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National Aeronautics and Space Administration
Precision Cleaning of Oxygen Systems and Components

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Executive Summary

Due to the impending phase out of Class II Ozone Depleting Substances, NASA and Department of Defense (DOD) entities are presented with a risk to mission for maintaining clean oxygen line systems and components. After a review of current commercially available alternatives as documented in a White Paper prepared by ITB in 2006, it was concluded that no viable and environmentally preferable solution is at a technology readiness level commensurate with demonstration / validation requirements. It was further concluded that it might be advantageous for NASA to strengthen its relationship with the Green Chemistry community; that this quickly growing field may discover or design the next generation of cleaning product chemistries. Yale University was chosen because of it world-renowned Green Chemistry program and existing relationship between member(s) of the faculty and NASA.

Early in the period of performance a site visit was completed at Tinker Air Force Base in Oklahoma City, OK to witness oxygen line cleaning of systems and components, and to gain valuable insight from Air Force subject matter experts. In consultation with NASA personnel at White Sands Test Facility (WSTF), a lab study was performed by the team at Yale to bring them up to speed on oxygen line cleaning. Many of the testing protocols were already assembled in a previous project for the Joint Group on Pollution Prevention (JG-PP). The first phase of lab experimentation was conducted to verify that Yale could achieve results comparable with previous studies and to lock down the process for future testing. Sample contaminants and cleaners were provided by personnel at WSTF as well as Asahi Glass Chemicals Group, the manufacturer of AK-225g (in-kind). The second phase of lab experimentation was meant to develop a list of non ozone depleting candidates for further evaluation and eventual demonstration / validation.

The main portion of this report discusses findings of the team, from establishing a baseline through non-volatile residue measurements to flow testing and investigating potential classes of compounds and solvents. One limiting factor in the selection of alternatives is the flammability in an oxygen rich environment. Future work in for this application will likely involve optimizing the characteristics of the cleaning compounds to maximize cleaning performance while minimizing risks of flammability.

Quarterly status reports were prepared and delivered to ITB throughout the period of performance. These reports were used by ITB to keep NASA Headquarters Environmental Management Division (HQ EMD) apprised of project progress. ITB is pleased to have provided programmatic and project development support services to NASA for the past year. The objectives and tasks identified in the SOW have been met and worked by ITB to provide significant benefit to NASA risk mitigation activities. These results have aided immeasurably in identifying NASA as a key leader in searching for replacements of Class II Ozone Depleting Substances, and strengthened strategic partnerships for the group.

Introduction

Currently, NASA uses Dichloropentafluoropropane (HCFC-225), a Class II ozone depleting substance (ODS), to clean contaminated oxygen systems. Starting in 2015, the Montreal Protocols and Clean Air Act prohibit the production and importation of all hydrochlorofluorocarbons (HCFC), except for limited use in refrigeration applications. Thus, a new non-ozone depleting solvent needs to be developed for use in cleaning. Optimally, such a solvent should also be environmentally benign or green to avoid needing to replace the new solvent with yet another solvent in the future due to other environmental concerns.

Work for the first year consisted of two parts. The first part was developing a method of testing the cleaning efficiency of potential solvents. Stainless steel coupons were contaminated with a known weight of various contaminants and contaminant combinations and then immersed in solvent for ten minutes. The coupons were then removed and dried in an oven until all solvent had evaporated. Once dry, the coupons were weighed and the mass of the non-volatile residue (NVR) left on the coupon was determined. The cleaning efficiency of the solvents is reported as percent cleaning, with 100% cleaning being zero NVR left on the test coupon. The second half of the first goal was to use the develop method to perform baseline testing on current solvents.

The second part of the work was to begin exploring alternative cleaning solvents. A variety of hydrofluorocarbons (HFCs) were tested. Preliminary testing was also performed with ionic liquids and aqueous surfactant solutions. Once potential solvents were identified, an analysis of the performance and environmental characteristics of each was to be conducted.

Four contaminants were specified for use in testing. These are Mil-Spec-H-5606 (5606), a hydraulic fluid, Mil-H-83282B (83282), another hydraulic fluid, diethylhexyl sebacate (Sebacate), and WD-40. The structures of these contaminants are all similar, with long aliphatic hydrocarbon chains of lengths between fifteen and fifty. Contaminants were tested both individually and in combination. All combinations were done with equal weights of the constituent contaminants.

Summary

Goals

1. Create baseline procedure for testing non-volatile residue testing and perform testing using current and past solvents. Testing is to be performed using a range of contaminants commonly encountered in aviation oxygen systems.

2. Create a list of potential non-ozone depleting solvents replacement solvents. Evaluate the cleaning efficiency and environmental characteristics of each potential solvent.

Year 1 Milestones

- Completed literature review on state of science for precision of oxygen systems and potential alternatives, including aqueous surfactant systems, supercritical fluids, ionic liquids, and fluorinated compounds.
- Completed JTR NVR testing of combinations of contaminants.
- Completed JTR NVR testing of current alternative (HFE 7100) under varying time and temperature conditions.
- Completed JTR NVR testing of a series of fluorinated alternative candidates to evaluate structure-solvent performance relationships.
- Completed flow testing for deionized water and HFE 7100.
- Completed initial testing using surfactant solutions.

The following report details information about the completed experiments and the results obtained. A full literature review is attached in Appendix A. Experimental average cleaning values and standard deviations are attached in Appendix B.

Baseline NVR Testing

To effectively evaluate the effectiveness of new solvents, it was necessary to establish a baseline of solvent effectiveness. Testing was done using HCFC-225, the current solvent, CFC-113, the Class I ODS replaced by HCFC-225, deionized (DI) water, and one potential new solvent HFE 7100, a mixture of methylnonafluorobutyl ether and methylnonafluoroisobutyl ether. The prior solvent, CFC-113 offered the best cleaning performance, but was replaced by HCFC-225 when Class I ODSs were phased out in the 1990's. As such, CFC-113 is included to show the optimal performance for any new solvent. Solvent structures and physical properties are listed in Appendices C and D respectively.

Figure 1 shows the baseline cleaning results.

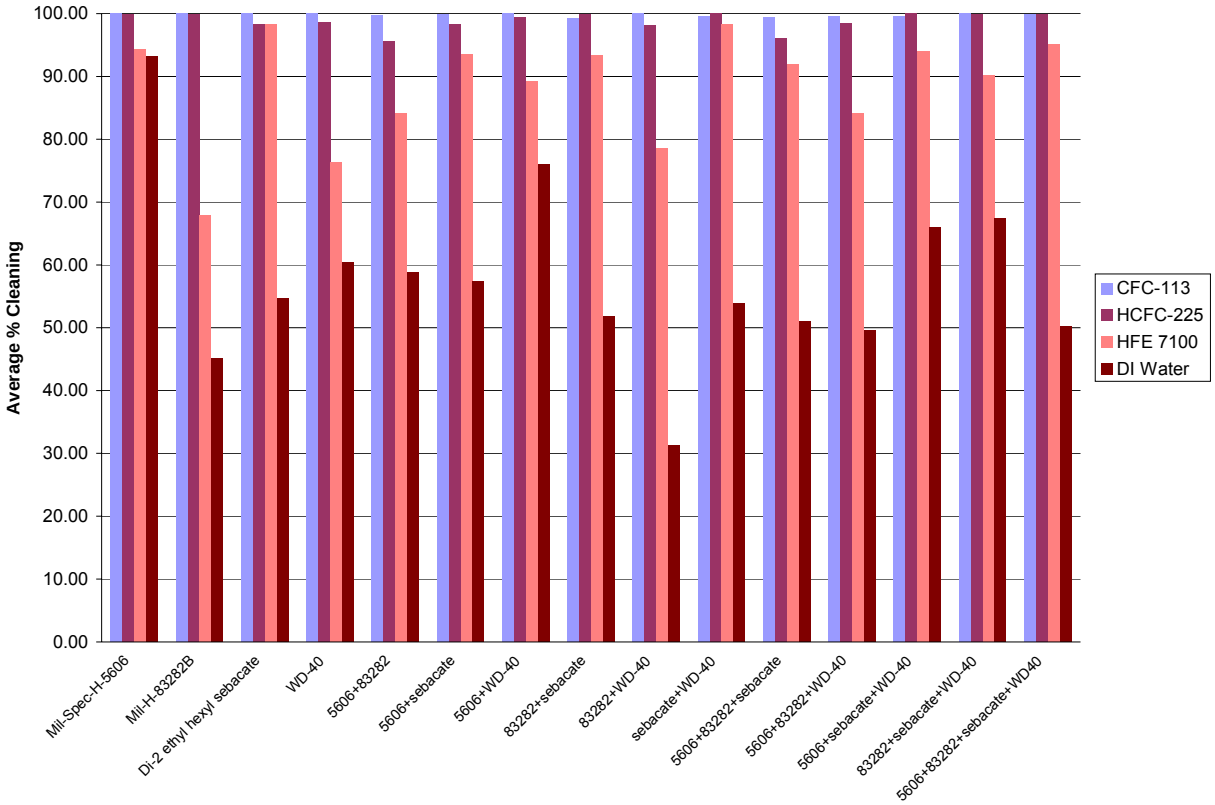

Figure 1: Baseline NVR immersion test results. Testing based on JTR procedure.

As can be seen in Figure 1, CFC-113 and HCFC-225 offer excellent cleaning performance for all tests. The use HFE 7100 results in lesser cleaning performance, but is still above 70% clean for all tests except Mil-H-83282B. DI water is shown to offer the lowest levels of cleaning.

Flow Testing

It may be possible to enhance the performance of solvents through the addition of energy to the system. One of the major obstacles to degreasing surfaces is the adhesion of the various oils to the surface itself, which prevents the transfer of the contaminants to the cleaning solvent. The addition of mechanical energy may help to overcome the adhesive force.

