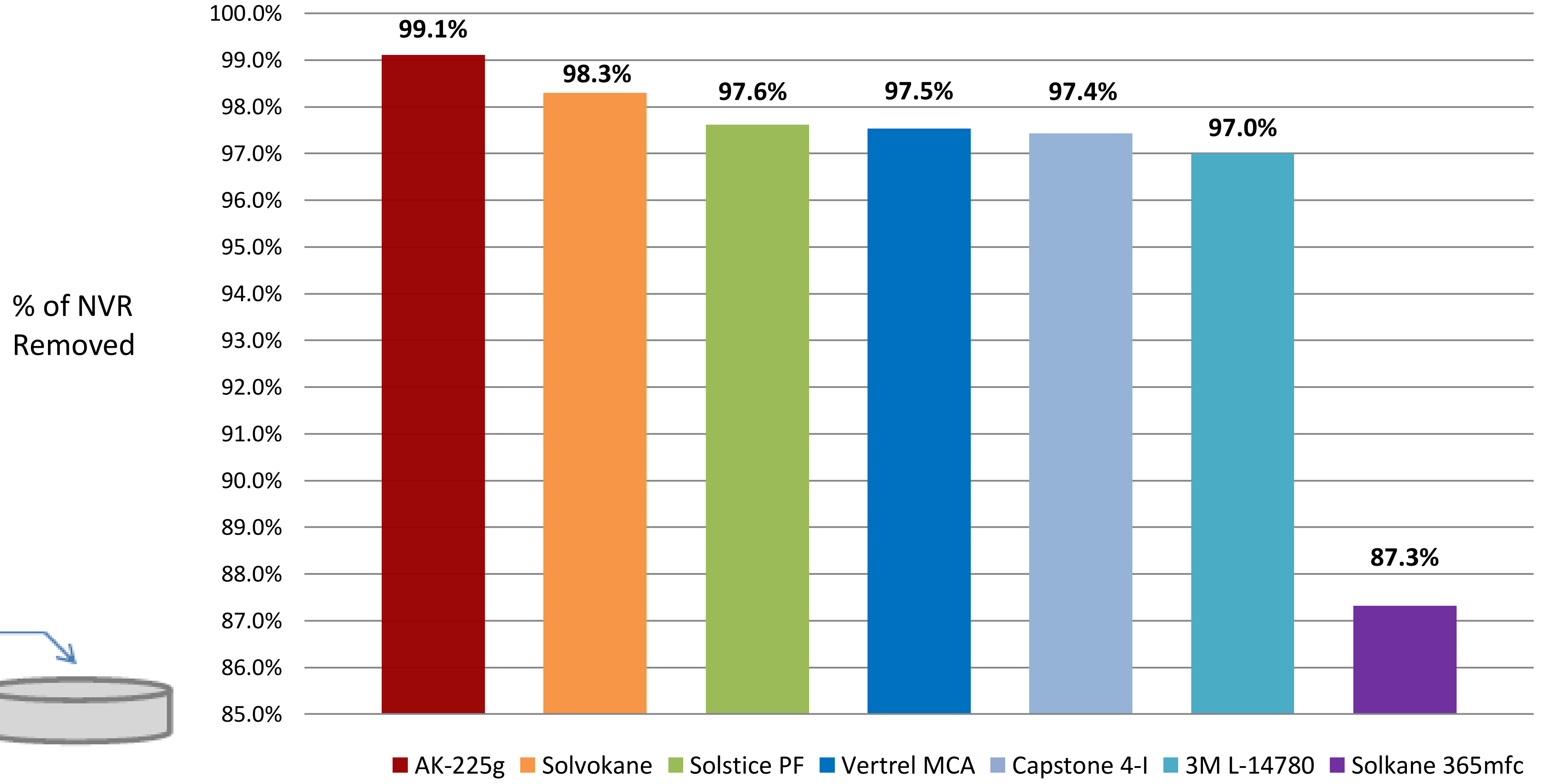
Di-2-ethylhexylsebacate (gauge calibration oil), Monoplex DOS

WD 40 (medium-heavy hydrocarbons)

Krytox GPL103 (fluorocarbon lubricant for oxygen systems)



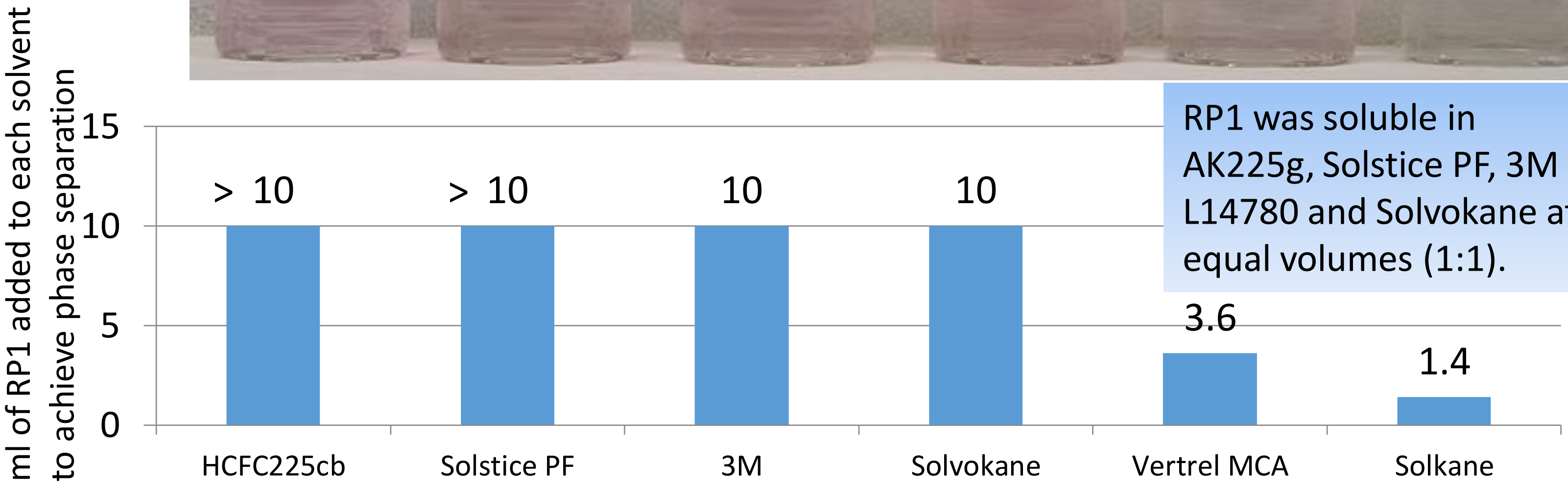
Std. qty of the NVR mix from the carrier solvent (AK225G) is applied to the dish and dish is flushed 3X with test solvent.



% of NVR Removed
Average-. Each Solvent was Tested 10 times

NVR Miscibility /Saturation Tests for the Candidate Solvents

Vol. of RP1 (NVR) required to achieve saturation (separation) is reported in the below graph. Each bottle contains 10ml of solvent. RP1 is predominantly C9-C16 (w/ sulfur < 30 ppm) & aromatics 5% Max.



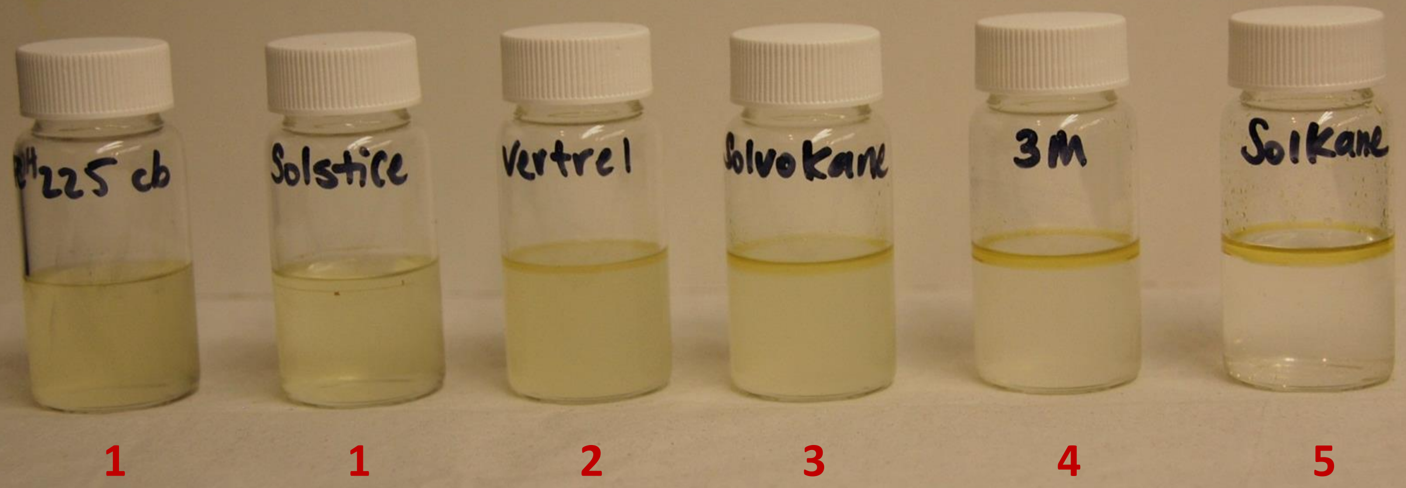
RP1 was soluble in AK225g, Solstice PF, 3M L14780 and Solvokane at equal volumes (1:1).

