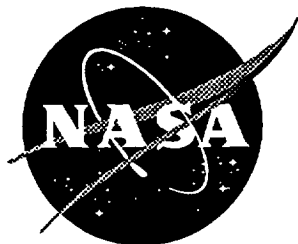


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Evaluation of Alternatives for Trichlorotrifluoroethane (CFC-113) to Clean and Verify Liquid Oxygen Systems

Michelle L. Morris
Langley Research Center, Hampton, Virginia

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National Aeronautics and
Space Administration
Langley Research Center
Hampton, Virginia 23681-0001

Abstract

Researchers at NASA Langley Research Center (LaRC) investigated several alternatives to the use of trichlorotrifluoroethane (CFC 113) in oxygen cleaning and verification. Options included several replacement solvents, Non-Destructive Evaluation (NDE) and Total Organic Carbon (TOC) analysis. Among the solvents, 1,1-dichloro-1-fluoroethane (HCFC 141b) and dichloropentafluoropropane (HCFC 225) are the most suitable alternatives for cleaning and verification. However, use of HCFC 141b is restricted, HCFC 225 introduces toxicity hazards, and the NDE and TOC methods of verification are not suitable for processes at LaRC. Therefore, the interim recommendation is to sparingly use CFC 113 for the very difficult cleaning tasks where safety is critical and to move to an aqueous-based cleaning system for components. Meanwhile, evaluation must continue on new solvents and procedures to find one suited to LaRC's oxygen cleaning needs.

Keywords: trichlorotrifluoroethane, CFC 113, solvents, oxygen cleaning, verification.

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Evaluation of Alternatives for Trichlorotrifluoroethane (CFC 113) to Clean and Verify Liquid Oxygen Systems

1.0 INTRODUCTION

The Montreal Protocol and the Clean Air Act specified that production of chlorofluorocarbons (CFCs) will cease December 31, 1995. CFC 113 is used for precision cleaning of sensitive aerospace equipment, electronics and liquid oxygen (LOX) systems. It is also used to verify the cleanliness level of equipment after it has been cleaned.

The 8-Foot High Temperature Tunnel (8'HTT) at NASA Langley Research Center (LaRC) is a core aerothermal facility where new high-speed engine concepts are tested. It uses many high-pressure gases to simulate Mach 7 conditions, among them methane, air, silane and liquid oxygen. The cleaning process relies heavily on trichlorotrifluoroethane (CFC 113) for the LOX injection ring and its accompanying components and to verify the cleanliness of those parts. Therefore, it is imperative that a replacement method of cleaning and verifying the LOX system be found.

NASA LaRC has investigated several alternatives including non-destructive evaluation (NDE) methods, total organic carbon (TOC) analysis and many alternate solvents. Methods were evaluated on their ability to remove contaminants, ability to detect remaining contaminants, material compatibility, health and environmental effects and cost.

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2.0 OBJECTIVE

The purpose of this investigation is to find a suitable replacement for CFC 113 to be used in the LOX cleaning and verification processes and thereby eliminate the Center's need for CFC 113.

3.0 BACKGROUND

NASA LaRC's mission is to conduct research in aeronautics and aircraft structures and transfer that knowledge to industry. The 8'HTT is an aerothermal test facility where hypersonic flight conditions can be simulated. The facility stores air, methane, hydrogen, silane and LOX, all at high pressure, to be used during a run. Many of these gases are flammable and present dangerous conditions, but the one of primary concern is LOX.

LOX is injected into high pressure air, mixes upstream and flows toward the nozzle past the methane spray bar (Figure 1). Methane is injected into the oxygen-enriched air and is