Mechanical energy was added by flowing solvent over the metal coupons. The solvent was applied through a pump, and impacted the surface roughly perpendicularly. The flowrate of the solvent was two liters per minute with the solvent flowing for two minutes. The results of these tests are shown in Figures 2 and 3. The contaminant for both tests was Mil-Spec-H-5606.

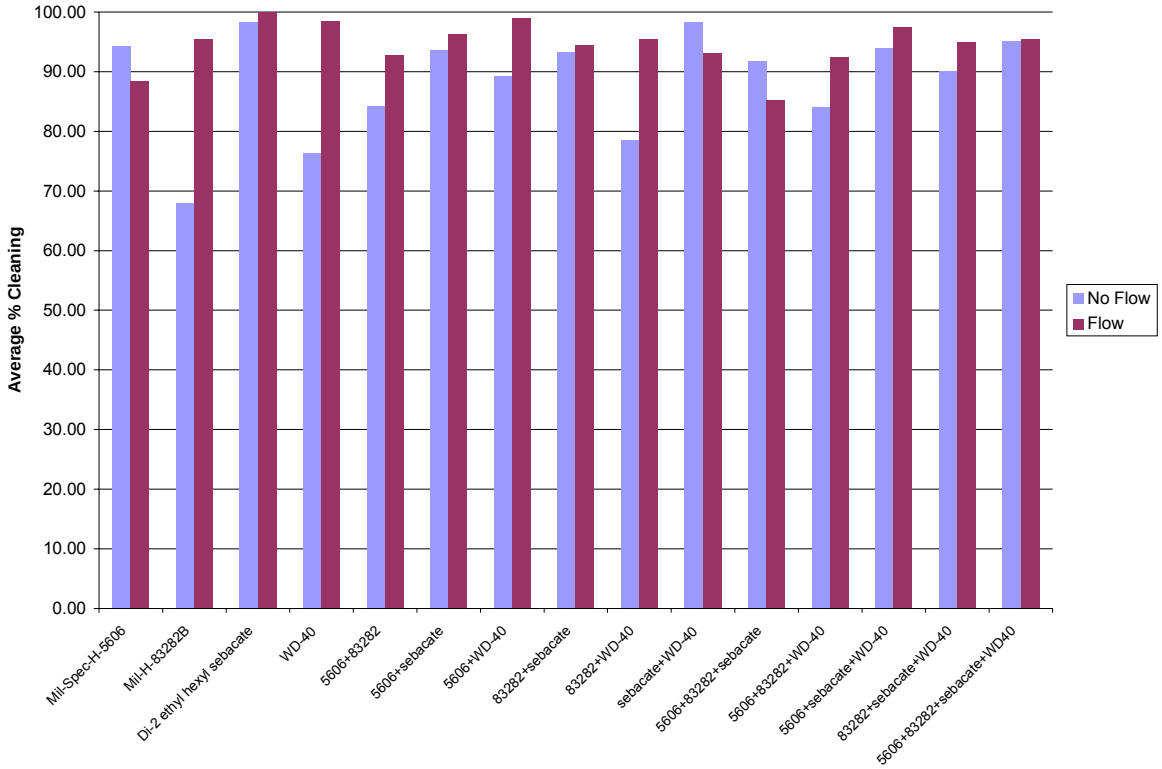

Figure 2: HFE 7100 immersion test results and flow test results. Flowrate was 2 liters/min.

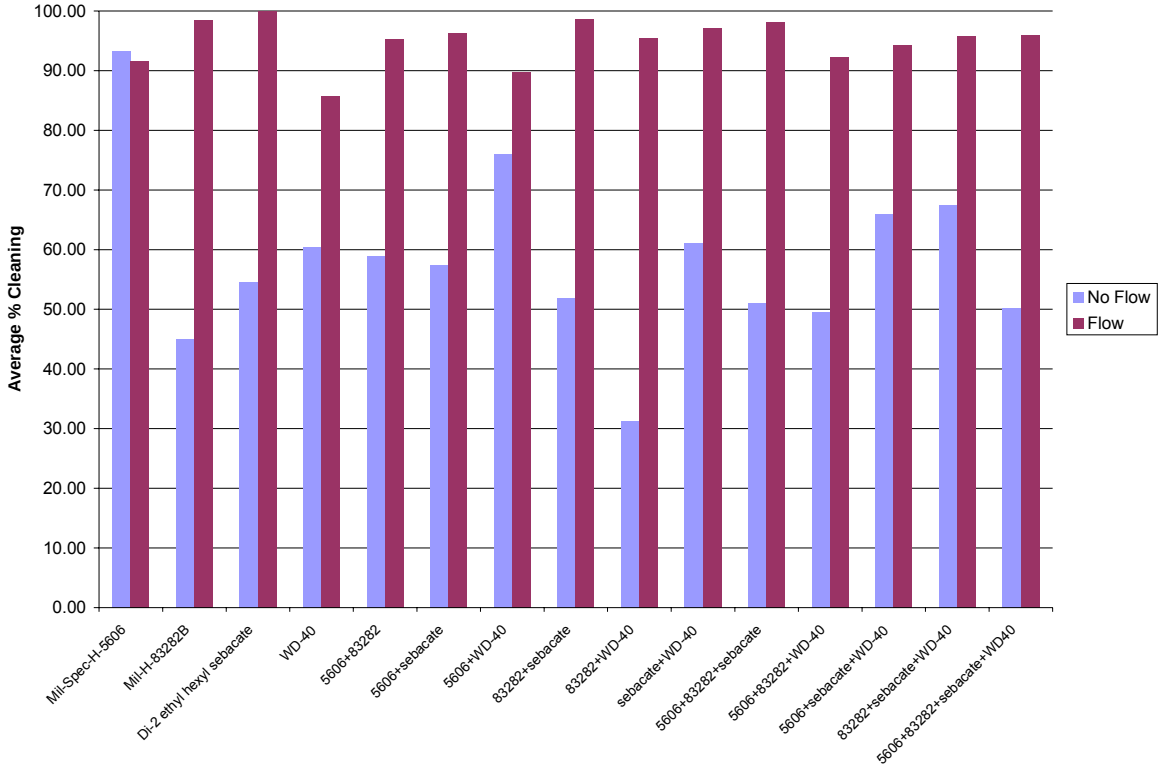

Figure 3: DI water immersion test results and flow test results. Flowrate was 2 liters/min.

As can be seen in Figure 2, the addition of mechanical energy to the system offers comparable or improved cleaning for each contaminant or contaminant combination.

Elevated Temperature Testing

Another potential means of adding energy to the system is elevating the solvent temperature. Changes in temperature are known to affect the solubility behavior of compounds. Figure 4 shows the cleaning efficiency of HFE 7100 with Mil-Spec-H-5606 as a contaminant. Temperatures range from 30°C to 65°C.

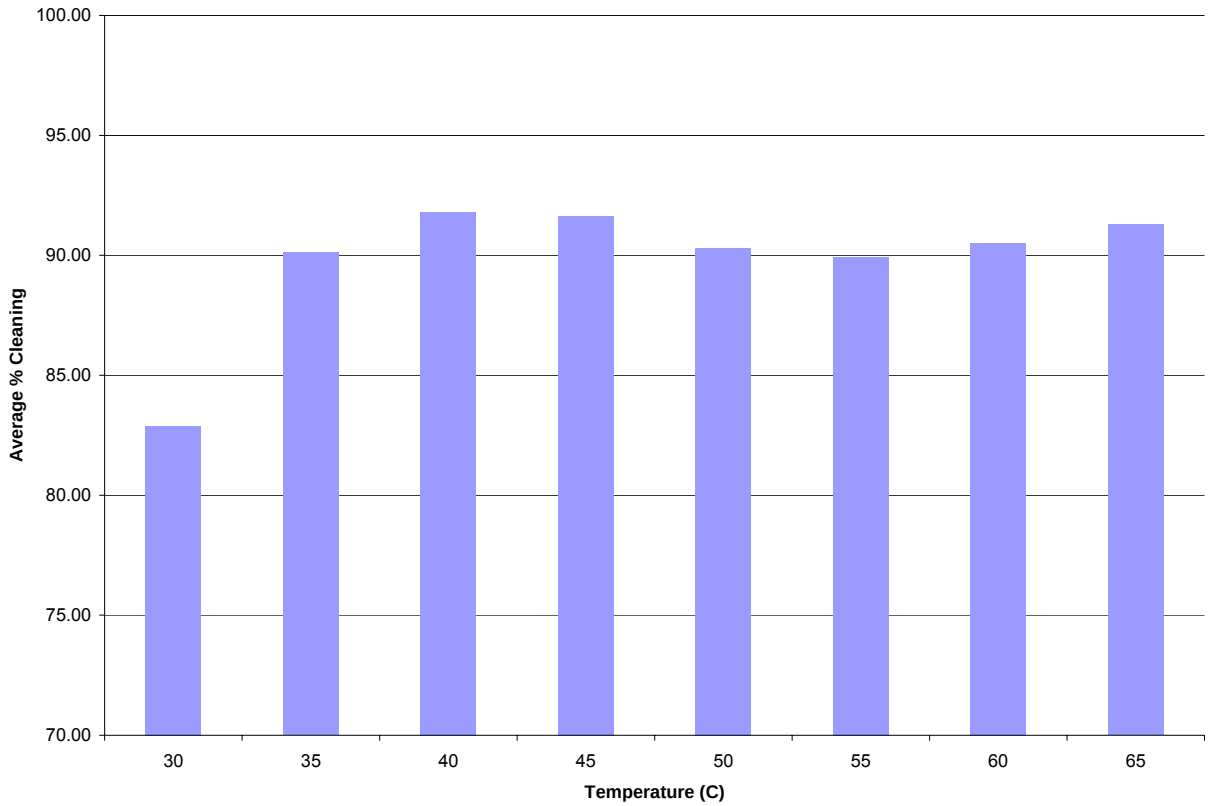

Figure 4: HFE 7100 cleaning performance at elevated temperatures with Mil-Spec-H-5606 as the contaminant.