1	1	1	1	2	3

Solvent Solubility Ranking for RP1

Miscibility /Saturation Response of the Candidate Solvents to Heavy Weight (85-140W) Gear Oil (Petroleum-Based)

150 mg of Gear Oil was added to each bottle (10ml solvent)



Solubility Ranking of Heavy Wt. Gear Oil in Candidate Solvents

The Gear Oil was fully miscible in Solstice PF & HCFC225cb (AK225g)
3ML14780 & Solkane were the least miscible solvents

NVR Miscibility Range of the Candidate Solvents

0.95ml of Hydraulic Fluid was added to each bottle containing 10ml of solvent)

MIL-PRF-8382 – ester based hydraulic fluid

Conc. for each bottle = 0.95ml Hyd. Fluid /10 ml Solvent

At the this conc., a phase separation occurs in Vertrel MCA (is partially miscible), the remaining three solvents are fully miscible (no stratification or phase separation occurred).

NVR Miscibility Range of the Candidate Solvents

Next, 1.3 ml of Hydraulic Fluid was added to each bottle containing 10ml of solvent

MIL-PRF-8382 – ester based hydraulic fluid

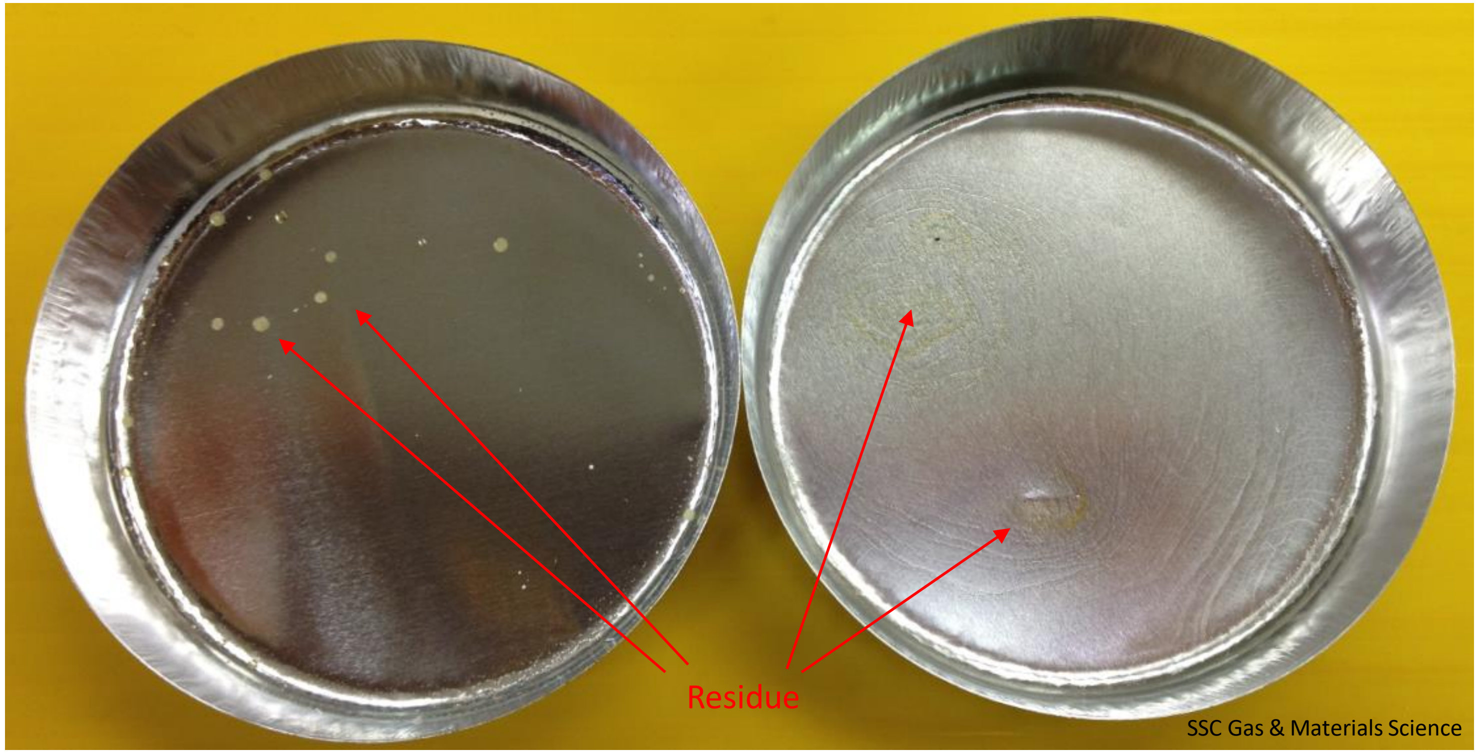
Conc. for each bottle = 1.3ml Hyd. Fluid /10 ml Solvent

Separation occurs with Solvokane at this conc. Solstice PF and the Control (AK225g) are fully miscible (no stratification or phase separation were observed).

Solstice PF and HCFC 225G exhibited the highest miscibility.

Solubility transport of NVR is similar to HCFC225.

Solvent Background NVR
Gravimetric NVR Results of L-14780 and Vertrel MCA



L-14780: 5.7mg/200mL NVR

Vertrel MCA: 2.5mg/200mL NVR

IR analysis of the NVR shows a typical stabilizer used for t-DCE.

Residue observed in the MCA is consistent with alkane hydrocarbons. May be a contaminant or from a stabilizer.

Product Consistency

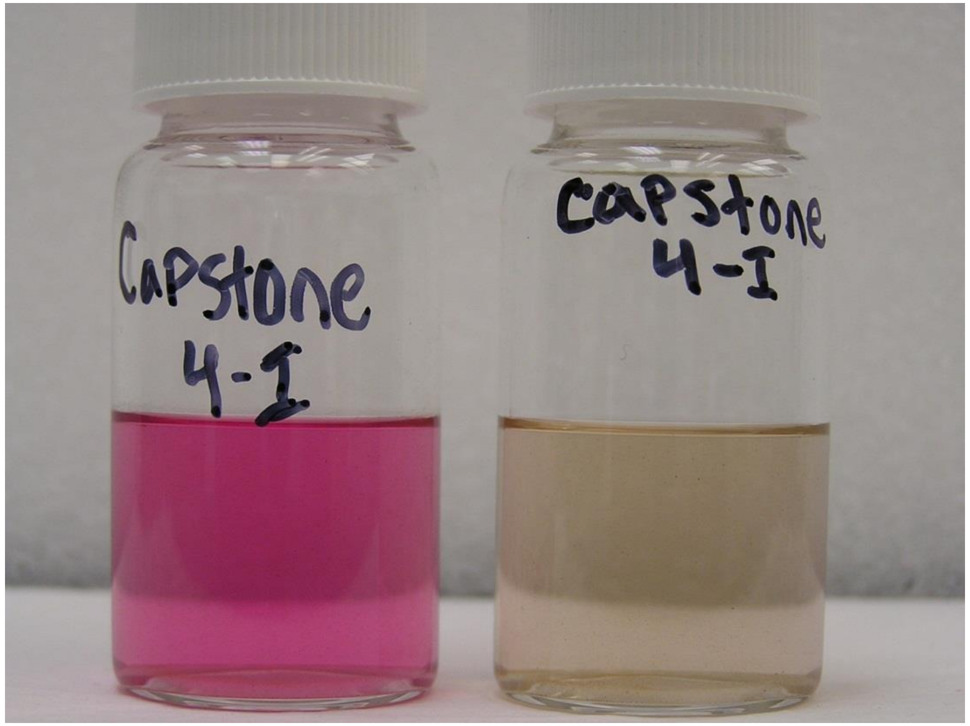
Different lots showed different background NVR levels. Some lots had very low NVR, < 1mg/200ml or < 2ppm.

NVR Residue in Solvents

- Precautions associated with use of azeotropic solvents and solvents containing trans-1,2 dichloroethylene (t-DCE) and stabilizers.
- Such solvents include 3M L-14780 and Vertrel MCA
- Azeotropic Mixtures
  - Azeotropic proportions may vary in applications of varying temperatures and pressures.
  - This will lead to varying flammability/ oxygen compatibility characteristics.
  - Product shelf life is affected by stabilizers and their respective concentrations

- Stabilizers
  - Stabilizer packages are generally a combination of organic compounds that are susceptible to degradation.
  - Variations in quantity and type of stabilizer can affect flammability / oxygen compatibility of solvent.
  - For oxygen use, vendor must commit to a specified stabilizer package or lot acceptance testing must be performed.

Stability of Capstone 4I (PFBI)