8-Ft. HTT COMBUSTOR

LOX MODE OPERATION

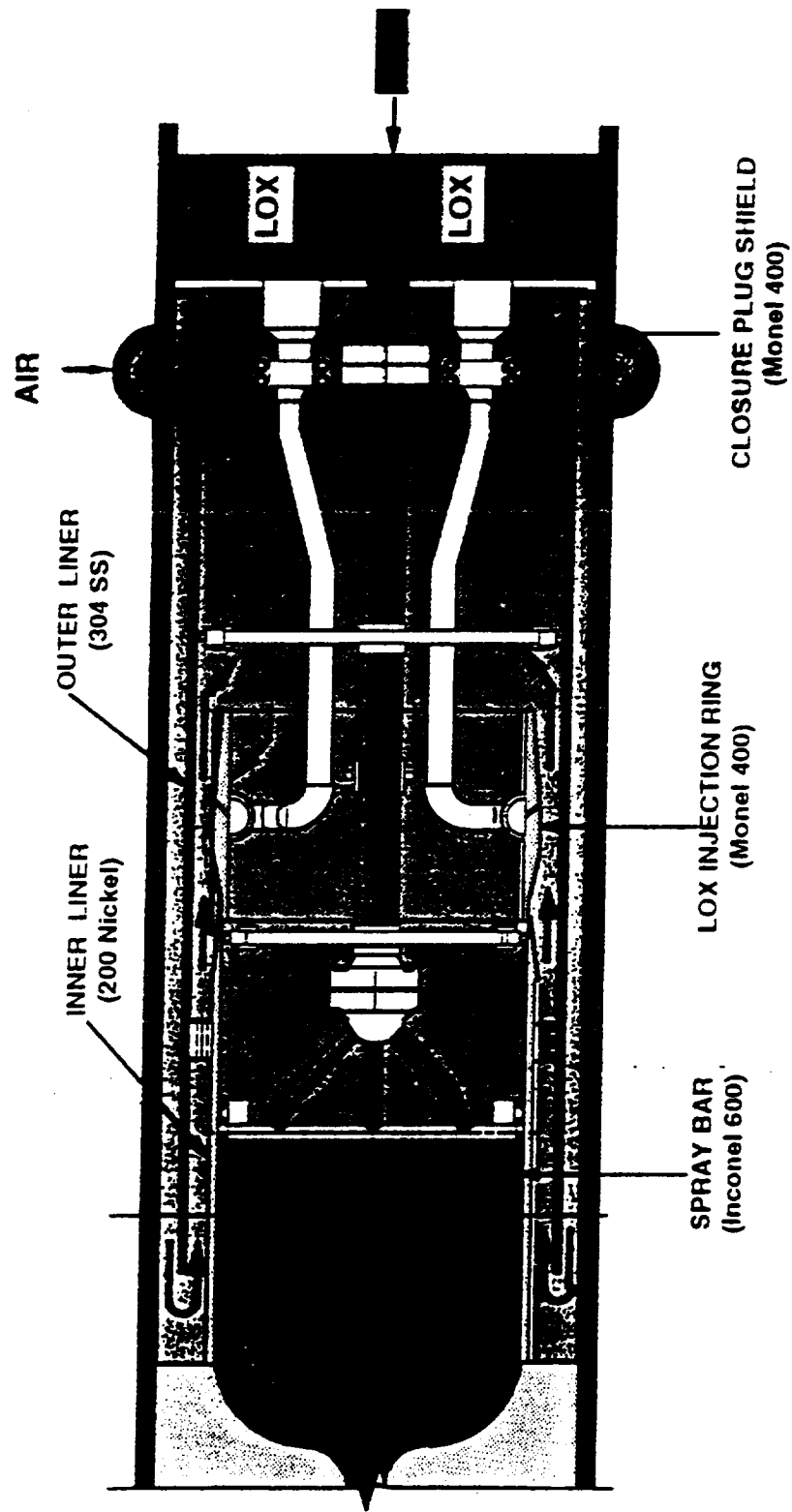


Figure 1

ignited a few inches from the spray bar. By the time the gas mixture reaches the test section, the oxygen content is back to 21 percent, simulating flight conditions.

Explosion hazards are a constant concern at the facility, and cleaning the 8'HTT oxygen system is a very important part of its operation and safety. Cleaning eliminates stray hydrocarbon greases that might combust and particles that might cause an impact explosion. The LOX injection ring is cleaned to Level 300A after every 10 run starts. The (A) designation stipulates that the non-volatile residue (NVR) shall be less than 10 ppm. Level 300 particle limits are defined in Table 1.

Table 1: Level 300A Particle Limits

Particle Size (microns)	Number Allowed
< 100	Unlimited
100 - 250	93
>250 - 300	3
>300	None

The current cleaning process is divided into two areas: components and the LOX injection ring.

For components, the parts are precleaned with brushes and hot water, then placed in ultrasonics with an aqueous alkaline solution of ten percent Brulin 815GD followed by a hot water rinse, and in some cases an acid dip. After cleaning, the parts must be undergo a verification process to certify their cleanliness. Currently, this verification is still performed with CFC 113 because of its previous history of reliable results.

The LOX injection ring is cleaned by clamping a gasket over the injection ring ports and filling the ring and four sections of LOX piping with CFC 113. The solvent is drained from the pipes and ring and purged with dry, oil-free GN₂ and repeated twice more. On the third fill and drain cycle, a sample of solvent is collected and analyzed for nonvolatile residue (NVR) and particulates. If the sample passes the tests (<1 mg/ft² and class 300 particles), the LOX injection ring is considered clean and ready to run. The LOX pipes are capped with polyethylene to prevent recontamination [1].

In spite of the GN₂ purge, the pipe geometry is such that solvent collects in the low points and cannot be completely removed without excessive time and purging. It is estimated that one to four gallons of solvent remain in the low points after cleaning and during the beginning of a run. Since the ends of the pipes are covered, evaporation will not remove the solvent. There are no low point drains due to concerns about introducing another contamination path into the LOX system. Therefore, any solvent chosen to replace CFC 113 for cleaning the LOX injection ring and pipes must be LOX compatible and non-flammable.

4.0 NDE METHODS OF VERIFICATION

A new verification method of NDE, Optical Scanning for Electron Emissions (OSEE), was investigated. Researchers developed this method to test flight hardware. The OSEE probe emits a beam of ultraviolet light at either 185 or 254 nanometers and collects the electrons emitted from the surface as the light strikes it. The results are dependent both on the substrate and on the contaminant. Both must be known and the results compared to previously generated curves to get an accurate answer. The developers also recommend using OSEE in an argon atmosphere for best results.

At the 8'HTT the contaminants that might be present on the surface of the pipes are not completely known, so this method would be of minimal use. Also, it is a new technology

and is still in the prototype stage. A compact instrument is needed, one that can be fed into the LOX pipes, which have a 3 1/2" inner diameter and complex geometry. For this method to work, a great deal of time and money must be spent to develop a small prototype detector and to generate the needed curves. Therefore OSEE is not a viable candidate for verification at the 8'HTT.

Another method of verification is carbon coulometry. In this method, the metal surface to be measured is placed inside a high temperature furnace where the carbon in the surface contamination is converted to carbon dioxide and measured with an infrared (IR) detector. The main drawback to this method is the size of the test specimen, which must be less than 0.75 inches wide and four inches long. This method could be used with witness plates but was deemed unsuitable for the 8'HTT due to the size restrictions.

5.0 TOC METHOD OF VERIFICATION

Total Organic Carbon Analysis (TOC) measures the total carbon concentration in a water sample. It vaporizes a small (200 microliter) sample of water, converting any carbon into carbon dioxide and measuring it with an IR detector. Experiments were conducted to find a relationship between parts per million (ppm) carbon from TOC and mg/ft² of non-volatile residue (NVR) obtained by the gravimetric methods. Experimental procedures were derived from Kennedy Space Center's aqueous TOC testing [2]. Three contaminants were tested: Oster Oil and Cool Tool, both hydrocarbon oils, and Silicon Dielectric, a silicon grease.