Cleaning efficiency increases from 30°C to 35°C, but does not increase thereafter. The high energy requirements to heat large quantities of solvent likely preclude the adoption of elevated temperature cleaning procedures.

Hydrofluorocarbons

One class of compounds that has been the focus of considerable attention as a potential replacement for ODSs is hydrofluorocarbons (HFC). These compounds have the same basic structure, an aliphatic carbon chain, as the CFCs and HCFCs that need to be replaced. The similarity in underlying structures means that HFCs have very similar properties as their CFC

and HCFC analogs. There is no chlorine or bromine in these compounds, making HFCs non-ozone depleting.

Preliminary testing was performed using a variety of monofluorinated compounds. The solvents consisted of 1-fluoroheptane, 1-fluorononane, 1-fluorododecane, and 1-fluorotetradecane. Two aromatic fluorinated compounds, 1-fluorobenzene and 4-fluoro-2-methylanisole were also tested. Immersion testing was first performed using pure solvents. Testing was also performed using HFCs diluted with ethanol. Fluorobenzene was diluted to 25 weight percent, while the other HFCs, excluding fluoromethylanisole, were diluted to 33 weight percent. Ethanol was also tested to provide a baseline for the diluted solvent testing. All tests were performed using Mil-Spec-H-5606 as the contaminant. The results of this testing are shown in Figure 5.

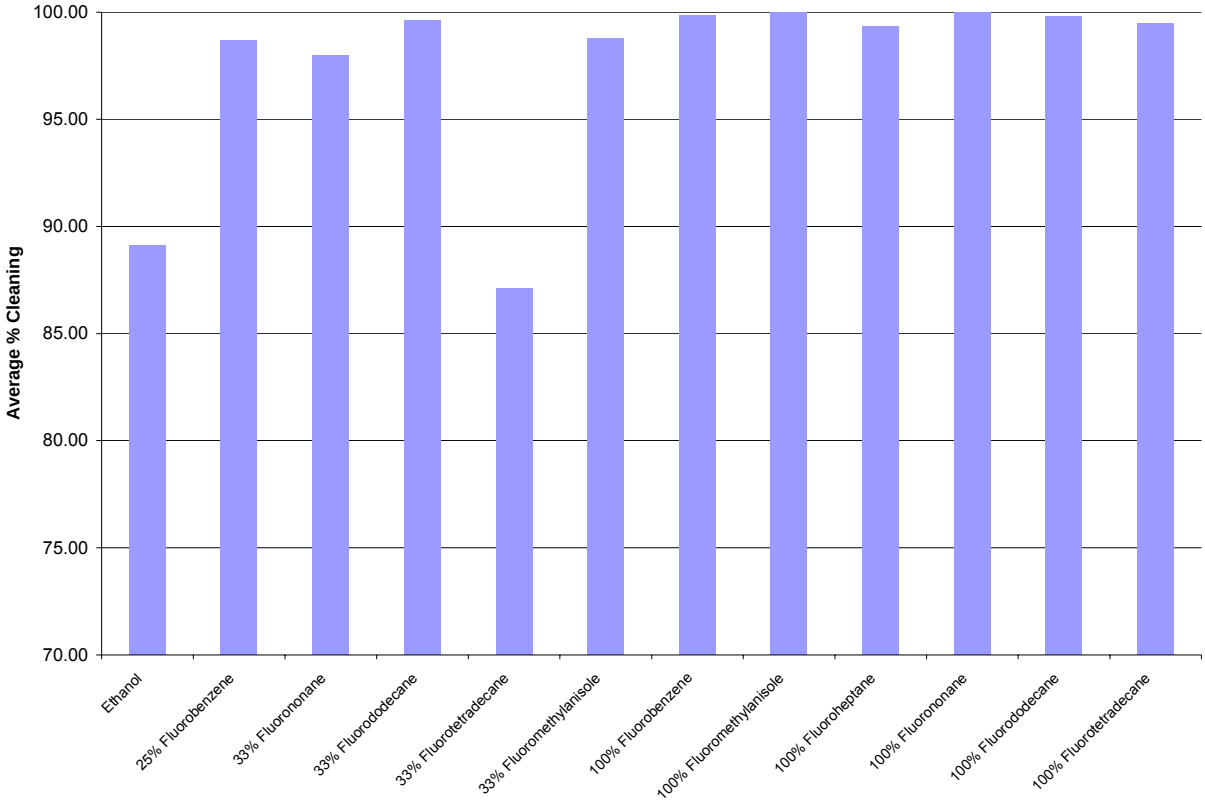

Figure 5: Preliminary HFC NVR test results using Mil-Spec-H-5606.

All of the neat solvents performed well, resulting in high levels of cleaning. All of the diluted solvents, with the exception of diluted 1-fluorotetradecane, also performed well. The diluted 1-fluorotetradecane offers cleaning similar to that of neat ethanol. This is due to the phase separation that occurs between ethanol and 1-fluorotetradecane at these concentrations.

Further testing was performed using neat 1-fluoroheptane as a solvent. Testing was done using all four of the specified contaminants, as well as mixtures of these contaminants. The results of this work are shown in Figure 6. Due to the limited amount of fluoroheptane available, testing

was not performed for the 5606/Sebacate/WD-40, 5606/83282/Sebacate, and 5606/83282/Sebacate/WD-40 combinations.

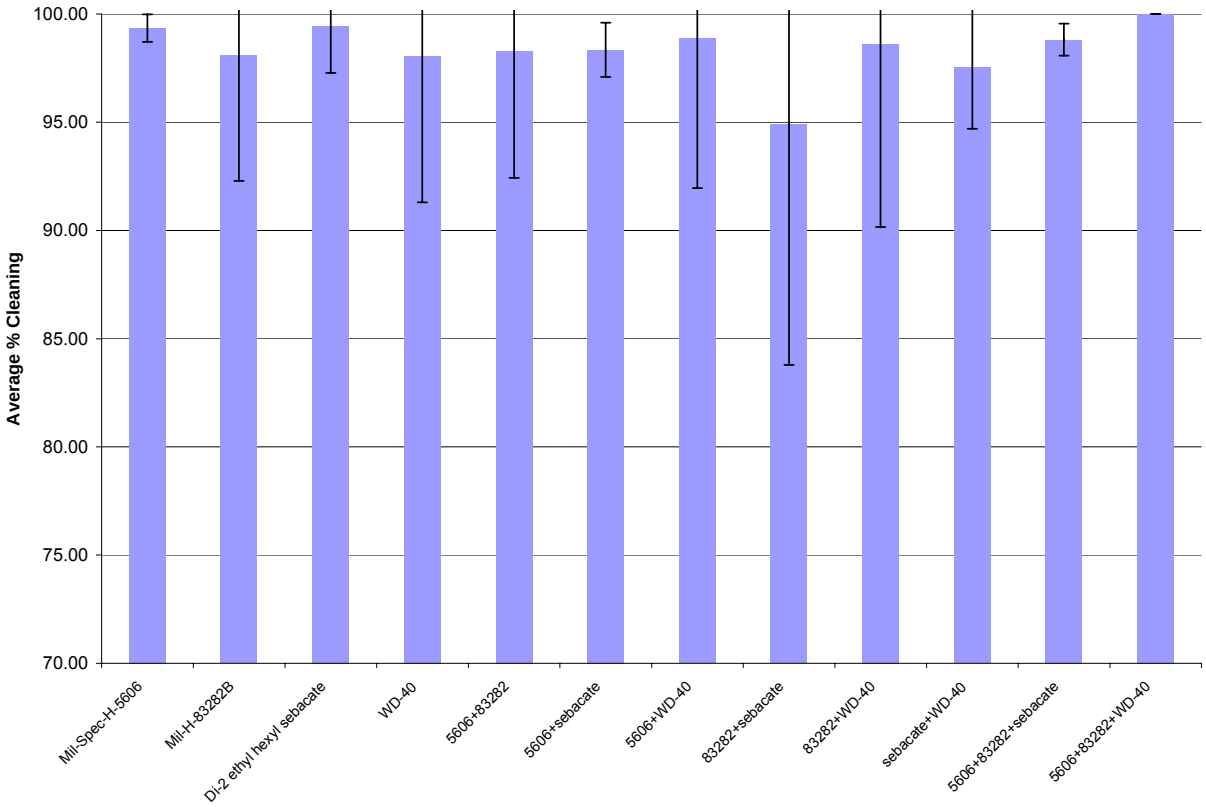

Figure 6: Cleaning efficiency of 1-fluoroheptane with both single contaminants and contaminants mixtures. Error bars show the 95% CI.

All contaminants and contaminant combinations are cleaned effectively by 1-fluoroheptane. The minimum cleaning performance is greater than 94%, with most contaminants being cleaned at greater than 97% efficiency.

The use of HFCs to clean oxygen systems will likely be severely limited by the flammable nature of these compounds. One way to decrease the flammability of these compounds is by increasing the degree of fluorination [1]. Perfluorinated compounds (PFC), that is fully fluorinated compounds, are known to be largely non-flammable. The adoption of such PFCs for cleaning purposes is hindered by the serious environmental limitations these compounds bring with them.