PFBI After 4 hrs Exposure to Light

PFBI - Immediately Poured from an Amber Bottle

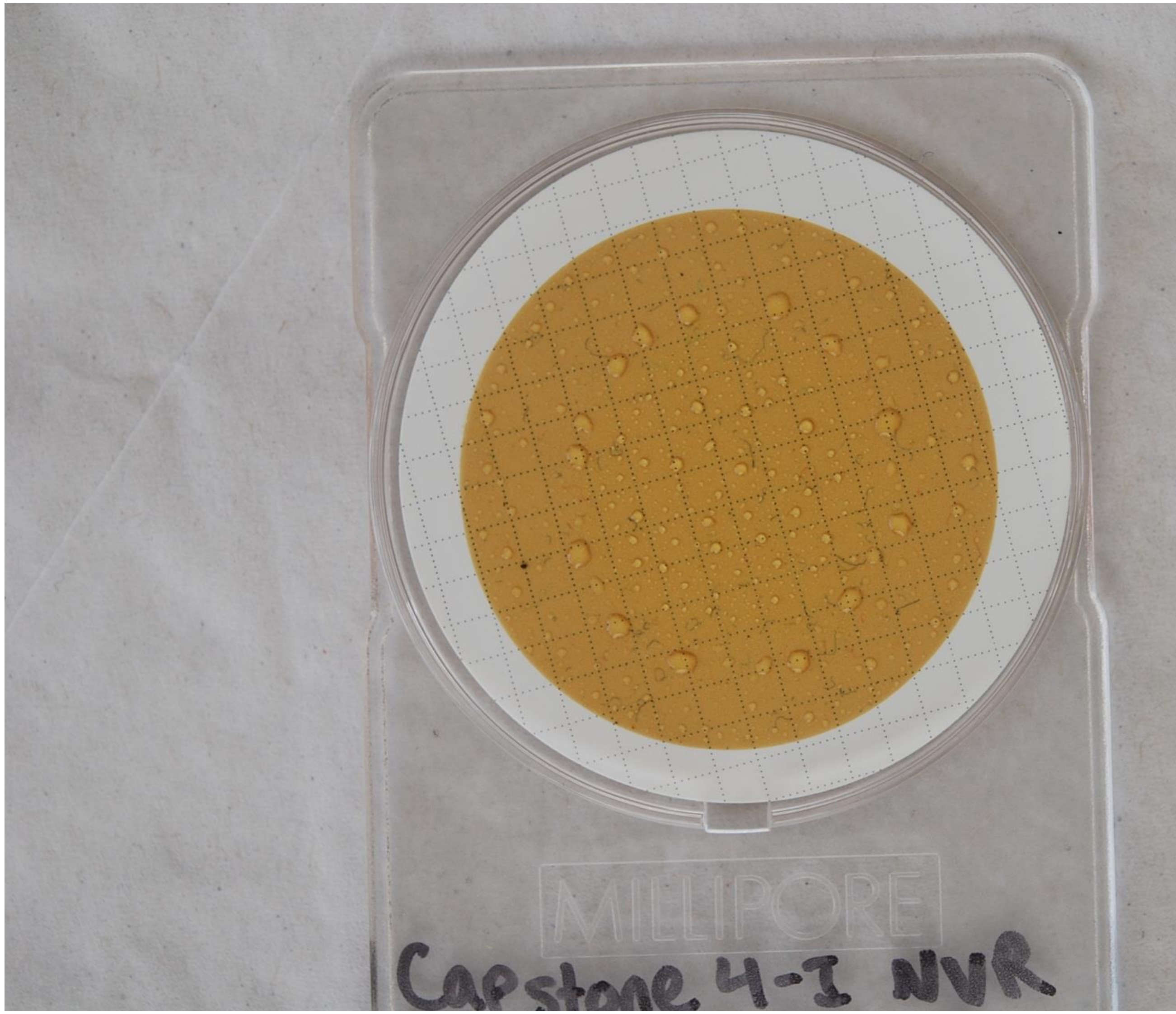
Photo reactivity
Liberates iodine when exposed to light.

Stability / Corrosion
Reacts with iron and steel alloys. Product purity varies from lot to lot.

Contamination
High particulate levels are generated after exposure to iron / steel.

Limited Availability
Vendor has shown no commercial interest to produce PFBI as a precision cleaning solvent.

High Cost
>4X than HCFC225



Filtered particulate matter associated with Capstone 4I from Lot 18.

Moisture forms on the filter pad as it sits in the lab.

Heavy Particulate Contamination in Capstone 4-I.

Capstone 4-I was found to be highly contaminated with particulates. Filtered particulate matter draws moisture in from the atmosphere.

Metals Compatibility

Liquid and Vapor Phase Immersion of Metal Specimens for Corrosion Testing per ASTM F483.

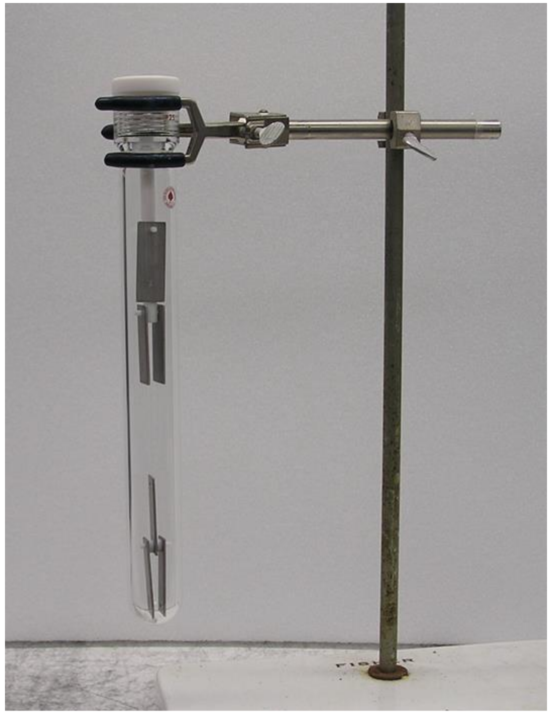
Specimens were inspected and weighed at 24 hours and 168 hours

Four Solvents

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

Thirteen Metals

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



Coupons are placed in a sealed high pressure borosilicate glass tube. Glass tube is placed in a constant temp bath at the solvent's boiling point.

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

Ferrous Based Coupons	Wt. Change from Vapor	Wt. Change From Liquid	Wt. Change Control Coupon	Appearance Sample vs Control
A286	-0.1 mg	-0.3 mg	0.0 mg	No Change
304L	-0.1	-0.1 mg	-0.1 mg	No Change
440C	0.2 mg	0.0 mg	0.1 mg	No Change
17-4 PH	0.2 mg	0.1 mg	0.0 mg	No Change
AISI 4140	0.2 mg	-0.5 mg	-0.4 mg	No Change

Non Ferrous Based Coupons	Wt. Change from Vapor	Wt. Change From Liquid	Wt. Change Control Coupon	Appearance Sample vs Control
Eligiloy	0.0 mg	0.0 mg	0.0 mg	No Change
Inconel 718	0.0	0.0 mg	0.1 mg	No Change
Monel 400	0.0 mg	-0.1 mg	-0.1 mg	No Change
Naval Brass	-0.1 mg	-0.1mg	0.0 mg	No Change
Tin Bronze 510	-0.2 mg	-0.2mg	-0.2 mg	No Change
Al 6061 T6	0.0 mg	-0.1 mg	0.0 mg	No Change
Al 2219 T6	0.0 mg	0.0 mg	0.1 mg	No Change
Al Li 2195 T8	0.1 mg	0.0 mg	0.1 mg	No Change

Metals Corrosion Testing Results for Solstice PF, ASTM F483

All solvents were tested at their boiling point except for Solstice PF. Solstice PF was tested at 72°F for168 Hours. Boiling point for Solstice PF is 66°F.

Delayed Corrosion was Observed on 4140 steel Coupons exposed to L14780. Test was Repeated and Confirmed.

Nonmetals Compatibility

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

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

Four Solvents

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

Nine Nonmetals

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

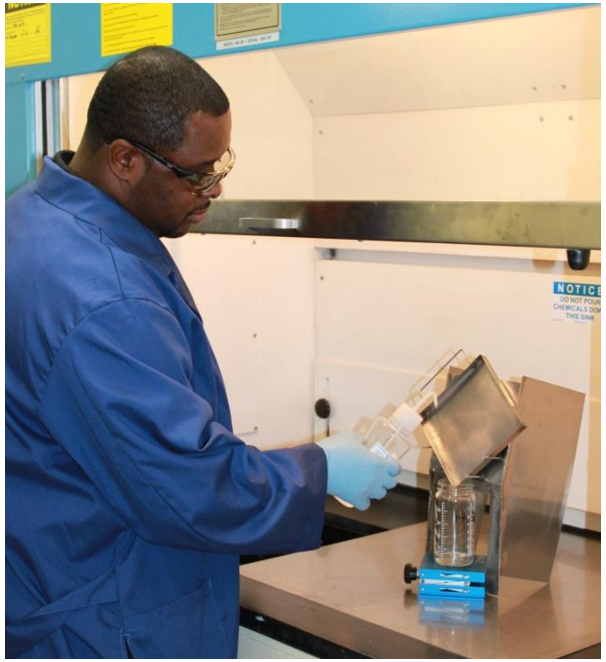
Summary
The three candidate solvents performed equal to or better than AK225G.

Cleaning Effectiveness Tests

MSFC Nonvolatile Residue Removal Efficiency Test

This test simulates an NVR verification sampling procedure.

Individual contaminants were applied to a test panel and dried, flushed with the test solvent, and the effluent was dried and weighed. The panel was sampled again with AK-225G to measure nonvolatile residue not removed by the test solvent.



Three Solvents

- AK-225G
- Solstice PF
- 3M L-14780

Eight Contaminants

- Mineral Oil
- WD-40
- MIL-PRF-83282 Hydraulic Fluid
- Mobil DTE-25 - Weld machine hydraulic fluid
- Di-2-ethylhexylsebacate
- Simulated fingerprint
- Krytox 240AC grease
- Big Red crane grease - heavy paraffinic grease

Initial contamination was ≈ 10 mg/panel
(1/4 ft^2 panels → yields ≈ 40 mg/ft^2)

NVR for each contaminant was measured gravimetrically. Each test was repeated 3 times. MSFC NVR results were consistent with the SSC NVR Screening Tests which used a mixed contaminant mixture.

Particulate Matter Removal

Wetting Index was used to estimate the ability of solvents to enter into tight spaces and to lift and remove particulates from surfaces. Solvents with a higher wetting index will perform better at removing particulates.

The Wetting Index combines the three most critical factors into a single index.

Wetting Index $= 10^3$ (Density) / Surface Tension x Viscosity

Low surface tension allows solvent to get into tight spaces

Low viscosity - flows easily around objects

High density lifts and floats away particles.

	Solstice PF-HP	HFE-7100	HCFC-225	CFC-113	nPB	TCE
Wetting Index	221	183	162	140	106	102
Surface Tension (dynes/cm)	12.7	13.6	16.2	17.3	25.9	26.4
Viscosity (cp)	0.45	0.61	0.59	0.65	0.49	0.54
Density (g/cm^3)	1.26	1.52	1.55	1.57	1.35	1.46

Initial LOX Impact Tests

- The ambient pressure LOX mechanical impact tests of candidate cleaning solvents to replace AK225G exhibited significant differences for reactivity when tested at WSTF and MSFC.
  - Both facilities used ASTM G86 for the standard method to determine the impact sensitivity in LOX at ambient pressure
- As a result of the discrepant results, a NASA Independent Assessment Team sponsored by the NASA Engineering & Safety Center (NESC) was formed to investigate the test variables responsible for the test inconsistencies.