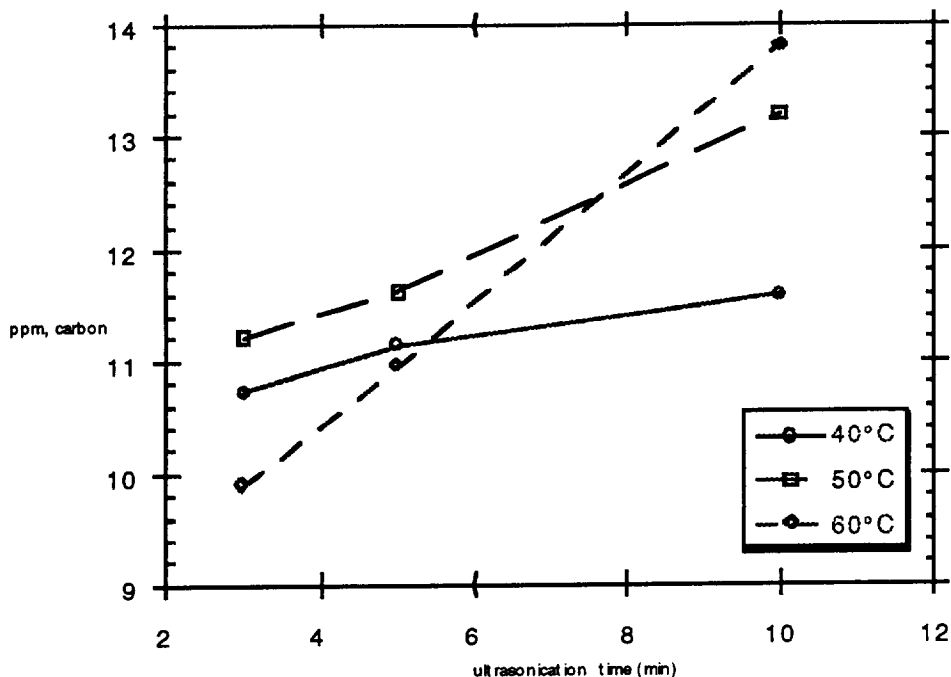
The test articles were stainless steel coupons, two inches square. The TOC analyzer was a Rosemount DC-190 from Dohrmann. A 27 kHz ultrasonic tank filled with warm deionized (DI) water was the final cleaning step.

The coupons were initially cleaned in CFC 113. A test solution was made from 100 mg of contaminant and 100 ml of CFC 113. The solution was shaken vigorously before being applied to the coupons. The solution was applied to the coupons with a 500 microliter pipette. Testing amounts were 0.5, 1.5, 2.5 and 5.0 ml of solution (or 1.5, 4.5, 7.5 and 15 mg of contaminant). The coupons were dried for four hours in an oven at 80°C. They were placed in a clean pan filled with 500 milliliters of warm DI water and subjected to ultrasonication for five minutes. A sample was drawn from the pan, injected into the TOC and tested for the amount of carbon.

Figure 2 shows the results of a 10 ppm aqueous carbon standard tested at three different temperatures and ultrasonicated for three different lengths of time. As the time increased, so did the TOC reading, until it measured more carbon in the tank than was actually there. The TOC reading also increased as a function of temperature. Therefore, both ultrasonication time and temperature affect the measurement. Based on these results the test water temperature was set to 50°C.

A solid correlation between TOC measurements of ppm carbon and the mg/ft² of contamination was sought. If a linear correlation was found, the slope could be used to convert ppm into the standard test measure of mg/ft².

Figure 2: TOC vs Time



Two assumptions were made for this analysis:

- The total amount of carbon in a hydrocarbon or silicon contaminant averages 60 percent.
- If the total surface area of articles to be tested is less than one square foot, it is assumed to be equivalent to 1 ft².

Initial testing showed the relation between TOC measurement and the contaminated test coupons to be mostly linear, but the slope varied from 2.0 to 4.5.

The cut-off point for failing a part is 1 mg/ft², equivalent to three to four ppm carbon on the TOC. The TOC lower detection limit is approximately one ppm, and the DI water used for testing typically contains one ppm of carbon. Therefore the decision range for pass/fail verification is only 1-2 ppm above the noise level. Only 500 milliliters of water were used, just enough to cover the coupons. To completely cover large fittings, filters, and flex hoses more water must be added, which will decrease the overall concentration of carbon in the ultrasonic tank. That will decrease the TOC measurement, possibly down into the noise level and make accurate measurements impossible.

The TOC method has several problems that make it unacceptable as a verification tool:

- It is operator dependent.
- It is unreliable.
- The level of contamination being measured is so low (1 mg/ft²) that readings are barely above the noise level of the TOC.
- Less than 50 percent of the components that come in for cleaning can be verified with the TOC due to restrictions on component size from the ultrasonic pan size and water volume.

- It can take four or more hours for the TOC to reach a steady state after being shut off for a weekend. It can take a week to reach steady state after being shut off for a month. Since LaRC's workload is infrequent, the TOC will not see continuous operation. Therefore, a large percentage of time will be spent getting the TOC ready for operation.

- It cannot be used for measuring cleanliness of the LOX injection ring due to the large amount of water that would be needed to flush the ring.

6.0 SOLVENT EFFICIENCY TEST

The objective of this test was to determine the cleaning power of the solvent without major mechanical agitation. The majority of testing is to find a replacement for CFC 113 used to cleaning the LOX injection ring. As such, the solvent must be a good cleaner for several contaminants (silicon, hydrocarbon, fluorocarbon), and it must do so without needing mechanical agitation such as scrubbing or ultrasonics.

6.1 Test Solvents

Several solvents were tested for their ability to clean common contaminants found in the 8'HTT. The test solvents are listed in Table 2. They include hydrochlorofluorocarbons (HCFC) both neat and azeotroped, a hydrofluorocarbon (HFC), a perfluorocarbon (PFC), a halogenated hydrocarbon and water. Their properties are listed in Table 3.

Table 2: Test Solvents

Chemical Name	Trade Name	Chemical Formula
HCFC 141b, neat	Genesolv 2000 ^a	1,1 dichloro-1-fluoroethane
HCFC 141b, w/ 4% IPA	Genesolv 2004	1,1 dichloro-1-fluoroethane
HCFC 225, neat ^b	AK 225	Dichloropentafluoropropane
HCFC 225, w/ 4% EtOH ^b	AK 225AES	Dichloropentafluoropropane
HFC 43-10mee	Vertrel XF	Dihydroperfluoropentane
PFC	PF 5080	C ₈ F ₁₈
Borothene	Borothene	Halogenated hydrocarbon ^c
Deionized Water, 100 °C	DI Water	H ₂ O
Deionized Water, 25 °C	DI Water	H ₂ O

a - Genesolv 2000 from Allied Signal was the brand tested, but many companies sell HCFC 141b under different trade names.

b - A mixture of 45 percent 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC 225ca) and 55 percent 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC 225cb); the mixture is referred to as HCFC 225

c - Manufacturer's Proprietary Information

Table 3: Solvent Properties

Solvent	BP (°C)	FP (°C)	Surface Tension (dynes/cm @ 25°C)	Vapor Pressure (psia; 25°C)	PEL ^a (ppm)	NVR ^b (ppm)	LOX ^c
CFC 113	48	None	17.3	6.46	1000	2	Yes
Genesolv 2000	32	None	19.3	11.5	500	60 ^e	Yes
Genesolv 2004	29	None	18.5	10.2	400	0.55	Yes
AK 225	54	None	16.2	ND	25 ^d	10	Yes
AK 225 AES	52	None	16.8	ND	25 ^d	19.5	Yes
Vertrel XF	55	None	14.1	4.4	200	ND	Yes
PF 5080	101	None	15	0.85	ND	ND	ND ^f
Borotheene	76	None	ND	ND	50	57.5	ND
DI Water	100	None	163.7	0.967	NA	ND	Yes