Although very few studies have focused on the environmental persistence of HFCs, increasing fluorination generally leads to increased resistance to degradation [2]. It has been shown that terminal hydrogen carbon bonds are required for efficient degradation, as these bonds offer sites for the molecule to be attacked [3]. Furthermore, it appears that increasing the carbon chain lengths leads to increased environmental persistence [3] as well as increased bioaccumulation [4].

Flammability testing has been performed on many polyfluorinated compounds [5,6]. Results indicate that saturated HFCs with fluorine occupying greater than 62.5% of the potential hydrogen sites are generally non-flammable [6].

The selection of HFCs to test is also limited by the physical properties of the compounds. If the chain length is too short, the solvent will be a vapor at one atmosphere and room temperature. A vapor would not be suitable for cleaning purposes. A review of physical property data suggests that HFCs with chain lengths of four or less will thus be unsuitable for use in cleaning [7].

Chain lengths of five to seven carbons offer a balance between the bioaccumulation and persistence concerns and any phase limitations. In order to be non-flammable, pentane will need to have at least eight fluorine atoms (octafluoropetane), hexane will need to have at least nine fluorine atoms (nonafluorohexane), and heptane will need to have at least ten fluorine atoms (decafluoroheptane). By using HFCs that have the fewest fluorine atoms needed to be non-flammable, the environmental persistence issue should be mitigated as much as possible.

Aqueous Surfactants

Aqueous solutions are attractive for green cleaning purposes, as water is an inherently benign solvent. Surfactants are molecules composed of a hydrophobic tail and hydrophilic head group. As a result, in water, surfactants self assemble into units called micelles. The interior of a micelle is composed of the hydrophobic tails, while the hydrophilic head groups are in contact with the surrounding water. Compounds, such as oils, that are not generally soluble in water, can be solubulized as their presence in the interior of micelles is thermodynamically favorable. Aqueous surfactant solutions have long been using for cleaning and degreasing applications in industry [8,9]. Surfactants offer a number of potential solutions to this engineering problem. There are a number of types of surfactants, such as anionic, cationic, and non-ionic surfactants. The behavior of surfactants in solution can be modified by changing the properties of the system, like temperature, surfactant concentration, pH, and ionic strengths [8,9].

Initial immersion testing was done using two common surfactants, sodium dodecylsulfate (SDS) and cetyl trimethylammonium bromide (CTAB). SDS is an anionic surfactant and CTAB is a cationic surfactant. Testing with SDS was done with 0.01M and 0.1M solutions. Testing with CTAB was done with a 0.01M solution. Immersion testing was performed for each individual contaminant as well as a combination of all four contaminants. The results, along with the baseline results for DI water, are shown in Figure 7.

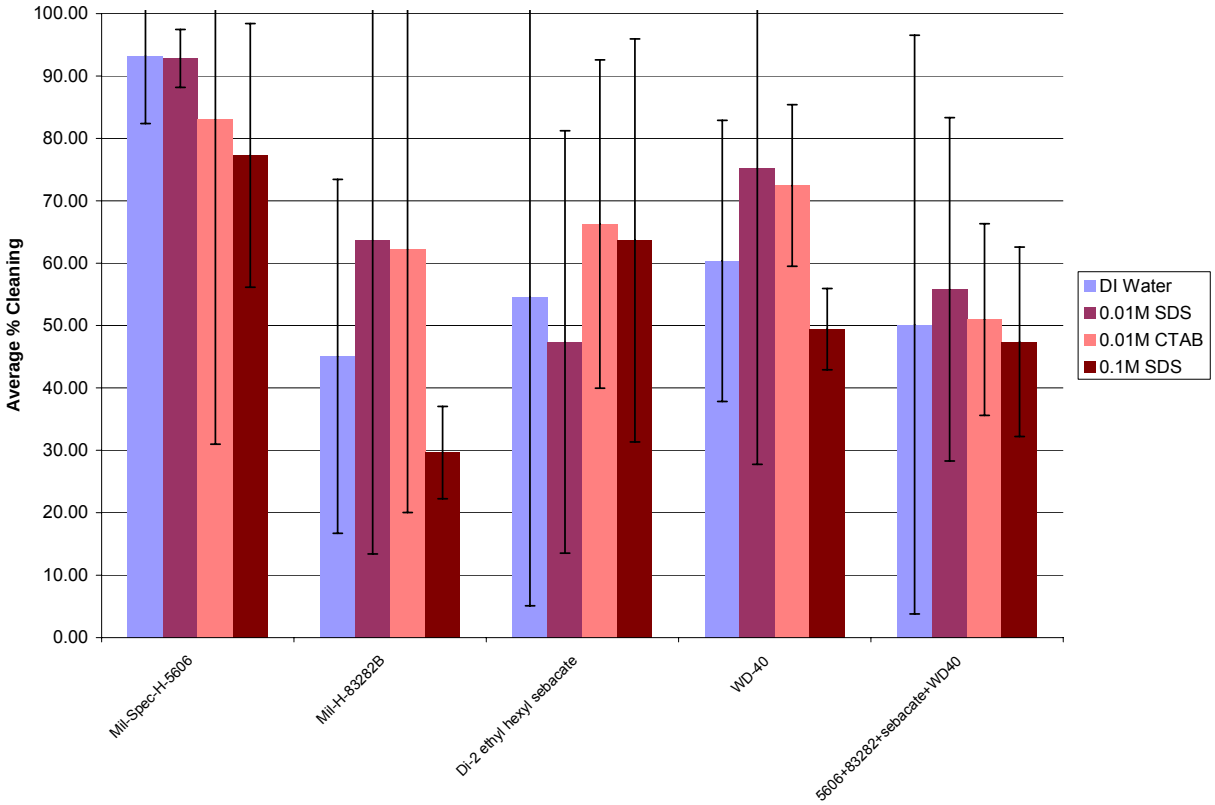

Figure 7: Surfactant cleaning results. Error bars show the 95% CI.

This testing did not yield promising results. For most of the surfactant concentrations and contaminants, the average percent cleaning was comparable to that of DI water. The limiting factor here may be that while surfactants are proven to be able to solubilize oils into aqueous phases, the solution is doing nothing to overcome the adhesion between the contaminants and metal coupons. The addition of mechanical energy via flow may help to overcome the adhesive force.

Surfactants do come with a few potential limitations. By introducing new non-volatile materials into the system, there is a chance of depositing a new contaminant into the system. Flowing surfactant solutions can promote foaming, which can increase the amount of residue left behind. The addition of a second rinse to the cleaning procedure may serve to remove any additional surfactant residue, although no testing has been done, at this time, to quantify either the amount of likely surfactant residue or the efficacy of additional rinsing in removing surfactant residue.

Room Temperature Ionic Liquids

Another class of solvents that has been of interest to the green engineering/chemistry movement over the last two decades is room temperature ionic liquids (RTIL). These are organic salts which are molten at temperatures less than 100C. They are attractive as solvents for a number of reasons, including their almost complete non-volatility and thermal stability over wide

temperature ranges. RTILs are also largely non-flammable. These properties make them candidates to replace the volatile organic compounds (VOCs) that are so prevalent in industry.

Estimates put the number of accessible RTILs, based on current cation and anion pieces, at greater than 10^{14} [10]. The properties of RTILs can be greatly changed by varying the ion pieces, as well as the tail lengths of the structures attached to the RTIL [11]. Due to the ability to change the properties of RTILs, as well as the large number of RTILs available, it should be possible to tailor RTIL properties for optimum performance in specific applications [11].

Initial testing was done using 2-ethylhexyl lactate (2EHL) as the solvent. This solvent has been used in industrial degreasing applications and is non-volatile as well as non ozone depleting. Testing was performed using all four contaminants and mixtures thereof. The results from this testing are shown in Figure 8.

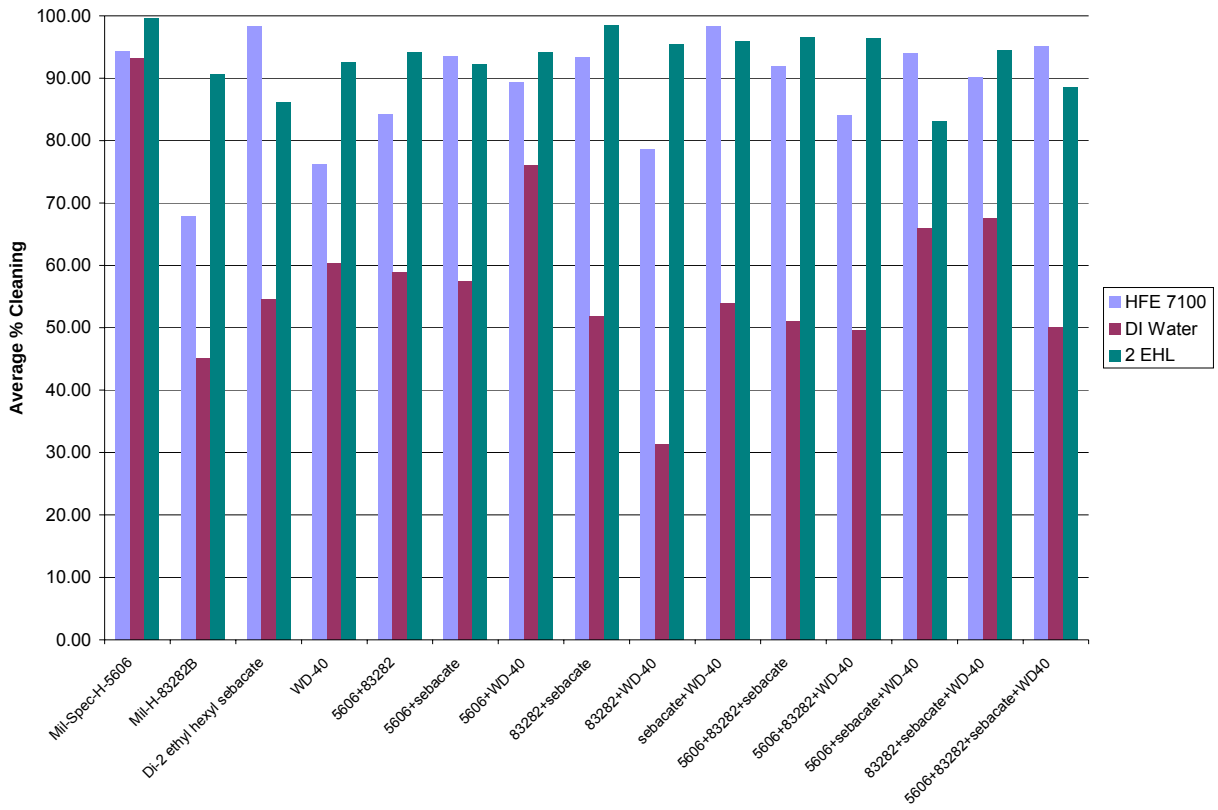

Figure 8: Cleaning efficiency using 2EHL as the solvent.