Independent Assessment Team Objective

- NESC Chief Engr at MSFC and the SSC Gas & Materials Science Lead scientist made up the Independent Assessment Team (IAT).
- IAT was responsible to identify the variables and conditions responsible for test variability and to establish a modified test protocol to ASTM G86 that would provide reproducible results for determining the impact threshold reactivity of the candidate solvents.

Initial LOX Impact Reactions Observed at WSTF Solstice PF

Energy (ft lbs)	Temp ^{0}F	% RH	Reaction Frequency	Reaction Rate	SST Disks
[1] Solstice PF, *Lot BA320B-10-118 (1.6 lb Cylinder) - June 23, 2014*					
72	66	28	2/5	40%	No
65	66	28	2/6	33.3%	No
60	66	28	1/11	9.1%	No
55	66	28	2/6	33.3	No
50	66	28	2/12	16.7%	No
45	66	28	0/3	0%	No
Solstice PF, Same Lot as Above - Different 1.6 lb Cylinder - June 27, 2014					
72	67	23	2/3	66.7%	No
65	67	23	2/4	50%	No
60	67	23	2/6	33.3%	No
55	67	23	2/10	20%	No
50	67	23	2/7	28.6%	No

[1] Solstice® is a registered trademark of Honeywell International, Morristown, N.J.
Solstice® performance fluid (PF) is also known as trans-1-chloro-3, 3, 3,-trifluoropropene (HCFO-1233zd(E)

Test Protocol
ASTM G86-98

Criteria for Acceptance
No reactions from 20 successive impact tests tested at 98 J (72 ft•lbf)

or

Not more than one reaction at 98 J (72 ft•lbf) after 60 successive impacts.

Initial LOX Impact Reactions Observed at MSFC Solstice PF

Energy (ft lbs)	Temp ^{0}F	% RH	Reaction Frequency	Reaction Rate	SST Disks
Solstice PF, Lot BA320BU-10-119 (1.6 lb Cylinder) - July 8, 2014					
72	75	65	0/10	0%	No
72	75	65	0/20	0%	Yes
72	75	65	0/5	0%	Yes
82.4	75	65	0/5	0%	Yes
Solstice PF, Lot BA320BU-10-110 (10 lb Cylinder) - July 10, 2014					
72	79	66	0/22	0%	No

Test Protocol
ASTM G86-98

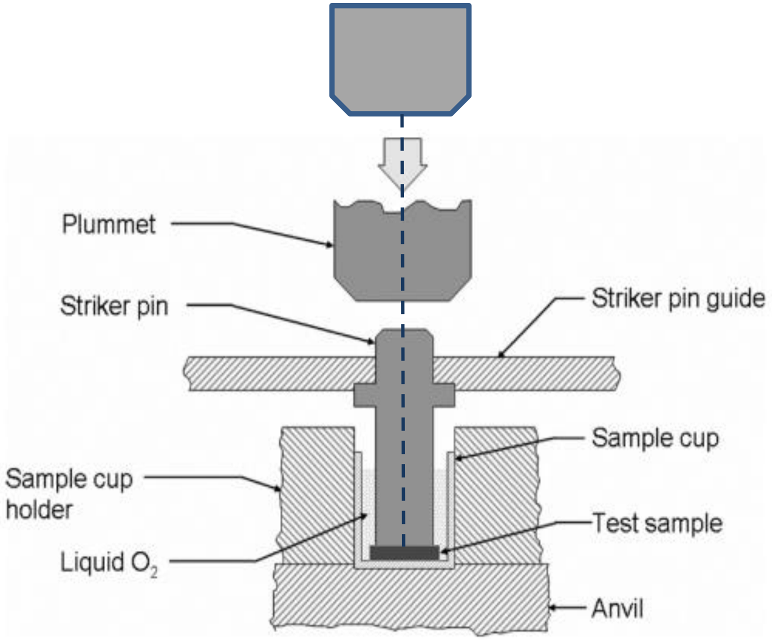
% RH during sample preparation – observed higher reactivity (sensitivity) when samples were prepared at lower %RH (NESC Independent Assessment Team)

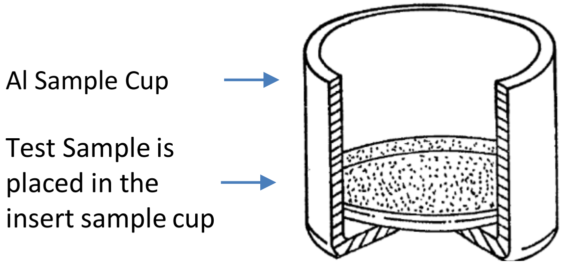
Ambient Pressure LOX Impact Tester at WSTF

Ignition Sensitivity of Materials to Mechanical Impact in Liquid Oxygen

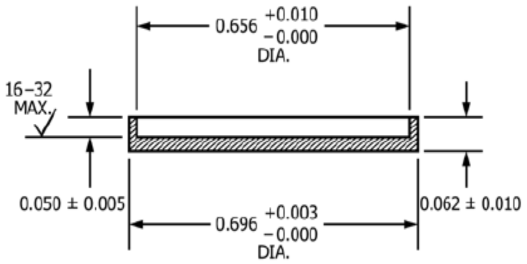
Plummet and Drop Tower Configuration

Moat and Sample Cup Holder

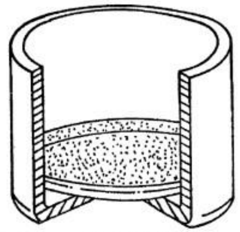




Insert Sample Cup

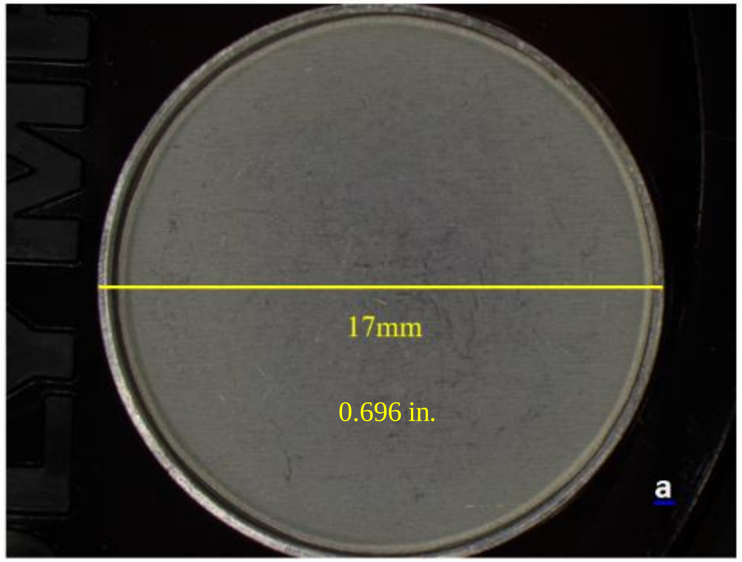


Rim height of the insert cup is 0.05 inches. Diameter is approx. 0.7 inches

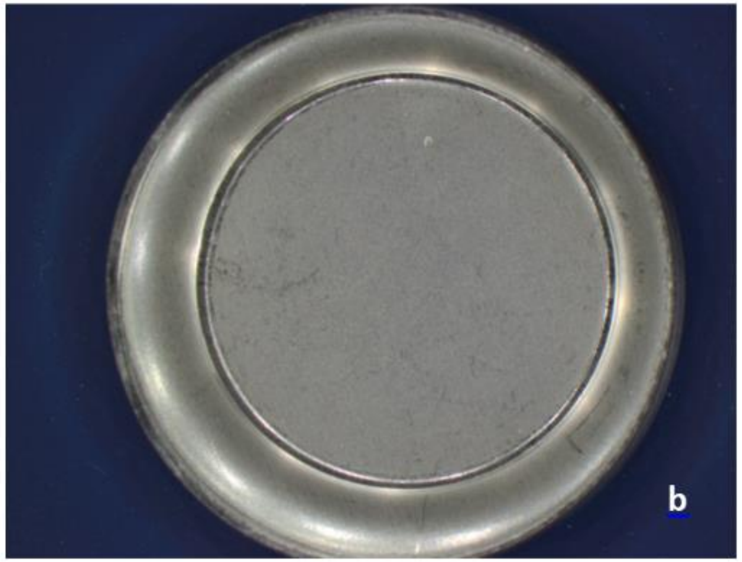


(b) TEST CUP WITH GREASE SAMPLE SHOWING INSERT CUP

Top. Diagram and dimensions of the insert cup.
Bottom. Insert sample cup is used to test liquids and greases and is placed in the tall aluminum cup. Diameter same as a quarter.



New Cup – Diameter ≈ the same as a dime. Has a lip (rim height) of 0.05 inches.

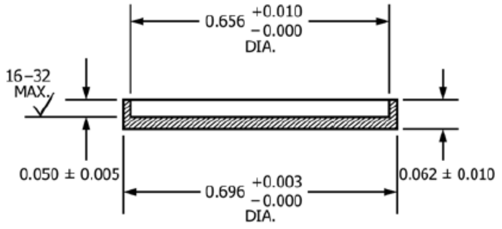


Cup after a near center impact at 72 ft. lbs.

The specimen shown in the upper right (b) received a near concentric impact that is uniform in terms of absorbed energy.