ND - Not Determined

NA - Not Applicable

^a - Permissible Exposure Limit^b - Non-Volatile Residue; baseline measurement of the solvent^c - LOX compatibility^d - Interim value; final value not established. Limit stated is for -ca isomer^e - Manufacturer believes our sample was contaminated. Normally <10 ppm^f - Manufacturer states PF 5080 is LOX compatible, but test results have not been established

AK 225 is made up of 45% HCFC 225-ca isomer and 55% HCFC 225-cb isomer. The -ca isomer has a PEL of 25 ppm, while the -cb isomer has a PEL of approximately 400 ppm. Since the two isomers have different boiling points, the -ca isomer can be distilled away leaving the less hazardous -cb isomer. However, that would effectively double the cost of the AK products. The NVR test showed a high result for AK 225AES. The manufacturer, Asahi Glass of Japan, responded that their products should have an NVR limit of 10 ppm maximum. Borotheene also has a very high NVR that does not meet LaRC's unused solvent specifications. Borotheene should respond well to purification by distillation, but no testing has been done.

6.2 Test Contaminants

Twelve contaminants were chosen for the solvent efficiency test (Table 4). They represent contaminants commonly found at 8'HTT and include hydrocarbon oils and greases, a silicon grease and LOX compatible fluorinated greases. Even though the LOX compatible greases do not have to be completely removed from the tunnel, they act as traps for hydrocarbons and particulates if they remain. Frequently, these fluorinated greases are the most difficult to remove and detect.

Table 4: Test Contaminants

Contaminant	Type
Silicone Dielectric	Silicon
Cimcool	Hydrocarbon
Oster Oil	Hydrocarbon
Molydee	Hydrocarbon
Blazer	Hydrocarbon
Cool Tool	Hydrocarbon
Tribolube 16	Fluorocarbon
Lubriplate	Hydrocarbon
Extreme Pressure Lube	Hydrocarbon
Krytox	Fluorocarbon
Fluorolube	Fluorocarbon
Tribol	Fluorocarbon

6.3 Contamination and Testing Procedure

The test articles were flat, stainless steel washers, 7/8" diameter. They were cleaned with CFC 113 and oven dried at 80°F prior to testing. A cleanroom sponge applicator was used to apply a thin layer of contaminant over 3/4 of the surface area. The washers were dried, weighed, placed in a small aluminum weighing pan and covered with 5-10 milliliters of solvent. The pan was gently agitated to simulate the conditions seen in the fill and drain cycle of the LOX injection ring. The washers were removed from the solvent and again oven dried. They were re-weighed and the difference in weight converted into percent contaminant removed.

7.0 MATERIAL COMPATIBILITY

Tests were conducted to determine what effects alternate solvents might have upon the materials present in the 8'HTT. These tests include measuring changes in dimensions, changes in hardness, visual inspections and NVR of the test solvent.

7.1 Test Materials

Ten materials present in the 8'HTT were tested: four metals and six softgoods. The materials are listed in Table 5. One common material in the 8'HTT that was not tested is Monel, both the K500 and the K400 series.

Table 5: Test Articles

Material	Composition	Original Dimensions
Copper	Metal	0.375" D x 2" L
15-5 PH Stainless Steel	Metal	0.5" D x 2" L
Mild Carbon Steel	Metal	0.5" x 0.5" x 2"
Brass	Metal	0.5" x 0.5" x 2"
Teflon	Elastomer	1" x .02" x 2.5"
Viton	Elastomer	0.375" D x 2.5" L
Fluorogreen	Elastomer	1.8" x 0.1" x 0.65"
Buna-N	Elastomer	0.375" D x 2.5"
VespeI	Elastomer	1" x 1" x 2.5"
Kel-F	Elastomer	1.25" D

7.2 Test Solvents

Four solvents were used in this test. They were chosen based on the results of the solvent efficiency test. The solvents are HCFC 141b azeotroped with four percent methanol (Genesolv 2004), HCFC 225 neat and azeotroped with four percent ethanol (AK 225 and AK 225AES) and Borothane.

7.3 Test Procedure

Prior to testing, each material was stamped with an ID code, measured for dimensions, tested for hardness and visually inspected for any signs of abnormalities. Hardness tests for metals were performed with the Wilson Rockwell Hardness Tester, bit B, except for the 15-5 stainless steel, which was tested with bit C. Hardness tests for the softgoods were performed with the Shore Durometer Hardness Type "A-2" and Type "D" instruments. Metal coupons were sandblasted to assure that all oxidized material was removed. The coupons were cleaned with CFC 113, dried and weighed.

Four series of tests were made, one per solvent. In each series, the coupons were placed in individual 60 milliliter bottles. Each bottle was filled with the series solvent until the coupon was half submerged in the liquid. The Kel-F coupon was completely submerged in solvent due to its small size. The bottle was tightly capped and kept at room temperature for 21 days.

The decision was made to run the tests at room temperature to avoid any problems associated with storing solvent above its boiling point in a sealed container. Since the solvent is normally in contact with the 8'HTT materials for a few hours at a time, and on rare occasions up to two days, 21 days was considered an adequate test period.

After 21 days, the coupons were removed from the solvent and allowed to dry at room temperature. Testing was conducted within three hours of removal from the solvent. The coupons were stored in a clean room for 24 hours, after which the tests were repeated to see if any changes had occurred.

After the coupons were removed from the bottles, an NVR test was performed on the solvent. The solvent was poured into a clean, dry aluminum weighing pan and boiled to dryness. The residue left in the pan was weighed and recorded.

8.0 RESULTS

8.1 Solvent Efficiency Test

The results of the solvent efficiency test are listed in Table 6. This is a preliminary test designed to point out three or four solvents suitable for further testing. Selection criteria was simply to find the solvent with the most consistently high removal efficiency for several contaminants.

Of all the solvents, CFC 113 had the highest overall efficiency at 95 percent. AK 225 and AK 225AES were nearly as good. Next were the Genesolv 2000 and 2004 products (HCFC 141b) with a respectable 80 percent average and Borothane at 78 percent. These solvents, which all contain chlorine, did very well removing the hydrocarbon oils and greases.