The use of 2EHL results in superior cleaning efficiency than DI water and is comparable to HFE 7100. This solvent offers inferior performance when compared to the HCFC-225 which is currently being used, as well as the original solvent CFC-113.

RTILs bring a number of engineering challenges with them. Most RTILs have high viscosities, ranging from ten to one thousand times that of water [10]. High viscosities coupled with low volatilities could result in substantial solvent residue after the use of RTILs for cleaning purposes.

As many RTILs are hydrophilic, it may be possible to either follow the initial RTIL cleaning with a rinse using another solvent, or to add water to the RTIL to decrease viscosity [12]. It may also be possible to emulsify hydrophobic RTILs [13].

Due to the large number of RTILs, no comprehensive study has been performed on the environmental fate and toxicity of these compounds. Some work has been done on the more common RTILs, such as those based on imidazolium and pyridinium cations. These cations are ring structures. Literature shows that toxicity of these compounds can range from an EC-50 of 1 ppm for 1-octyl-3-methyl imidazolium bromide to 2248 ppm for 1-butyl-3-methyl imidazolium bromide [14]. Generally, increasing both the alkyl chain lengths and number of alkyl chains on these ring structures seem to increase the toxicity of the RTILs [14].

While the almost non-existent vapor pressure of RTILs prevents air pollution from being a concern, there are concerns about the role RTILs may play in water pollution. Many RTILs are hydrophilic and work has been done that shows that RTILs like 1-butyl-3-methyl imidazolium chloride are not retained by adsorption into soil systems [15].

Conclusions

Testing procedures have been established to compare potential new solvents. Baseline testing was performed using CFC-113, HCFC-225, HFE 7100 and deionized water. The effect of flow on the cleaning efficiency of water and HFE 7100 as well as the effect of temperature on the cleaning efficiency of HFE 7100 has been examined. The addition of mechanical energy via flow appears to have the potential to enhance solvent performance while elevated temperature does not. This work fulfilled the requirements listed in the first half of the Statement of Work.

As required by the second half of the Statement of Work, a list of potential green solvents was compiled. These solvents were then tested for cleaning efficiency with a variety of contaminants commonly found in oxygen systems. A literature search was performed for the environmental properties of the new green solvents and the results were summarized.

Hydrofluorocarbons were tested as one potential alternative solvent. The use of a variety of HFCs with the contaminant Mil-Spec-H-5606 resulted in high levels of cleaning. All contaminants and most contaminant combinations were tested with 1-fluoroheptane with no test resulting in a cleaning performance lower than 94%. If concerns about solvent flammability and suitability for use in an oxygen environment can be resolved, HFCs appear to offer a promising path to explore for non-ozone depleting solvent alternatives.

Aqueous surfactant solutions using sodium dodecylsulfate and cetyl trimethylammonium bromide were examined. Neither surfactant resulted in high levels of cleaning. This may be due to the adhesive forces between contaminants and the test coupons. If surfactants were to be used as a cleaning solution, concerns about surfactant residue would need to be investigated, and, if necessary, mitigated.

One room temperature ionic liquid, 2-ethylhexyl lactate, was tested as a solvent. While this compound did offer superior performance to HFE 7100 in certain cases, its overall performance

was still substantially less than the ozone depleting solvents that need to be replaced. The use of ionic liquids as a solvent also raises residue concerns, but these may be able to be addressed via careful selection of the RTIL or through mixing the RTIL with other green solvents.

Future Work

- Continue work with HFCs of chain lengths between five and seven. Determine degree of fluorination necessary for non-flammability.
- Investigate flow as a means of overcoming adhesion for solvents exhibiting cleaning efficiencies less than 100%.
- Continue testing RTILs. Investigate RTIL/water mixtures and emulsions as a means of overcoming RTIL limitations.
- Perform oxygen compatibility testing on promising solvent alternatives.
- Perform analysis of environmental properties on promising solvent alternatives.

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APPENDIX A - Literature Review

Currently, NASA uses Dichloropentafluoropropane (HCFC-225), a Class II ozone depleting substance (ODS), to clean contaminated oxygen systems. Starting in 2015, the Montreal Protocols and Clean Air Act prohibit the production and importation of all hydrochlorofluorocarbons (HCFC), except for limited use in refrigeration applications. Thus, a new non-ozone depleting solvent needs to be developed for use in cleaning. Optimally, such a solvent should also be environmentally benign or green to avoid needing to replace the new solvent with yet another solvent in the future due to other environmental concerns.

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Room Temperature Ionic Liquids

Another class of solvents that has been of interest to the green engineering/chemistry movement over the last two decades is room temperature ionic liquids (RTIL). These are organic salts which are molten at temperatures less than 100C. They are attractive as solvents for a number of reasons, including their almost complete non-volatility and thermal stability over wide temperature ranges. RTILs are also largely non-flammable. These properties make them candidates to replace the volatile organic compounds (VOCs) that are so prevalent in industry.

Estimates put the number of accessible RTILs, based on current cation and anion pieces, at greater than 10^{14} [10]. The properties of RTILs can be greatly changed by varying the ion pieces, as well as the tail lengths of the structures attached to the RTIL [11]. Due to the ability to change the properties of RTILs, as well as the large number of RTILs available, it should be possible to tailor RTIL properties for optimum performance in specific applications [11].

RTILs bring a number of engineering challenges with them. Most RTILs have high viscosities, ranging from ten to one thousand times that of water [10]. High viscosities coupled with low volatilities could result in substantial solvent residue after the use of RTILs for cleaning purposes. As many RTILs are hydrophilic, it may be possible to either follow the initial RTIL cleaning with a rinse using another solvent, or to add water to the RTIL to decrease viscosity [12]. It may also be possible to emulsify hydrophobic RTILs [13].

Due to the large number of RTILs, no comprehensive study has been performed on the environmental fate and toxicity of these compounds. Some work has been done on the more

common RTILs, such as those based on imidazolium and pyridinium cations. These cations are ring structures. Literature shows that toxicity of these compounds can range from an EC-50 of 1 ppm for 1-octyl-3-methyl imidazolium bromide to 2248 ppm for 1-butyl-3-methyl imidazolium bromide [14]. Generally, increasing both the alkyl chain lengths and number of alkyl chains on these ring structures seem to increase the toxicity of the RTILs [14].

While the almost non-existent vapor pressure of RTILs prevents air pollution from being a concern, there are concerns about the role RTILs may play in water pollution. Many RTILs are hydrophilic and work has been done that shows that RTILs like 1-butyl-3-methyl imidazolium chloride are not retained by adsorption into soil systems [15].

Supercritical Fluids

Supercritical fluids (SCF) are currently being used in a variety of applications in industry. Currently, the most common SCF is carbon dioxide. Carbon dioxide's critical point is 31°C and 73 atmospheres, which are relatively easy conditions to reach. Supercritical carbon dioxide (SCCO2) has been used for degreasing purposes in the leather industry [16]. SCCO2 has also been shown to be effective in oils from metal substrates [17]. Studies on the efficiency of contaminant removal using SCCO2 show that increasing pressure or temperature leads to improved cleaning performance [17].

Performance Indicators

Several indicators exist as to how well a solution will perform beyond simple non-volatile residue testing. Such tests include determining changes in contact angle, determining the release time for a single drop of contaminant, and observing other physical alterations to the system [18,19,]. Of particular interest is the determination of changes in contact angle. A variety of influences affect the solution's ability to increase and decrease the contact angle of a contaminant droplet [8,18,19].

One factor affecting the contact angle of a droplet is the pH of the solution. It was found that each type of surfactant (anionic, cationic, etc) responded differently to changes in pH [8]. This research shows that certain solutions work best in acidic environments while others have increased efficacy in basic environments. It is interesting to note that despite changes in pH producing dramatic results in increasing the efficacy of a solution, of the solutions tested, none of them were able to achieve more than 50% total removal of the non volatile residue present [18].

The efficacy of the solution can also be altered by changing the electrostatic charge of the substrate. Each type of surfactant reacts differently, resulting in increased efficacy depending on the nature of the potential (negative, positive, none) [19]. For the proper potential applied to the system, the contact angle increases, the time for the first droplet to be released decreases and there is a greater amount of the contaminant removed.

The changes that occur within the system that result in higher efficacy have a means of being observed prior to determining the actual efficacy. Literature has shown that the observation of

the release of the first droplet of contaminant is a quality indicator of the overall efficacy of the cleaning system [18,19]. These studies have shown that the faster the drop is released, the greater the efficacy of the system.