Test Variable – Off Centered Initial Impacts Non Uniform / Edge Promoted Reactions

Impact Position of the Insert Cup
An edge promoted reaction from a single impact is due to an alignment offset between the center of the striker pin and the center of the insert sample cup that rests freely on the bottom of the tall aluminum sample cup or from movement of the insert sample cup after placement in the impact tester.



Rim height of the insert cup is 0.05 inches. Diameter is approx. 0.7 inches (similar to a dime).

Test Variable - Rebound Impacts
Non Uniform / Edge Promoted Reactions

Various rebound impacts that resulted in flash, audible & charring reactions.

During a rebound, the plane of the striker pin and the plane of in the insert sample cup can vary and may reduce the impact area. The energy per unit area from a reduced impact area is therefore increased causing a higher temperature in a localized region of the sample.

Preparation of Liquid Samples Referenced in NHB 8060.1B, 1C & NASA STD 6001 and NASA STD 6001A

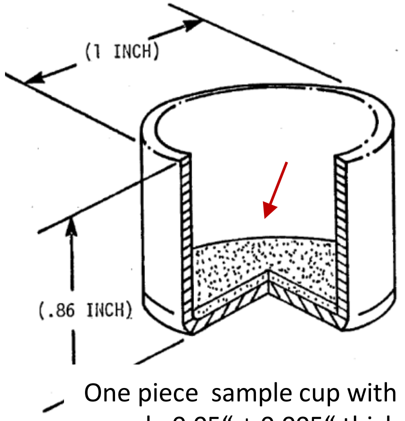
NHB 8060.1B & 1C & NASA STD 6001
(09/1981 thru 03/2008)
ASTM D2512-82

Par. 413, p. 4-66, sub section b, par (2),
Liquid sample will be transferred to the one piece aluminum specimen cup (fabricated from 5052 H32 aluminum alloy). Using micro burette deliver a sample thickness of 1.27 ± 0. 13 mm (0.050 ± 0.005 in.)
Illustration shows no special insert sample (grease) cups are used when testing liquids (see red arrow).

NASA STD 6001A References ASTM G86
(04/2008 to present)

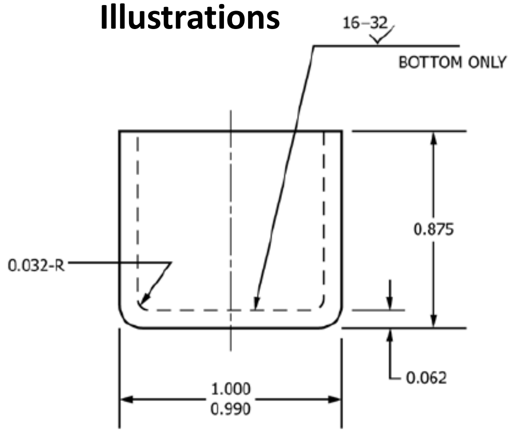
Special insert cup used for liquids, greases and semisolids. The Insert cup is placed in the one piece aluminum cup. Any 3000 or 5000 series aluminum alloy.

NHB 8060.1B Illustrations

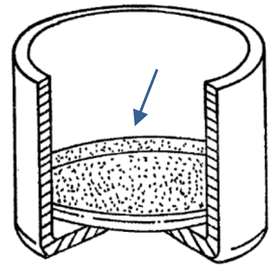


One piece sample cup with liquid sample 0.05" ± 0.005" thick
Al Alloy, any 3000 or 5000 series

ASTM D2512-82 Illustrations

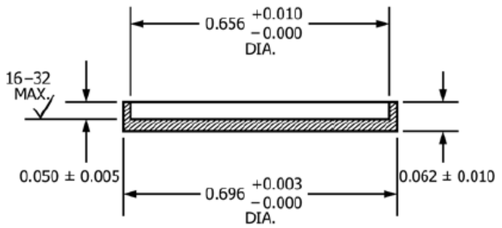


One piece aluminum sample cup is used for liquids 0.05" ± 0.005" thick. Al alloy, 5052-H32



(b) TEST CUP WITH GREASE SAMPLE SHOWING INSERT CUP

Special insert cup used for greases and liquids. The Insert cup is placed in the one piece aluminum cup. Any 3000 or 5000 series aluminum alloy.



NOTE 1—Material: aluminum alloy QQ-A-318 (5052), temper H-32. All dimensions in inches.
FIG. 7 One-Piece Insert Cup

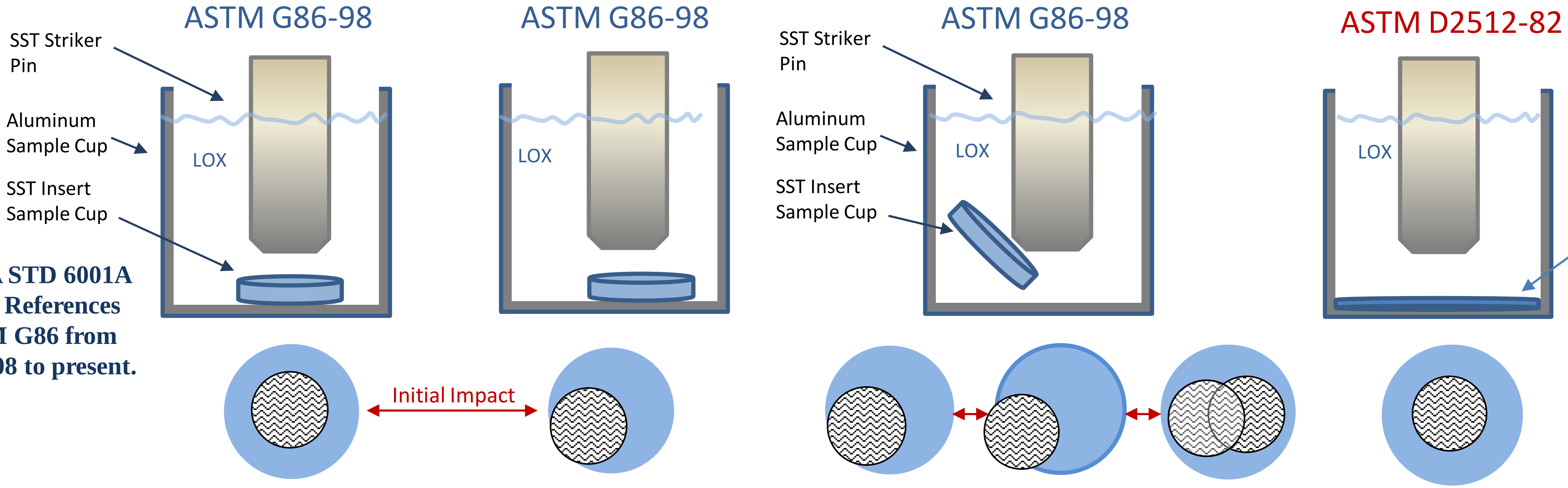
Special insert (aluminum) cup is used for greases and semisolids. The Insert cup is placed in the one piece aluminum cup.

D2512-82
No Insert Cups are Used for Liquid Samples

G86-98a
Insert Cups Are Used for Liquid Samples

LOX Impact Testing of Liquid Samples
ASTM G86-98a vs. ASTM D2512-82

NASA STD 6001A & 1B References ASTM G86 from 04/2008 to present.



NHB 8060.1B & 1C & NASA STD 6001 (09/1981 thru 03/2008) References ASTM D2512-82

Sample is placed in the bottom of the aluminum sample cup – No SST Insert cups are used.

Uniform impacts if insert sample cup and striker pin are aligned. Difficult to control in LOX.

Rim /Edge Impact from alignment offset between insert sample cup and striker pin during the initial impact.

Rebound impacts are not consistent when using the insert sample cup.

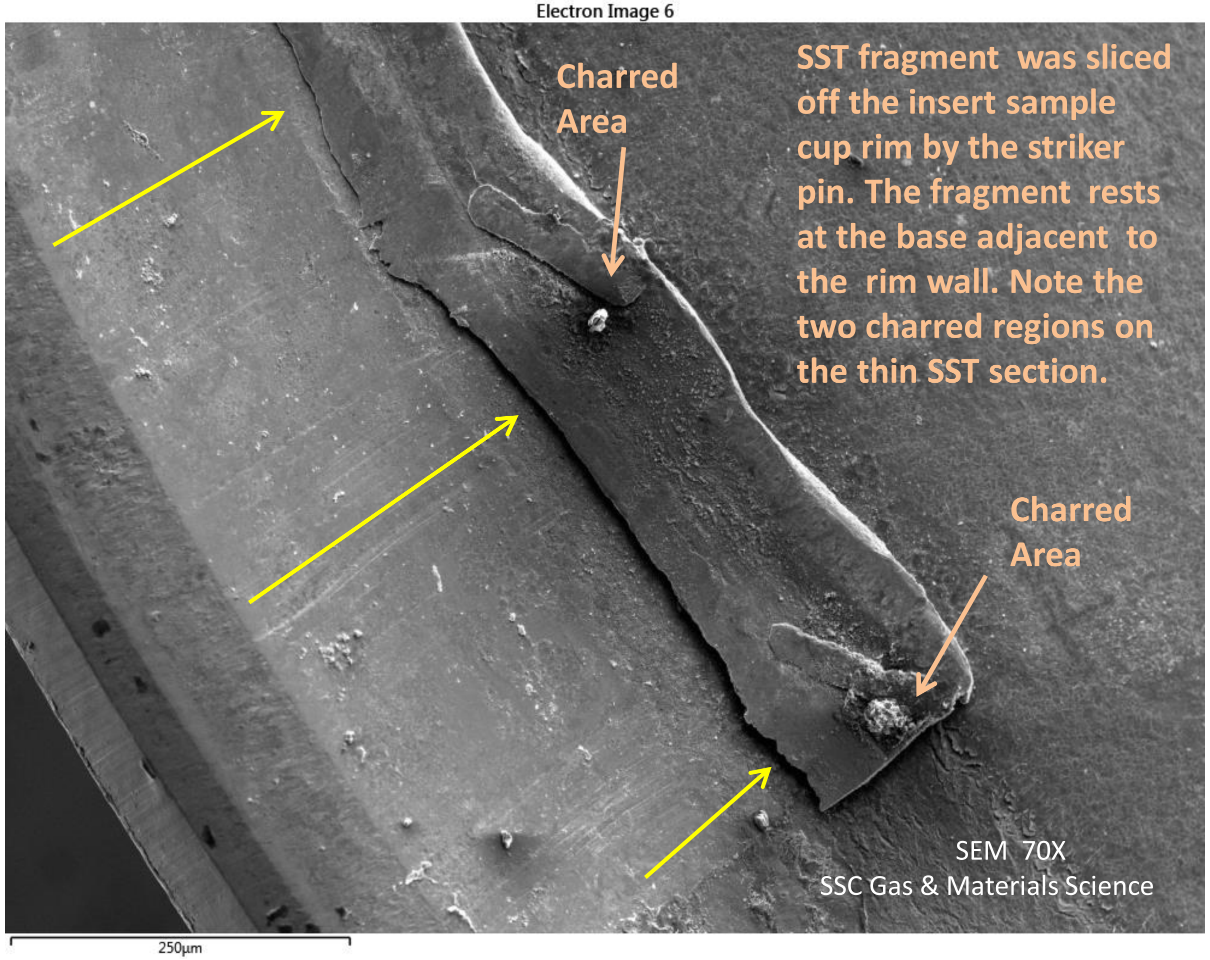
All Impacts are more uniform – eliminates edge promoted impacts from the SST insert cups.