Table 6: Solvent Efficiency Test - Percent Contaminant Removed

CFC113	Genesolv 2000	Genesolv 2004	AK 225	AK 225- AES	PF 5080	Ventrel XF	DI Water 100 °C	DI Water 25 °C	Boroethene
Silicone	100	96	99	100	94	7	12	0	86
Diclectric									
Cincool	94	54	89	100	100	61	69	81	58
Oster Oil	100	100	99	100	100	82	45	65	44
MolyDec	96	98	98	100	100	1	34	6	5
Blazer	100	100	100	99	97	34	64	18	12
Coul Tool	100	95	99	100	100	18	48	37	10
Tribolube 16	73	11	7	69	74	66	69	24	10
Lubriplate	89	88	89	75	94	12	31	71	44
Ext. Press.	100	100	96	100	92	0	0.5	63	38
Lube									
Krytox	90	20	90	86	96	98	96	16	2
Fluorolube	100	98	97	100	100	91	99	8	0
Tribol	100	100	95	100	84	34	94	16	16
Average ^a	95	80	81	94	94	42	55	33	19
									78

^a - This is an average of each solvent's ability to remove contamination. It should not be the sole discriminator of a solvent's performance. Some solvents perform better on some contaminants than others.

The purely fluorinated solvents, PF 5080 and Vertrel XF did poorly on all contaminants except the fluorinated greases (Krytox and Fluorolube). This is a good example of like dissolving like.

As expected, water performed very poorly with hot water being marginally more effective than room temperature water.

8.2 Material Compatibility Tests: Metals

None of the metals were significantly affected by any of the solvents except for the mild carbon steel. It rusted heavily while immersed in Boroethene. Other solvents caused some staining, but no rusting.

Copper:

Table 7 shows the results from the copper tests. There were no significant negative impacts from any of the solvents tested. Genesolv 2004 did produce some slight staining and discoloration on the coupons, but no rust was apparent.

Table 7: Copper Compatibility Tests

	Weight Gain (g)	Abnormalities/ Corrosion	Hardness g	% Linear Swell
Genesolv 2004				
Test 1 a	58.45947	No	42	
Test 2 b	NC d, e	Yes f	45	< 1
Test 3 c	NC e	Yes f	46	< 1
AK 225				
Test 1	59.06163	No	44.5	
Test 2	NC	No	46.5	< 1
Test 3	NC	No	46	< 1
AK 225AES				
Test 1	59.63432	No	46	
Test 2	NC	No	45	< 1
Test 3	NC	No	45	< 1
Boroethene				
Test 1	58.93778	No	45.5	
Test 2	NC	No	45	< 1
Test 3	NC	No	46	< 1

NC - No Change.

a - Original test series.

b - Test series repeated after 21 day immersion.

c - Test series repeated 24 hours after removal from solvent.

d - Changes less than 1 mg are not reported.

e - Numbers for Test 2 and Test 3 represent the delta from the original value in Test 1.

f - Staining and discoloration were seen on the half immersed in the solvent, but no corrosion.

g - Tested using the Rockwell B hardness bit.

15-5 Stainless Steel:

Table 8 lists the results of the compatibility tests for 15-5 Stainless Steel. No adverse effects appeared in any of the tests.

Table 8: 15-5 Stainless Steel Compatibility Tests

	Weight Gain (g)	Abnormalities/ Corrosion	Hardness ^c	% Linear Swell
Genesolv 2004				
Test 1	52.47202	No	32	
Test 2	NC a, b	No	31	< 1
Test 3	NC	No	33	< 1
AK 225				
Test 1	53.14119	No	32	
Test 2	NC	No	32	< 1
Test 3	NC	No	33	< 1
AK 225AES				
Test 1	52.83139	No	30.5	
Test 2	NC	No	31	< 1
Test 3	NC	No	32	< 1
Borotheene				
Test 1	51.83476	No	31	
Test 2	NC	No	32	< 1
Test 3	NC	No	33	< 1

NC - No Change.

a - Changes less than 1 mg are not reported.

b - Numbers for Test 2 and Test 3 represent the delta from the original value in Test 1.

c - Tested using the Rockwell C hardness bit.

Mild Carbon Steel:

Table 9 lists the compatibility results for mild carbon steel. The only adverse effect was caused by Borothane. It caused the steel to rust heavily.

Table 9: Mild Carbon Steel Compatibility Tests

	Weight Gain (g)	Abnormalities/ Corrosion	Hardness ^c	% Linear Swell
Genesolv 2004				
Test 1	38.18680	No	82	
Test 2	NC a, b	No	90	< 1
Test 3	NC	No	93	< 1
AK 225				
Test 1	37.82920	No	80	
Test 2	NC	No	89	< 1
Test 3	NC	No	90	< 1
AK 225AES				
Test 1	37.90452	No	86	
Test 2	NC	No	89	< 1
Test 3	NC	No	92	< 1
Borothane				
Test 1	37.90551	No	82.5	
Test 2	0.006	Yes ^d	90	< 1
Test 3	0.005	Yes ^d	92	< 1

NC - No Change.

a - Changes less than 1 mg are not reported.

b - Numbers for Test 2 and Test 3 represent the delta from the original value in Test 1.

c - Tested using the Rockwell B hardness bit.

d - Heavy rust was present on the submerged half. Rust spots were visible on the top half of the coupon, which was exposed to the vapors.

Brass:

Brass, like the other metals, showed little sign of negative impacts. Borothene caused some staining on the coupon, but no rust. The results are listed in Table 10.

Table 10: Brass Compatibility Tests

	Weight Gain (g)	Abnormalities/ Corrosion	Hardness ^c	% Linear Swell
Genesolv 2004				
Test 1	71.75291	No	82	
Test 2	NC a, b	No	90	< 1
Test 3	NC	No	93	< 1
AK 225				
Test 1	71.29208	No	80	
Test 2	NC	No	89	< 1
Test 3	NC	No	90	< 1
AK 225AES				
Test 1	71.21857	No	86	
Test 2	NC	No	89	< 1
Test 3	NC	No	92	< 1
Borothene				
Test 1	71.73793	No	82.5	
Test 2	NC	Yes d	90	< 1
Test 3	NC	Yes d	92	< 1

NC - No Change.

a - Changes less than 1 mg are not reported.

b - Numbers for Test 2 and Test 3 represent the delta from the original value in Test 1.

c - Tested using the Rockwell B hardness bit.

d - Slight staining was present, but no corrosion.