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APPENDIX B - Experimental Data

Baseline NVR Immersion Testing and 2EHL

	CFC-113		HCFC-225		HFE 7100		DI Water		2ehl	
Contaminant	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ
Mil-Spec-H-5606	100.00	0.00	99.84	0.25	94.27	4.84	93.24	3.92	99.58	0.04
Mil-H-83282B	100.00	0.00	99.84	0.33	67.93	12.11	45.06	10.21	90.61	3.17
Di-2 ethyl hexyl sebacate	100.00	0.00	98.24	1.90	98.33	3.33	54.60	17.83	86.12	1.10
WD-40	100.00	0.00	98.67	1.41	76.28	2.81	60.37	8.12	92.55	2.49
5606+83282	99.68	0.33	95.62	7.38	84.17	7.12	58.89	4.82	94.24	1.00
5606+sebacate	99.91	0.09	98.31	3.39	93.57	5.13	57.46	8.30	92.17	1.01
5606+WD-40	100.00	0.00	99.36	0.95	89.28	7.10	76.02	3.21	94.24	0.10
83282+sebacate	99.18	0.82	99.92	0.17	93.27	7.05	51.79	17.61	98.53	0.69
83282+WD-40	100.00	0.00	98.10	2.91	78.52	14.53	31.30	12.24	95.41	1.22
sebacate+WD-40	99.47	0.19	100.00	0.00	98.33	2.09	53.87	12.14	95.96	2.31
5606+83282+sebacate	99.37	0.27	96.00	5.15	91.85	8.18	50.95	7.93	96.47	0.48
5606+83282+WD-40	99.54	0.19	98.41	2.00	84.09	9.73	49.54	8.44	96.41	0.31
5606+sebacate+WD-40	99.58	0.17	99.95	0.09	94.02	5.13	66.00	20.40	83.05	0.00
83282+sebacate+WD-40	100.00	0.00	99.93	0.14	90.18	9.55	67.45	24.77	94.55	0.48
5606+83282+sebacate+WD40	99.82	0.18	99.93	0.14	95.12	7.31	50.16	16.70	88.59	0.14

NVR Flow Testing

	HFE 7100		DI Water	
Contaminant	μ	σ	μ	σ
Mil-Spec-H-5606	88.41	10.39	91.53	0.00
Mil-H-83282B	95.49	2.49	98.46	1.08
Di-2 ethylhexyl sebacate	100.00	0.00	100.00	0.00
WD-40	98.50	0.63	85.67	3.34
5606+83282	92.76	1.85	95.25	0.71
5606+sebacate	96.31	0.76	96.33	0.90
5606+WD-40	98.94	0.30	89.69	3.64
83282+sebacate	94.45	1.70	98.52	0.85
83282+WD-40	95.43	0.22	95.51	1.50
sebacate+WD-40	93.08	0.71	97.17	0.89
5606+83282+sebacate	85.19	4.20	98.14	0.49
5606+83282+WD-40	92.46	0.04	92.30	0.37
5606+sebacate+WD-40	97.50	0.44	94.22	0.00
83282+sebacate+WD-40	94.92	0.85	95.85	0.24
5606+83282+sebacate+WD40	95.43	0.54	95.93	0.47

NVR Immersion Testing at Elevated Temperature Using Mil-Spec-H-5606

	HFE 7100			
Temperature (°C)	1	2	μ	σ
30	80.00	85.77	82.88	2.88
35	90.12	-	90.12	-
40	89.98	93.65	91.81	1.84
45	91.64	-	91.64	-
50	90.30	-	90.30	-
55	89.92	-	89.92	-
60	90.52	-	90.52	-
65	91.28	-	91.28	-

Preliminary HFC NVR Immersion Testing Using Mil-Spec-H-5606

Solvent Solution	μ	σ
Ethanol	89.10	3.94
25% Fluorobenzene	98.68	0.22
33% Fluorononane	98.00	1.37
33% Fluorododecane	99.64	0.06
33% Fluorotetradecane	87.08	3.86
33% Fluoromethylanisole	98.79	0.42
100% Fluorobenzene	99.83	0.17
100% Fluoromethylanisole	100.00	0.00
100% Fluoroheptane	99.34	0.05
100% Fluorononane	100.00	0.00
100% Fluorododecane	99.79	0.21
100% Fluorotetradecane	99.48	0.52

1-fluoroheptane NVR Immersion Testing

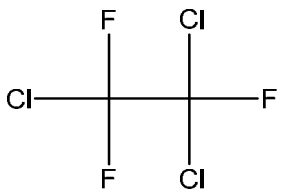
	1-fluoroheptane	
Contaminant	μ	σ
Mil-Spec-H-5606	99.34	0.05
Mil-H-83282B	98.09	1.35
Di-2 ethyl hexyl sebacate	99.45	0.50
WD-40	98.05	1.57
5606+83282	98.29	1.36
5606+sebacate	98.35	0.29
5606+WD-40	98.86	1.61
83282+sebacate	94.90	2.58
83282+WD-40	98.61	1.96
sebacate+WD-40	97.53	0.66
5606+83282+sebacate	98.81	0.17
5606+83282+WD-40	100.00	0.00

Surfactant NVR Immersion Testing

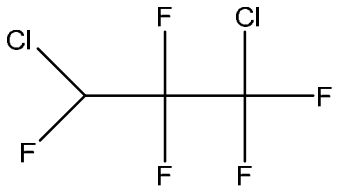
	0.01M SDS		0.01M CTAB		0.1M SDS	
Contaminant	μ	σ	μ	σ	μ	σ
Mil-Spec-H-5606	92.82	0.36	83.05	4.10	77.26	4.91
Mil-H-83282B	63.61	11.67	62.22	9.80	29.65	1.72
Di-2 ethyl hexyl sebacate	47.37	7.86	66.28	6.12	63.65	7.51
WD-40	75.16	3.73	72.45	1.02	49.44	1.51
5606+83282+sebacate+WD40	55.81	10.70	50.97	4.82	47.38	3.53

APPENDIX C - Solvent Structures

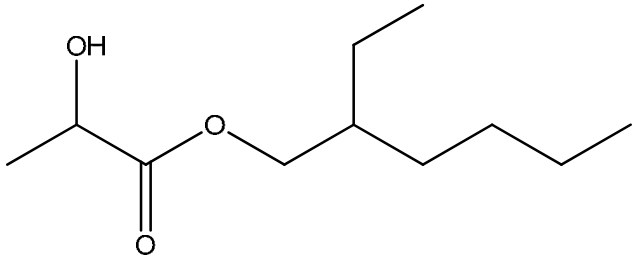
CFC-113



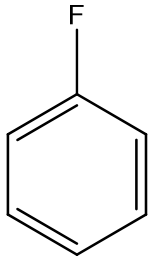
HCFC-225cb



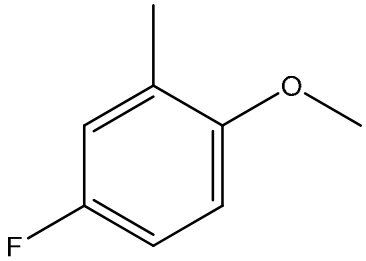
2-ethylhexyl lactate



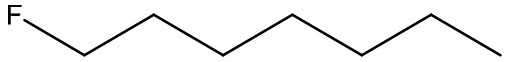
1-fluorobenzene



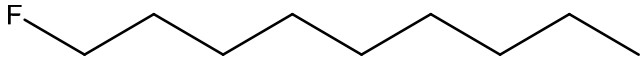
4-fluoro-2-methylanisole



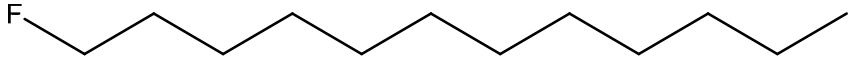
1-fluoroheptane



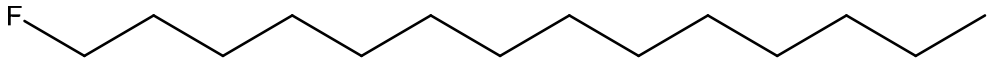
1-fluorononane



1-fluorododecane

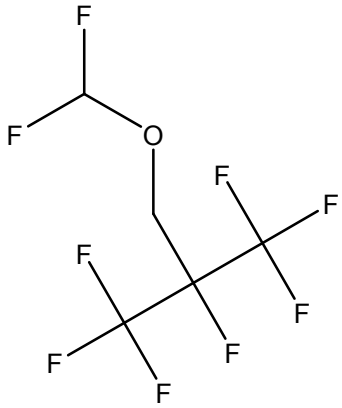


1-fluorotetradecane

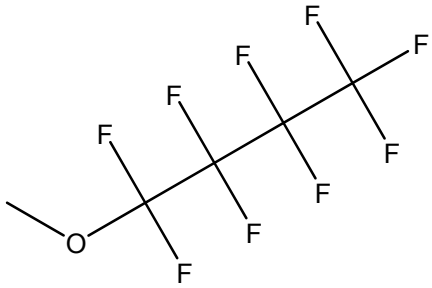


HFE 7100

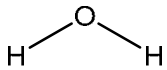
methylnonafluoroisobutyl ether



methylnonafluorobutyl ether



Water



APPENDIX D - Solvent Physical Property Data

Solvent	CAS No.	MW AMU	Boiling Point °C	Viscosity mPa-s	Density g/cm^3	Vapor Pressure mm Hg
CFC-113	76-13-1	187.4	48	0.68 (20°C)	1.564 (25°C)	285 (20°C)
2 ethylhexyl lactate	186817-80-1	202.3	246	7.7 (25°C)	0.939 (20°C)	0.015 (20°C)
1-fluorobenzene	462-06-6	96.1	84-85	-	1.025 (20°C)	60 (19.6°C)
1-fluorododecane	334-68-9	188.3	225-227	-	0.811 (25°C)	0.14 (25°C)
1-fluoroheptane	661-11-0	118.2	119.2	-	0.790 (25°C)	20.4 (25°C)
1-fluorononane	463-18-3	146.3	166-169	-	0.801 (25°C)	2.5 (25°C)
1-fluorotetradecane	593-33-9	216.4	259	-	0.816 (25°C)	0.02 (25°C)
4-fluoro-2-methylanisole	399-54-2	140.2	178	-	1.046 (25°C)	1.4 (25°C)
HCFC-225	507-55-1	202.9	56.1	0.59 (25°C)	1.578 (25°C)	263 (25°C)
HFE 7100	163702-08-7 163702-07-6	250	61	0.6 (23°C)	1.5 (25°C)	202 (25°C)
Water	7732-18-5	18	100	1 (20°C)	0.997 (25°C)	23.8 (25°C)