The majority of the reactions were from non-uniform impacts & were due to:

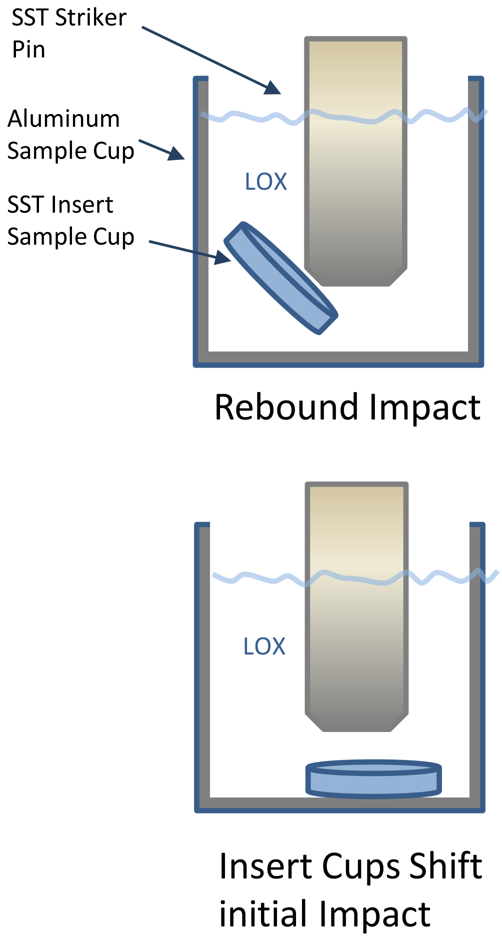
- The edge of striker pin impacts the inner rim wall and/or the striker pin hits the rim of the insert cup.
- How well the insert sample cup was centered in the tall aluminum sample cup.

Rebound impacts occurred after relocation and a change of orientation of the sample cup following the initial impact. Also, the rebound energy imparted to the sample is unknown.

Striker Pin Impact On the Inner Rim Wall of the Insert Sample Cup

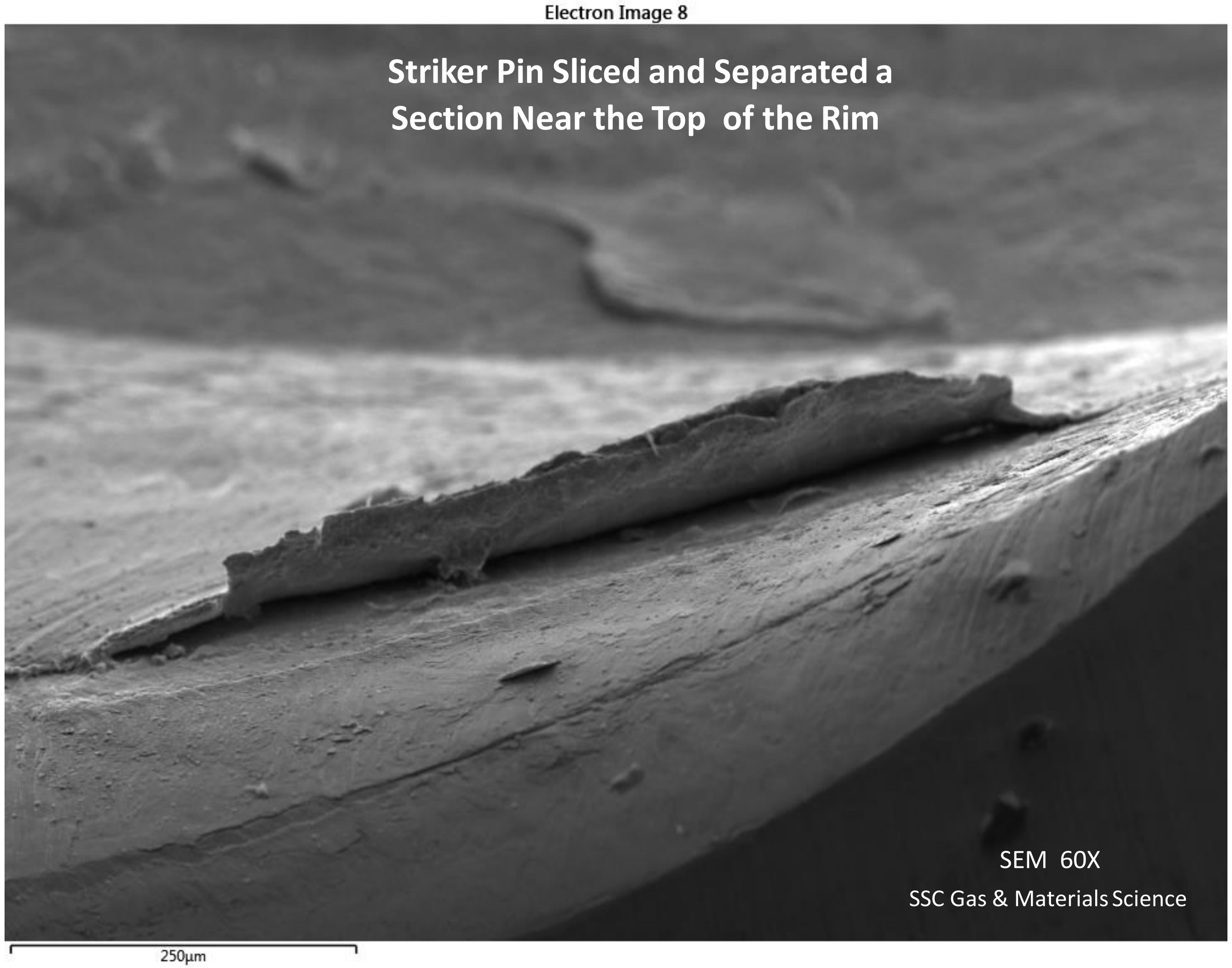


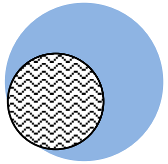
SEM Image after the striker pin impacted the rim wall of the insert cup. Rim wall is subjected to a high strain rate from the sudden eccentric loading.



Edge of Striker Pin Impacts the Inner Rim Wall of the SST Insert Cup.

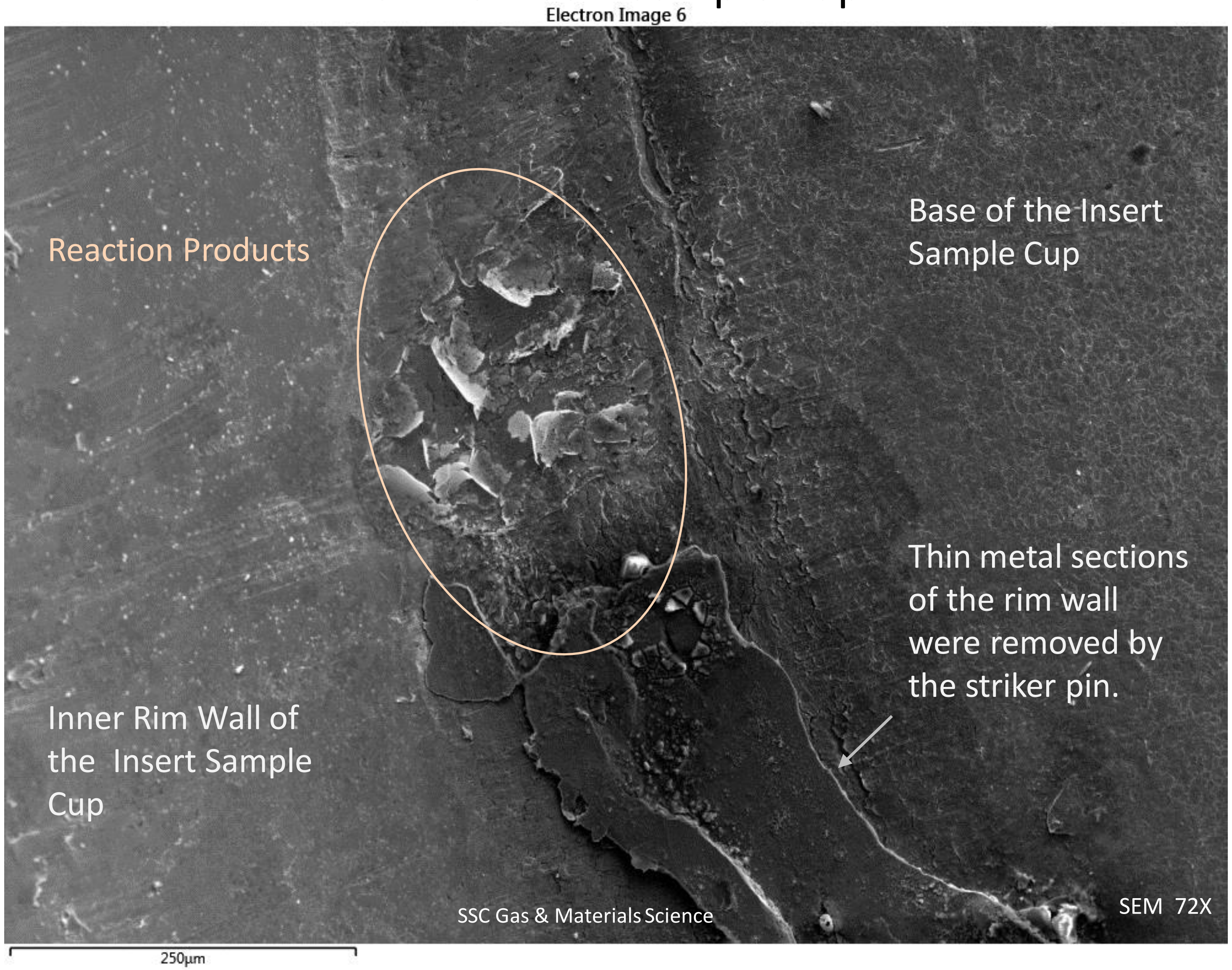
Striker Pin Impact On the Inner Rim Wall of the Insert Sample Cup