8.3 Material Compatibility Test: Elastomers

Many of the elastomers absorbed the solvents during the 21 day immersion test causing weight gain and swelling. However, most of the elastomers released the solvents during the 24 hour drying period after removal from the solvent. Viton and Buna-N showed extreme incompatibility to all four solvents tested.

Teflon:

The Teflon experienced some slight weight gain, especially from the AK 225 products. However, after 24 hours of drying the weight of the coupons was decreasing back to the original value. Test results are shown in Table 11.

Table 11: Teflon Compatibility Tests

	Weight Gain (g)	Abnormalities/ Corrosion	Hardness ^c	% Linear Swell
Genesolv 2004				
Test 1	1.81413	No	93	
Test 2	0.003 a	No	90	< 1
Test 3	0.001	No	91	< 1
AK 225				
Test 1	1.80163	No	94	
Test 2	0.027	No	90	< 1
Test 3	0.022	No	93	< 1
AK 225AES				
Test 1	1.81938	No	92	
Test 2	0.023	No	91	< 1
Test 3	0.019	No	93	< 1
Borotheene				
Test 1	1.79079	No	93	
Test 2	NC b	No	90	< 1
Test 3	-0.003	No	94	< 1

NC - No Change.

a - Numbers for Test 2 and Test 3 represent the delta from the original value in Test 1.

b - Changes less than 1 mg are not reported.

c - Tested using the Shore Durometer Hardness Type "A-2" and Type "D."

Viton:

Viton experienced severe compatibility problems with all four solvents. Each coupon gained a large amount of weight, 10 to 45 percent of the original weight. The weight was decreasing even 24 hours after removal from the solvent. They also had a considerable amount of swelling. However, little change in the hardness of the coupons was seen. If contact between Viton components and the alternate solvent can be limited and the component dried thoroughly afterwards, many of these problems can be avoided. Test results are listed in Table 12.

Table 12: Viton Compatibility Tests

	Weight Gain (g)	Abnormalities/ Corrosion	Hardness ^c	% Linear Swell
Genesolv 2004				
Test 1	4.64764	No	78	
Test 2	1.991 a, b	No	75	13.4
Test 3	1.001 a	No	75	7.9
AK 225				
Test 1	4.71314	No	75	
Test 2	2.087 a	No	75	10.2
Test 3	1.368 a	No	75	6.2
AK 225AES				
Test 1	4.65443	No	77	
Test 2	2.25 a	No	75	14.9
Test 3	1.557 a	No	79	11.6
Borotheene				
Test 1	4.66173	No	77	
Test 2	0.370	No	79	1.9
Test 3	0.776	No	80	1.6

a - Weight of the coupon was decreasing while being weighed.

b - Numbers for Test 2 and Test 3 represent the delta from the original value in Test 1.

c - Tested using the Shore Durometer Hardness Type "A-2" and Type "D."

Fluorogreen:

Fluorogreen did well in the compatibility tests. It did gain some weight during the immersion tests, with the coupons in the AK 225 products gaining the most weight. However, the weights decreased after drying at room temperature for 24 hours. The linear swelling was slight and no changes in hardness were detected. Results are listed in Table 13.

Table 13: Fluorogreen Compatibility Tests

	Weight Gain (g)	Abnormalities/ Corrosion	Hardness ^b	% Linear Swell
Genesolv 2004				
Test 1	3.3739	No	95	
Test 2	0.057 ^a	No	93	0.8
Test 3	0.0316	No	94	0.6
AK 225				
Test 1	3.48714	No	95	
Test 2	0.122	No	93	0.5
Test 3	0.067	No	93	0.5
AK 225AES				
Test 1	3.39428	No	95	
Test 2	0.112	No	93	1.4
Test 3	0.064	No	93	1.3
Borothane				
Test 1	3.55723	No	94	
Test 2	0.016	No	95	< 1
Test 3	0.004	No	94	< 1

^a - Numbers for Test 2 and Test 3 represent the delta from the original value in Test 1.

^b - Tested using the Shore Durometer Hardness Type "A-2" and Type "D."

Buna-N:

The Buna-N components exhibited a severe incompatibility with all solvents. There was a significant weight gain in all coupons; in many cases, the amount gained exceeded the original weight. All of the coupons had lost weight by the following day, but whether they would return to their original weight is unknown. However, the linear swelling that occurred was significant and after 24 hours still had not approached the original value. All of the samples experienced a loss of hardness, probably as a result of absorbing large amounts of solvent and partially dissolving, as indicated by the NVR tests. Table 14 lists the test results.

Table 14: Buna-N Compatibility Tests

	Weight Gain (g)	Abnormalities/ Corrosion	Hardness c	% Linear Swell
Genesolv 2004				
Test 1	5.85041	No	76	
Test 2	6.65 a, b	No	72	16.3
Test 3	1.883 a	No	71	7.2
AK 225				
Test 1	5.85278	No	79	
Test 2	7.1 a	No	73	19.7
Test 3	3.941 a	No	71	12.3
AK 225AES				
Test 1	5.90026	No	77	
Test 2	8.1 a	No	74	21.9
Test 3	3.936 a	No	71	11.7
Borotheene				
Test 1	5.84914	No	80	
Test 2	7.2 a	No	70	15.7
Test 3	1.633 a	No	73	11.9

a - Weight of the coupon was decreasing while being weighed.

b - Numbers for Test 2 and Test 3 represent the delta from the original value in Test 1.

c - Tested using the Shore Durometer Hardness Type "A-2" and Type "D."

Vespel:

Vespel is stable with respect to these solvents. The coupons experienced a slight weight gain, especially with Borothene. Unlike previous materials, the weight gain with Vespel appears to be permanent. No other adverse effects were noted. Results are listed in Table 15.

Table 15: Vespel Compatibility Tests

	Weight Gain (g)	Abnormalities/ Corrosion	Hardness ^b	% Linear Swell (5)
Genesolv 2004				
Test 1	54.44768	No	82	
Test 2	0.028 ^a	No	82	< 1
Test 3	0.026	No	82	< 1
AK 225				
Test 1	53.04403	No	85	
Test 2	0.002	No	85	< 1
Test 3	0.004	No	84	< 1
AK 225AES				
Test 1	52.42409	No	84	
Test 2	0.001	No	84	< 1
Test 3	0.003	No	84	< 1
Borothene				
Test 1	51.52913	No	81	
Test 2	0.456	No	81	< 1
Test 3	0.376	No	81	< 1

a - Numbers for Test 2 and Test 3 represent the delta from the original value in Test 1.

b - Tested using the Shore Durometer Hardness Type "A-2" and Type "D."