APPENDIX E - Oxygen Cleaning White Paper (2006)

Overview: During the mid 1990's, efforts were initiated to find replacement technologies for Class I ODC cleaning solvents routinely used for oxygen systems and component cleaning. CFC-113 (Freon) was the industry standard for oxygen cleaning and is no longer produced. 1,1,1, Trichloroethane was another. The immediate and best replacement for Freon was HCFC-141b, a Class II ODC. The manufacturer of HCFC-141b phased the product out of production in December 2003. Field testing and demonstrations qualified the next successful and available product for oxygen cleaning; which was AK-225g (*1,3-dichloro-1,1,2,2,3-pentafluoropropane, CF2Cl-CF2-CHFCl)*, however, this was also a Class II ODC which begin being phased out in Europe by 2008 and the U.S. by 2015. We have entered into a follow on technology gap from previous replacement programs. An environmentally acceptable product has yet to be developed. Exemptions may be necessary is no suitable products are developed by the future phase out dates.

Status of Technology: The NASA AP2 office contacted the agencies listed below associated with known oxygen cleaning and product development to investigate any potential technology breakthroughs for an oxygen cleaning solvent.

- U.S. Air Force is continuing to look at Ikon P (*1-iodononafluorobutane, CF2I-CF2-CF2-CF3),* now know as PFBI, as a possible next qualifying oxygen cleaning solvent. NASA experts question pursuing the product development. The product passes all tested cleaning requirements, but issues still exist for possible implementation:

- *Failed some LOX impact tests (but burn resistant)*
- *Must Examine environmental, toxicity and oxygen compatibility issues, Toxicity evaluations expected to be complete Jan 2007*
- *Also, a concern with shelf life as the product tends to degrade during extended storage*

The Air Force Research Laboratory also initiated a SBIR study for replacing CFC-113 for oxygen cleaning. The contract was awarded to Mainstream Engineering Corp. in Rockledge, FL. The effort concluded in 2005 and resulted in the recommendation of a 25%/75% mixture product with a commercial name of QwikClean ®, (*Mixture of 25% 4-bromo-3-chloro-3,4,4-trifluoro-1-butene and 75% 1-chloro-2,2,2-trifluoroethyl difluoromethyl ether)*. The company has filed a patent application as well. The final report claims the product cleans as well as CFC-113 and AK-225g. Some toxicology testing has been done, but full toxicology testing for government requirements has not been completed on the product and funding is being sought to conclude the testing.

The following excerpt was provided by Mr. Dennis Schroll, a recognized Air Force authority in oxygen cleaning, and member of the NATO STANAG (Standardization Action Group), and the Oxygen Standardization Coordination Group (OSCG). Note, this excerpt also mentions the status of the JGPP Oxygen Line Cleaning System Program:

e. THE MONTREAL PROTOCOL

From the USA position paper, the Panel noted the following:

Montreal Protocol. The USAF continues to evaluate Iodoperfluoro-carbons (PFBI) as an oxygen compatible cleaning solvent. The Air Force Research Labs (AFRL) at Wright-Patterson AFB was funded to conduct a toxicological study of PFBI this year. The study is scheduled to be completed in September 2006. One concern is that this product is not in production so the amount of time needed to field this product is a concern.

The Air Force is seeking a replacement for HCFC-225g (AK-225G) to use in Europe as 225g is set to be phased out of use in Europe in December of 2008 under EU regulations. In the United States 225g is scheduled to be phased out under the Clean Air Act in 2015 although under the Montreal Protocol it could continue to be used through 2030. Various groups within the US Air Force and Navy are considering petitioning the EPA asking for an extension to use 225g through 2030 as agreed to under the gradual phase-out under the Montreal Protocol. The EPA may be receptive to the idea as there aren't many viable replacements for 225g to use for precision cleaning in the aerospace industry.

The Oxygen Line Cleaning Technology which was presented at the 1st GGSP meeting in San Antonio, Texas began its demonstration and evaluation phase in early 2006. The technology is being evaluated at Luke AFB in Arizona. The system, which uses HFE-7100, will be used to clean the oxygen lines and LOX converters on all the aircraft stationed at Luke AFB. All the servicing carts, gaseous and liquid, will be cleaned as well. The types of contaminants found will be classified and evaluated. At the end of a three month period the equipment and aircraft will be cleaned again to measure how much additional contamination has built up. A report of this activity and the contaminants identified will be presented to the GGSP upon completion of the project.

- 3M Corporation is continuing to work with their line of HFE's and HFC's. They currently produce several good cleaners such as HFE-7100, -7200, however they do not clean as well and can not serve as a verification fluid as desired, they were rated as marginally acceptable in Air Force field tests. At the time of discussion, no new products were mentioned being ready for demonstration/validation.

-AGA Chemicals (Asahi Glass Group), the makers of AK-225g are also continuing developmental work with their own HFE's and HFC's. At the time of discussion, no other product was approaching testable status, but they do have their HFE version presented to the EPA for acceptance.

-Du Pont is the manufacturer of the Vertrel MCA ® brand cleaner. This cleaner also rated marginally acceptable in the Air Force Field tests and just failed the NASA LOX impact testing with 2 reactions out of 70 impacts. DuPont is developing another variant of its Vertrel line that could be ready for testing in approximately 6 months. The product is of course proprietary, still a HFC, but will not be a Class II ODC.

- European Response: At the time of this paper, we are still awaiting a response from out counter parts at the European Space Agency (ESA). We tried to contact Mr. Barrie Dunn or someone from his department. We did contact the European Commission Directorate-General Environment Unit C4, Ozone Layer Protection Team (EU equivalent of our EPA) and they stated they have granted several exemptions where no replacements are available and expect future requests. The exemption requests will be assessed on a case by case basis as foreseen under Regulation (EC) No 2037/2000. They state that some progress has been made on a number of alternatives, but expect to continue to process exemptions. No details were provided as to any technical aspects of European progress on alternatives.

U.S. EPA Response: Mr. Tom Land, Manager, International Programs, Stratospheric Protection Division, has recognized these applications use quantities that are "very, very small".

Cleaning Requirements: In response to our inquiry, DuPont asked the prize question of "What are the cleaning requirements?". Of course there is no simple answer. I followed up with our WSTF and Boeing experts (Dr. Harold Beeson and Mr. Eric Eichinger) and the answer is always dependant upon the application. Mr. Eichinger summed it up best by breaking down the scenario into 4 areas of application with the primary driver being identified from the application.

- Cost: If you are open flushing items, expensive solvents are not practical to lose to the atmosphere. Solvents such as AK-225g and HFE-7100 average about $10,000.00 per barrel.

- Toxicity: For breathing systems, toxic agents are not practical for use compared to systems using oxygen as an oxidizer such as propulsion purposes.

- Compatibility: This becomes critical depending on the exposed environment. Incompatible substances will cause fires or explosions and must be verifiably removed in the cleaning process.

- Performance: The safest cleaning agent may not be aggressive enough for the cleaning task at hand, or may not be compatible on some materials of a system such as seals and fittings.

Our best general cleaning requirements are outlined in the Joint Test Protocol of the JGPP Non-ODC Oxygen Line Cleaning project which can be viewed at http://www.jgpp.com. From there, other specific cleaning requirements must be addressed individually based on applicability. For example, on the Orbiter program, Boeing Corp. had additional cleaning requirement for some adhesives not associated with routine oxygen system cleaning.

Conclusion: Two potential U.S. products could be ready for market soon, pending final testing, a DuPont Vertrel ® variant product, and QwikClean ® from Mainstream Engineering Corp. Due to their proprietary natures, exact specifications and environmental acceptability of the products won't be fully known until the information is released publicly. They will not be Class II ODC's. The Air Force in continuing with development of PFBI with hopes of overcoming its shortfalls in compatibility and shelf life.

Some processes require a two step approach, a cleaning step and a verification step. A final verification rinse may still be necessary with an approved qualified product such as Freon or AK-225g. This would be dependant upon the application requirements. For some applications, a replacement environmentally friendly product may help reduce dependence on ODC's but not totally eliminating the need.

One overarching concern with company investments in environmentally preferable chemicals is defining what will become an acceptable GWP (Global Warming Potential). AGA emphasized that risk management is crucial in the development of a product that once complete, may slightly exceed a "yet to be determined" GWP threshold! European countries are treading very lightly on the topic due to the listed constraints of the Kyoto Protocol, and what may have to be acceptable versus having no replacement technologies at all. This is true for any entity conducting research for alternatives.

This paper should prove beneficial in circumstances where future exemptions may be necessary for NASA applications. Below is a list of contacts associated with the paper demonstrating the breadth of the inquiry for environmental alternatives for oxygen cleaning.