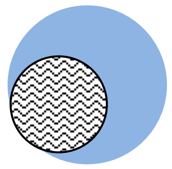




Edge of the Striker Pin Impacted the Inner Rim Wall

Striker Pin Impact On the Inner Rim Wall of the Insert Sample Cup



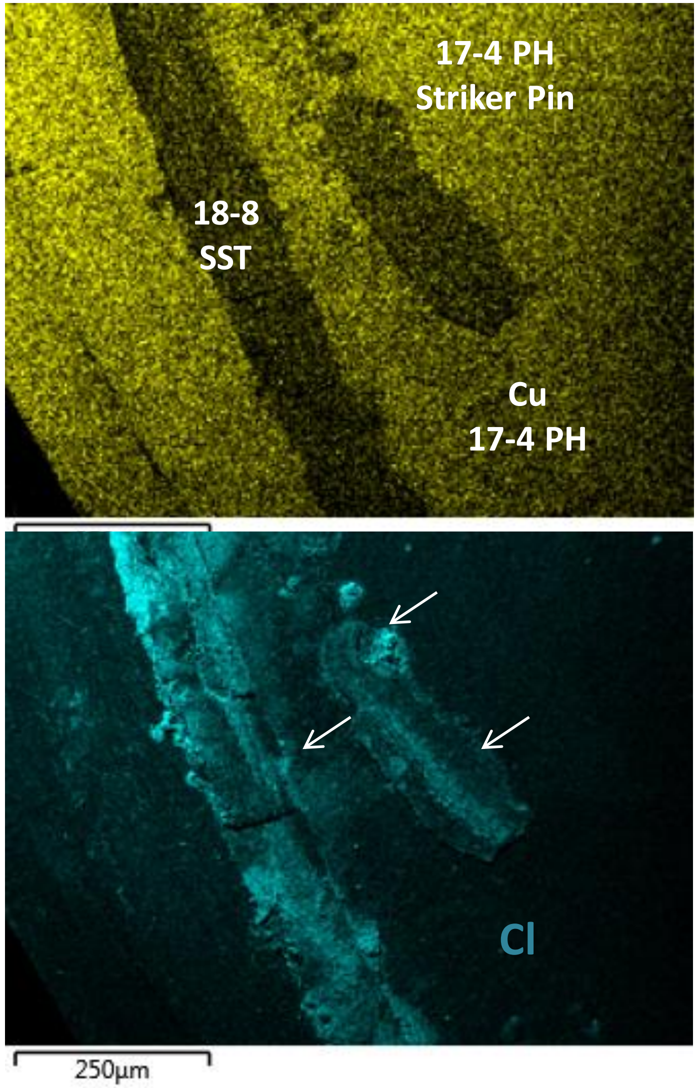


Edge of the Striker Pin Impacted the Inner Rim Wall

Striker Pin Impacted the Inner Rim Wall of the Insert Sample Cup

Top. A long ribbon fragment of the insert sample cup is fused to the striker pin.

Right. X- Ray maps showing the chlorine reaction products from Solstice PF. The reaction occurred on the thin section of the insert sample cup that was removed by the striker pin due to a non concentric (non- uniform) impact.



Oxygen Reactivity Data Summary

June 2016

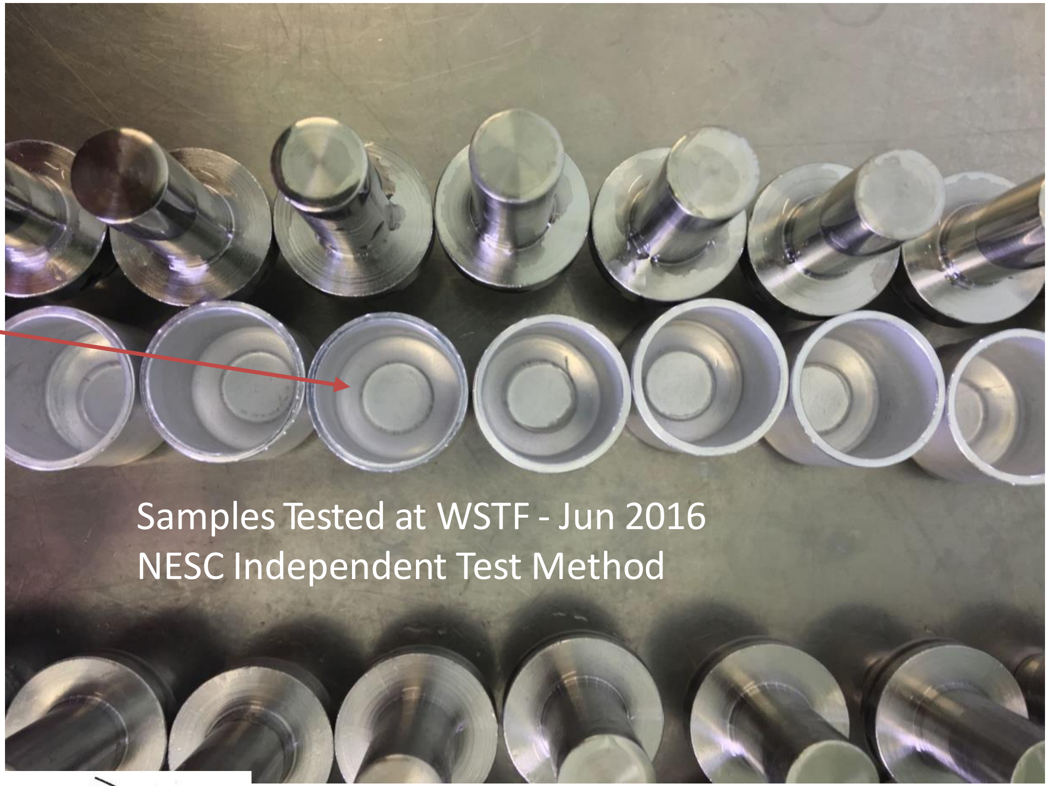
		Solstice (Propellant Version) Honeywell Lab ID 42208-37-B					Solstice PF Honeywell Lot BR 13019-50-42					Historical Data Solstice PF	
		Run 1	Run 2	Run 3	**Mean**	**Stand. Dev.**	Run 1	Run 2	Run 3	**Mean**	**Stand. Dev.**	**Mean**	**Stand. Dev.**
		(cal/g)	(cal/g)	(cal/g)	**(cal/g)**	**(cal/g)**	(cal/g)	(cal/g)	(cal/g)	**(cal/g)**	**(cal/g)**	**(cal/g)**	**(cal/g)**
HOC		2250.3	2294.7	2346.3	**2297.1**	**39.2**	2311.4	2240.0	2304.3	**2285.2**	**32.1**	**2447.7**	**22.4**
		(˚F)	(˚F)	(˚F)	**(˚F)**	**(˚F)**	(˚F)	(˚F)	(˚F)	**(˚F)**	**(˚F)**	**(˚F)**	**(˚F)**
AIT (2ksi)	0.2	TL	--	--	**--**	**--**	--	--	--	**--**	**--**	**--**	**--**
	0.5	TL	--	--	**--**	**--**	--	--	--	**--**	**--**	**--**	**--**
	0.7	402	--	--	**--**	**--**	--	--	--	**--**	**--**	**--**	**--**
	1	405	394	410	**403**	**7**	367	391	368	**375**	**11**	**360**	**5**
AIT (50 psia)	0.2	--	--	--	**--**	**--**	--	--	--	**--**	**--**	**--**	**--**
	0.5	--	--	--	**--**	**--**	--	--	--	**--**	**--**	**--**	**--**
	0.7	--	--	--	**--**	**--**	--	--	--	**--**	**--**	**--**	**--**
	1	456	472	492	**473**	**15**	463	497	461	**474**	**17**	**464**	**16**
13A Modified		**0/60 (~45% RH/ 49-50 ^{0} F) [1]**					**0/60 (~45% RH / 49-50 ^{0} F) [1]**					**0/60 (10-15% RH) [1]**	

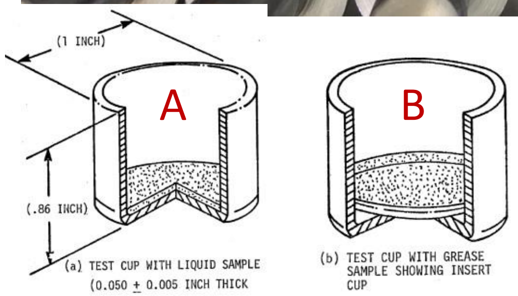
[1]Test 13A (Modified) 72 ft lbs (98J) – Solvent was filtered and dispensed directly into the tall aluminum cups (no insert sample cups were used as specified in D2512-82). Also, the plummet catcher was used to eliminate rebound (uncontrolled) impacts.