Kel-F:

Due to a shortage of available material to test, Kel-F was only tested with two solvents. Some linear swelling and weight gain was noticed. After 24 hours, the material had not recovered as quickly as other elastomers.

Table 16: Kel-F Compatibility Tests

	Weight Gain (g)	Abnormalities/ Corrosion	Hardness ^b	% Linear Swell
Genesolv 2004				
Test 1	1.17672	No	96	
Test 2	0.067 ^a	No	95	2.4
Test 3	0.058	No	95	2.2
AK 225				
Test 1	1.14633	No	95	
Test 2	0.09	No	95	2.0
Test 3	0.077	No	95	2.0

a - Numbers for Test 2 and Test 3 represent the delta from the original value in Test 1.

b - Tested using the Shore Durometer Hardness Type "A-2" and Type "D."

8.3 Material Compatibility Test: NVR

Table 17 compares the metal NVR results from the 21 day immersion test to the NVR results of clean, unused solvent. The reference line defines the cleanliness of the original solvent. LaRC specifications call for new solvent to have an NVR less than 10 ppm. The Genesolv 2004 product is extremely clean. The AK products are marginally acceptable, and the Borotheene product is too contaminated to use out of the drum without extensive purification first.

The test determines the effect of solvents on the test materials. If they are incompatible, the solvent will react adversely to the materials and increase the NVR, either through metal removal in the form of rust or solubilizing the polymeric materials. The solvent was not filtered before being boiled off, so the weight of any particulates is included.

The Genesolv had a mild effect upon the metals, producing 2-13 ppm NVR. The Borotheene had similar results, adding 4-5 ppm to the baseline. The AK 225 and AK 225AES had results that were less than the baseline readings. One possible explanation is that the contaminant in the original solvent settles out on the metal coupons, thus causing them to become more contaminated than before cleaning.

Table 17: Metals NVR Results

	Genesolv 2004 (ppm)	AK 225 (ppm)	AK 225AES (ppm)	Borotheene (ppm)
Reference ^a	0.55	10.0	19.5	57.5
Copper	2.5	5.4	9.4	61.6
15.5 Stainless Steel	6.9	7.5	4.9	61.8
Brass	13.6	8.0	16.6	62.6
Carbon Steel	26	8.4	25.3	110.9

a - Baseline NVR.

Table 18 lists the NVR measurements of the elastomers after the 21 day immersion test. Again, all elastomer results are compared to the solvents' baseline NVR. The results here do not indicate undesirable solvents as much as they indicate undesirable materials. Both Viton and Buna-N show extremely large NVRs after the 21 day immersion test. This data, coupled with their large weight gains, swelling, and softening for the Buna-N, indicate a severe negative impact by all solvents upon these materials.

In theory the solvents are absorbed by the elastomer and slowly dissolve it. The Viton or Buna-N materials in the 8'HTT can trap the replacement solvent and over the course of many days, slowly release vapors back into the tunnel and LOX injection ring. Even though all four solvents are non-flammable, this is a problem to avoid if possible.

For components, the Viton would be removed before cleaning. For the LOX injection ring, where softgoods such as gaskets and o-rings cannot be removed, the Viton would have to be replaced with a more resistant elastomer.

Table 18: Elastomers NVR Results

	Genesolv 2004 (ppm)	AK 225 (ppm)	AK 225AES (ppm)	Borotheene (ppm)
Reference a	0.55	10.0	19.5	57.5
Teflon	1.9	3.9	18.8	76
Viton	790.8	372.5	497.5	177.2
Fluorogreen	0	5.0	7.7	39.6
Buna-N	6515.5	3853.3	4865.3	2790.8
Vespel	2.5	16.8	20	59.6

a - Baseline NVR.

9.0 HEALTH AND ENVIRONMENTAL EFFECTS

9.1 Health Effects

Many of the solvents have much lower Permissible Exposure Limits (PELs) than CFC 113 (Table 3). This could cause problems with personnel working with the solvents while cleaning the LOX injection ring.

A great deal of care is taken that vapors from the cleaning solvent are contained. The solvent is pumped from a clean barrel into the pipes and drained into a waste barrel at the other end. The only vapors come from the open bung of the barrels.

However, since some of the solvent stays in the low points of the pipes, it is possible for vapors to be present in the working environment around the LOX injection ring. The pipe ends are covered with polyethylene, but the fit is not always perfect. Some of the solvents, such as HCFC 225ca and Borotheene have PELs low enough to force personnel to wear supplied air respirators while working closely with the solvent. In addition, they could release vapors that could adversely affect personnel nearby.

One possible solution is improving the facility by adding filtered ventilation systems to move more air through the work area.

None of the solvents pose a severe health hazard regarding skin contact. Personnel should use appropriate protective measures while working with the solvent, such as goggles, suitable gloves, and protective coats or aprons.

9.2 Environmental Effects

Any solvent chosen to replace CFC 113 must be acceptable to the Environmental Protection Agency (EPA). They define the regulations and restrictions governing the use of solvents commonly used in precision cleaning. CFC 113 is considered a Class I Substance under the Clean Air Act. HCFC 141b and HCFC 225 are considered Class II Substances. As such they are scheduled to be phased out of production by 2030, however HCFC 141b has an accelerated phase out schedule. It is due for phase out in 2003.

HCFC 141b has been defined by the EPA as "unacceptable" as a replacement for CFC 113 in cleaning applications with the following exceptions. The EPA has granted a waiver of continued use for one year (until 1997) to help industry move to an acceptable solvent. However, this only applies to companies who have been using HCFC 141b prior to this.

In addition, HCFC 141b is still an Ozone Depleting Substance (ODS). It has an ozone depleting potential (ODP) of 0.1 compared to CFC 113's ODP of 0.8 (Table 13).

Another environmental hazard associated with these solvents is the Global Warming Potential (GWP). This is caused by solvent vapors trapping heat in the earth's atmosphere and creating a global greenhouse effect. PF 5080 is a strong greenhouse gas (Table 19).