Persons/Agencies Contacted:

<u>Government Regulators:</u>

U.S. EPA: Mr. Tom Land, Manager, International Programs, Stratospheric Protection Division

European Commission: Mr. Marcus Wandinger; Directorate-General, Environment Unit C4, Ozone Layer Protection Team

<u>Space Agencies:</u>

NASA: Dr. Harold Beeson and Sarah Smith, White Sands Test Facility

European Space Agency: Mr. Barrie Dunn (awaiting response)

<u>Air Force:</u>

Mr. Dennis Schroll, T-6A Crew Systems Lead and Oxygen Standardization Coordination Group (OSCG) and NATO STANAG Member, and Mr. Bennet Curtis, Chief, Aerospace Fuel Laboratory.

<u>Organizations:</u>

C3P: Ms. Joana Vide Pereira (awaiting further input from ISQ, Portugal)

<u>Commercial Companies:</u>

Boeing Corp., Shuttle Orbiter Systems: Mr. Eric Eichinger

3M Corp.: Mr. David Hesselroth, 3M Electronic Markets Materials Division, Product Development/Technical Service Specialist.

DuPont, Micro Care Corp.: Mr. Thomas Tattersall

Asahi Glass Chemicals Group: Mr. David Ferguson

Mainstream Engineering Corp.: Mr. Bob Skinge

Statement of Work
For

Delivery Order (DO) BB
Titled

Precision Cleaning of Oxygen Systems and Components

Under NASA Contract Number NNH06CC40C
with ITB, Inc.

PR###########

August 23, 2007

APPENDIX F – Delivery Order 018 Statement of Work

Statement of Work
Precision Cleaning of Oxygen Systems and Components

1. PURPOSE

The purpose of this task is to provide engineering review, analysis, study and reporting of potential chemical alternatives for environmentally friendly oxygen systems and component cleaning that will replace existing Class I and II Ozone-Depleting Substances (ODS). Task efforts will be managed by the Contractor under the Technology Evaluation for Environmental Risk Mitigation (TEERM) Principal Center. This work will assist the government in identification of potential viable environmentally benign alternatives for oxygen system components and hardware cleaning that may be demonstrated and validated for future use.

The expectation of this Statement or Work (SOW) is to study and identify any new chemical products capable of replacing existing Class I and II ODS used for oxygen cleaning. This SOW should constitute the initial phase for potential follow on developmental project actions to potentially identify and eventually qualify new environmentally benign cleaning solvents for use on oxygen systems and components. If productive, identified alternatives will be incorporated into future demonstration/validation projects.

2. BACKGROUND

Limiting organic residues in high pressure oxygen systems is particularly important. The current method of cleanliness verification used by NASA requires an organic solvent flush of the critical hardware surfaces. The solvent is filtered and analyzed for particulate matter, followed by gravimetric determination of the Nonvolatile Residue (NVR) content of the filtered solvent.

Most of the organic solvents currently specified for use in oxygen system cleaning are ODS slated for elimination. These include chlorofluorocarbons (CFC), which are defined as Class I ODS, and hydrochlorofluorocarbons (HCFC), which are Class II ODS. In the mid 1990's, NASA and other aerospace organizations conducted many studies to replace Class I ODS such as CFC 113, and 1,1,1 Trichloroethane used in cleaning aviation oxygen systems and components. In some cases, Class II ODS, such as HCFC 141b and HCFC 225g, became the new oxygen system cleaning agent of choice. (Some hydrofluoroether (HFE) compounds were also qualified, but only for specific applications.) This conversion to HCFC was a temporary solution, however, because the Clean Air Act and Montreal Protocol have set finite caps and phase-out dates for Class II compounds.

Developing a long-term, sustainable solution to this challenge can be advanced through the engagement of Green Chemistry[1] and Green Engineering[2]. These fields are focused on reducing or eliminating the use and generation of hazardous substances; maximizing efficiencies; and considering economic and environmental costs and benefits across the life cycle of chemical products and processes. This is achieved by working at the molecular level and treating any adverse impacts – hazards - to human health and the environment as another physical-chemical property that can be controlled through molecular structure design. As the intrinsic hazard is decreased, there is less reliability on release and exposure controls and therefore less likely for failure. The ultimate goal would be completely benign materials or chemicals such that there is no need to control releases or exposure.

The design approaches and mechanisms used by these fields have been successfully demonstrated in numerous applications across a variety of sectors including metalworking and metal cleaning. They are unique in that green chemistry and green engineering provide approaches and strategies for innovation that contribute to economically beneficial solutions while mitigating risks to human health and the environment.

Dr. Zimmerman and Dr. Anastas of the Center for Green Chemistry and Green Engineering at Yale University maintain, in whole or part, authorship of the sole reference materials on the Principles of Green Chemistry and the Principles of Green Engineering. They are nationally recognized leaders in the areas of green chemistry and engineering. Also, they have delivered invited lectures on these topics to numerous organizations such as the US Army, NASA, Environmental Protection Agency, SC Johnson, the White House Office of Science and Technology Policy, the National Academies, and many for-profit entities.

3. OBJECTIVE

This SOW will engage academia's green engineering and environmentally benign design capabilities to overcome existing barriers of using Class I and II ODS as qualified cleaning agents for oxygen systems and related components. A thorough understanding of oxygen cleaning standards and cleanliness verification science must be examined and evaluated for potential exploitation by new chemical science to overcome the inclusion of environmentally hazardous components to achieve the desired results. The results of this project should produce a comparative baseline testing and validation as to the previous Joint Test Protocol (JTP), then develop and provide a listing of potential alternative cleaning agents for further testing.

[1] Anastas and Warner
[2] Anastas and Zimmerman

4. SCOPE

This statement of work shall utilize the existing JTP from the completed Joint Group on Pollution Prevention (JGPP) project; Non-ODC Oxygen Line Cleaning, project number J-99-CL-015 (available at http://www.jgpp.com) and the attached white paper; Advancements in Oxygen Cleaning Solvents as baseline products to identify current requirements, standards and specifications for aviation oxygen systems cleaning. Academia will explore new chemistry to meet or exceed existing cleaning technology with a goal of identifying environmentally benign potential alternatives that may result in follow on demonstration validation projects to qualify new or designer chemicals for implementation in oxygen systems cleaning.

5. REQUIREMENTS

The Contractor shall provide the necessary management, engineering, technical, and administrative personnel, material, and all other items essential to the performance of the assigned tasks.

5.1 General Requirements

5.1.1 Contractor Personnel Supervision

Contractor personnel shall not be under the direct supervision of any NASA or other Government personnel.

5.1.2 Security

Access to classified information is not required.

5.1.3 Travel

No travel is required.

5.2 Specific Requirements

In the first part of the test program, the Contractor shall demonstrate methods for cleanliness verification using ODS (baseline procedure) such as CFC-113 and HCFC 225. The Contractor shall evaluate organic solvent flush methods for NVR verification. Results will be compared with those from similar samples from another NASA-approved laboratory (e.g., NASA White Sands Test Facility). The Contractor shall evaluate the current method using a range of contaminants encountered in the production, maintenance, cleaning and processing of aviation oxygen systems and components, and oxygen components for space flight hardware. The nature of these contaminants and the appropriate substrate materials for rocket engine and hardware testing will be supplied by NASA.

In the second part of the test program, the Contractor shall develop a strategy for selecting and/or developing/designing alternative methods for cleanliness verification that do not require the use of ozone-depleting chemicals (either Class I or Class II) and

that minimize or eliminate the use of solvents regulated as hazardous air pollutants or smog precursors through green chemistry and green engineering. The Contractor shall develop a prioritized list of potential alternative cleaning agents and/or procedures that may include supercritical fluids, ionic liquids, or aqueous-based surfactant formulations as well as a qualitative and quantitative, where appropriate, analysis of the performance, environmental, and economic characteristics of each alternative.

In the next phase of the test program in Years 2 to 5 (beyond this current contract), the Contractor shall design, develop, and evaluate these 'green' alternatives and perform organic solvent flush methods for NVR verification, where appropriate and via other processes when necessary depending on the alternative solvent system. Results will be compared with those from the baseline method. The Contractor shall evaluate the alternative methods using a range of contaminants encountered in the production, maintenance, cleaning and processing of aviation oxygen systems and components, and oxygen components for space flight hardware, the nature of which has been previously provided by NASA.

6. PERIOD OF PERFORMANCE

The expected period of performance is September 2007 through September 2008.

7. DELIVERABLES

The Contractor shall submit Executive Progress Reports on a quarterly basis to coincide with regular NASA TEERM quarterly progress reporting, which presently begins October 10, 2007. The Contractor shall supplement the Executive Progress Reports with updates to the Precision Cleaning of Oxygen Systems and Components project content on the TEERM World Wide Web site.

The Contractor shall generate a draft and final report that summarizes all work performed under this SOW. The Contractor shall appropriately address Government review comments and incorporate them in the final report.

Item	Delivery Schedule
Quarterly Executive Progress Report	Due October 10, January 10, April 10, and July 10 in concert with Web update
Draft Final Report	30 days prior to end of period of performance
Final Report	12 months after contract award

The Contractor shall provide these documents in an electronic format including all task order products in appendices so all the products can be readily available for future use by the Government.

8. POINTS OF CONTACT

NASA CONTRACTING OFFICER'S
TECHNICAL REPRESENTATIVE
Mr. David Amidei
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School of Forestry and Environmental Studies
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APPENDIX G - Deliverables - Quarterly Status Updates and Trip Reports

The following attachments have been delivered previously and are available upon request.

G1. Trip Report – O2 Cleaning Meeting – Aug 2007
G2. Oct 07 – Dec 07
G3. Jan 08 – Mar 08
G4. Apr 08 – Jun 08