Samples Tested at WSTF - Jun 2016
NESC Independent Assessment

Solstice PF, 13A Test Results from the Modified Test Protocol Performed in Jun 2015 Yielded the Same Results (0/60) When Tested in Jun 2016

All Impacts are Uniform





Solvent samples were dispensed into the tall aluminum sample cup (**A**). The insert sample (grease) cups were not used for the modified tests (**B**).

All impacts were near dead center.

- Eliminating rebound impacts reduced the different point loadings.
- Excluding the insert sample cups eliminated any edge promoted reactions due to the plummet striking the raised edge (rim and rim wall) of the insert sample cup. Also, movement of the insert sample cup after placement in the impact tester would often result in non-centric impacts.
- Removing the insert sample cups also minimized the %RH effects (atmospheric moisture) during sample preparation. At high humidity, frost would accumulate on the rim of the insert cup and could quench reactions.

Oxygen Impact Sensitivity Results for L14780 & Solvokane

Solvent	Energy 40 ft lbs	Test Location	Test Method	Test Protocol
L14780	$\geq$ 40 ft lbs (Failed)	WSTF	13A	ASTM G86-98

Solvent	Energy 72 ft lbs	Test Location	Test Method	Test Protocol
L14780	0/20 (Passed)	MSFC	13A	ASTM G86-98
L14780	0/20 (Passed)	WSTF	Modified 13A	ASTM D2512-82
L 14780	0/70 (Passed)	WSTF	Modified 13A	ASTM D 2512-82

Solvent	Energy 10 ft lbs	Test Location	Test Method	Test Protocol
Solvokane	Note 1 (Failed)	WSTF	13A	ASTM G86-98
Solvokane	2/6 (Failed)	MSFC	13A	ASTM G86-98

[1] Lowest limit of impact tester. Threshold could not be determined.

L14780 passed the Modified 13A LOX Impact Tests at WSTF (the type and amount of stabilizer used can influence the results.

Oxygen Compatibility Ranking of Solvents vs. Other Non Metallic Materials Used in Oxygen Systems

Oxygen Compatibility Assessment

D240 HOC Energy Release (Damage Potential)

Materials with higher heats of combustion have greater likelihoods of propagating fires once they have been ignited.

MORE COMPATIBLE

Material	HOC (cal/g)
AK225G	1153
TFE Teflon	1701
3M L14780	1925
Vertrel MCA	2034
Fluorogreen	2402
Solstice PF	2448
Kel-F 81 (Neoflon)	2558
Viton A	3995
Vespel SP-21	7603
Nylon 6/6	7905
Buna -N	9909
Polypropylene	11107

LESS COMPATIBLE

WSTF Data

G72 Ignition Resistance Susceptibility (AIT)

Adiabatic compression is one of the most common ignition mechanisms for non metallic materials.

MORE COMPATIBLE

Material	AIT (^{0} C)
Flouorogreen	479
TFE Teflon	434
Kel-F 81 (Neoflon)	377
Vespel SP-21	321
AK225G *	230
Solstice PF *	182
Nylon	178
Vertrel MCA *	167
3M L14780 *	161
Viton A	155
Buna -N	142

LESS COMPATIBLE

* AIT for solvents performed at 2000 psig. Standard method is performed at 1500 psig.

Non Metallic Materials Commonly Used in Oxygen Systems vs Solvents

Conclusions

- NVR removal performance for Solstice PF was essentially equal to AK225G (Baseline Solvent).
- Solstice PF and AK225 had similar solubility / miscibility with the hydrocarbon fluids tested (RP1, Ester Based Hydraulic Fluid and Gear Weight OIl).
- Solstice PF has a higher wetting index than AK225G for removing particulate matter from complex shapes.
  - Ability to penetrate between closely spaced parts.
- Solstice PF has an acceptable flammability risk in oxygen - ranks well w/ other commonly used nonmetallic materials used in oxygen systems.
  - Mechanical Impact and AIT – Impact and Ignition Sensitivity
  - HOC – Energy Release / Damage Potential
  - No stabilizers (no excess NVR from stabilizers)
- Under the right conditions, all solvents (including AK225G) are reactive with oxygen.
  - Verify solvent/s used in oxygen systems are removed.

Conclusions

- Recommendations were made to the ASTM G04 committee for improvements to LOX Mechanical Impact (G86) testing of solvents / liquids.
  - Testing at only one NASA Facility would not have identified test discrepancies with G86 for mechanical impact testing.
  - No insert sample cups as stated in D2512-82 eliminates non uniform (edge) impacts and the effects of RH during sample preparation. Insert cups introduce an uncontrolled variable.
  - Filter solvents prior to testing – Inert particles in the solvent such as silicon oxides and other oxides may have a positive effect on reactivity. Many oxides are abrasive and can quickly expose fresh metal to oxygen when impacted.
- L-14780 requires resolution to reduce NVR from stabilizers for oxygen compatibility and product stability.
  - The reactivity of the stabilizer residue/s used in azeotropes has not been evaluated.
  - Stabilizers / additives can affect NVR results and must be controlled.
  - Additional testing would be required to qualify.
- Solvokane was the most reactive (failed LOX Impact and AIT tests) – eliminated as a candidate.
- Vertrel MCA has a relatively high 100 year global warming potential – less favorable for long term sustainability. Also, stabilizers can affect NVR and reactivity and would have to be controlled.
- The type of stabilizers used with azeotropes containing t- DCE and the associated NVR levels varied from lot to lot.
- The t-DCE component in the azeotrope solvents are not VOC exempt.

Acknowledgments

- **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.
- Thanks to the NASA Rocket Propulsion Test (RPT) Organization and for providing funding for this project.
- We gratefully acknowledge the support and samples provided by the solvent suppliers.

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WSTF: Susana Harper, Fred Juarez, Steve Peralta, Steve Bailey, John Bouvet, Horacio Perez, Christina Pina-Arpin, Joel M. Stoltzfus

NESC Steve Gentz at MSFC and Michael Smiles at SSC

.

Final Report

NASA/TP—2015–218207

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

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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

No claim is made regarding :

- **Safety/efficacy with materials or contaminants other than those tested**
- **Suitability with other systems (not evaluated).**

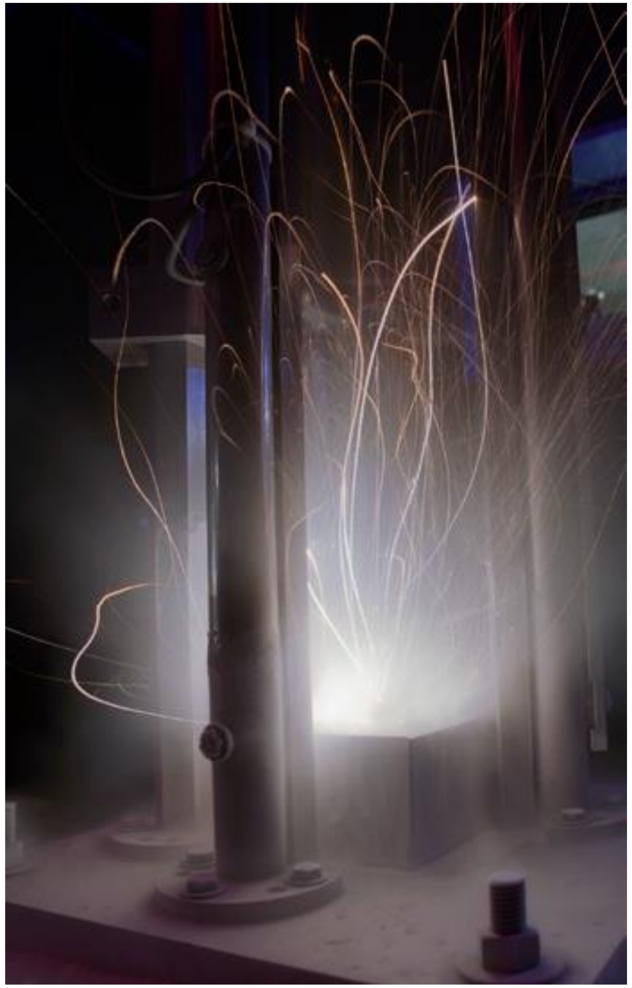
BACKUP CHARTS

Ranking Factors for Oxygen Compatibility

- Damage potential (HOC, ASTM D240)
  - Primary ranking driver against common O_2 system materials (Direct Comparison possible)
    - Solstice PF, L-14780, & Vertrel MCA within proven range
- Ignition Resistance (AIT, ASTM G72)
  - Solvents exhibit lower AITs than common O_2 softgoods
    - Increased severity of 2,000psi vs.1,500psi
  - Volatility affords higher ignition resistance
    - Evaporation & dissipation (ignition, sustained combustion, propagation)(AK-225G history of use)
- LOX Impact Testing (Modified D2512-82 instead of G86-98)
  - Reaction sensitivity at a specific impact energy.
  - Eliminates edge impacts from the insert sample cups and effects from relative humidity.
  - Filter the liquid prior to testing – remove particulates that may be reactive.

ASTM G72 (AIT)

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



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