Table 19: Environmental Effects of Test Solvents

Solvent	ODP ^a	GWP ^b
CFC 113	0.8	1.35
HCFC 141b	0.11	0.14
HCFC 225	0.03	ND
HFC 43-10mee	0	0.25
PF 5080	0	8.0
Borotheene	ND	ND

ND - Not Determined

a - Ozone Depleting Potential

b - Global Warming Potential

Finally, water has some environmental hazards associated with using it as a cleaner and verification agent. The restrictions on releasing wastewater into the nation's sewer systems are growing tighter. New regulations might force LaRC to pre-treat any wastewater before sending it to the wastewater treatment plant.

10.0 FINANCIAL CONSIDERATIONS

The cost of CFC 113 is \$22 per pound or \$286 per gallon (August 1995). As time goes by, the decreasing supply of CFC 113 and the increasing government taxes on it will drive the price higher. The actual production cost of CFC 113 is less than \$2 per pound.

The loss of one to four gallons of solvent every time the LOX injection ring is cleaned presents another problem for the 8'HTT. That is the amount of solvent estimated to be trapped in the low points after cleaning and purging the pipes. When the tunnel starts running, the trapped solvent is evaporated into the oxygen and exhausted into the atmosphere. That amount of solvent is lost forever and cannot be replaced, yet another reason to find an alternate solvent to replace CFC 113.

Many of the alternatives are as costly as CFC 113, but they will be available for many years. The costs of these alternatives are listed in Table 20.

Table 20: Cost of Alternative Solvents ^a

Solvent	Cost/Pound (\$/lb.)	Cost/Gallon (\$/gal)
CFC 113	22.00	286
HCFC 141b	3.20	41
HCFC 225	14.00	183
PF 5080	13.25	185
HFC 43-10mee	17.00	222
Borotheene	2.50	30
DI Water	0.12	1.00

a - Cost as of August 1995.

In addition, the supply of CFC 113 available to the 8'HTT is finite. If all the options have not been investigated and a safe and suitable alternative chosen, the change will be made in ignorance. That opens a Pandora's box of problems relating to safety, cleaning ability, material compatibility, health issues, cost and more.

A final cost consideration is any facility modifications that will have to be made as a result of changing to an alternate solvent. Such modifications might include installing a new, filtered ventilation system to increase the air circulation or safety precautions such as eye wash stations and safety showers.

11.0 CONCLUSIONS

The need to find a suitable alternate for CFC 113 is pressing. Alternatives exist, but many of them are unsuited to the extreme conditions of the 8'HTT. No NDE methods have been found that would work in the 8'HTT verification processes. The TOC method has been investigated, but it is too troublesome and ineffective to solve the problem. The last approach has been to search for an alternative solvent, which would require only a few modifications to the cleaning process and minor equipment changes. This seems the best choice for 8'HTT cleaning operations.

Regarding the cleaning ability of the solvents, HCFC 141b and HCFC 225 were the most effective. They functioned nearly as well as CFC 113. However, HCFC 225 has a low PEL that would pose significant health problems for workers.

HCFC 225 shows the best overall material compatibility followed by HCFC 141b. Borothene is unacceptable due to the high corrosion effects it has on carbon steel. Viton and Buna-N were adversely affected by all the solvents tested, indicating a need to keep these materials out of contact with the selected solvent or replace these tunnel components with a more resistant material. All the solvents tested have some type of negative impact on one or more of the materials. Further investigation must be conducted on material compatibility if an alternate solvent is chosen.

HCFC 141b is the best choice concerning health effects on personnel since it has a very high PEL. However, it is in disfavor with the EPA due to its ODP and Class II Substance designation. Even if used as a stopgap measure, research into alternatives must continue and a switch must be made as soon as a suitable one is found.

11.1 Future Plans

The issue is far from resolved. New products continue to come onto the market. DuPont and Allied Signal have formed a partnership to develop a new product: a hydrofluoroether (HFE), available for testing and commercial applications sometime in 1996. It is expected to have a cost similar to CFC 113. Much remains unknown about the product, including its cleaning ability, health effects and LOX and material compatibility, but many industry experts have expressed high hopes concerning its use in LOX applications.

Another product available for testing is Navy Oxygen Cleaner (NOC). It is currently being tested by the NAVSEA and NAVAIR departments of the Navy [3]. It is a semi-aqueous cleaner that works by mechanically removing contamination from the surface rather than dissolving it like solvents. Navy testing indicates very favorable results for component cleaning and line flushing. They are in the process of converting their NAVAIR cleaning operations to NOC procedures.

Much of the work discussed in this paper is based on the current cleaning procedures at 8'HTT. Those procedures were established many years ago when CFC 113 was inexpensive and plentiful, and ensuring a safe operation was the most important item. Now that costs of cleaning solvents are much higher than before, the cleaning procedures need to be re-evaluated. The question of "how clean is clean" should be asked. The fill

and drain cycle for cleaning the LOX injection ring has been used successfully for many years, but perhaps a more effective method exists. These new methods might require a longer downtime or more work for personnel, but they might make a less effective cleaner work as well as CFC 113. Several industry experts are reporting that the cleaning "process" is just as important as the solvent used and that even aqueous cleaning can be suitable if the correct process be determined for the task.

11.2 Recommendations

There was no one clear choice for replacing CFC 113 in the LOX injection ring cleaning and verification work. The best choice, HCFC 141b, is disallowed by the EPA. The second best cleaner, HCFC 225, is too toxic to use safely without major modifications to the facility and to the cleaning operations.

The 8'HTT has a reserve of CFC 113 that will last for years if used only to clean the LOX injection ring. That is the one area where cleaning requirements are the most stringent and safety is extremely important due to the trapped solvent in the tunnel. An alternate solvent cannot be recommend for the LOX injection ring at this time. If a future solvent proves to be acceptable, tunnel operations can immediately move to use it. In the meantime, research must continue into new solvents, and more importantly, into new cleaning procedures and facility modifications should a toxic solvent be chosen.

Component cleaning requirements for LOX compatibility and non-flammability can be relaxed slightly because the components can be thoroughly dried prior to use in the 8'HTT. Investigation into alternate cleaning products and processes is ongoing. Some new cleaners, such as NOC, provide their own verification process. For reasons relating to performance and safety, LaRC will concentrate on aqueous-based component cleaning. For component verification, CFC 113 will be used sparingly until an alternate verification solvent or method is approved by the Center.

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