National Aeronautics and Space Administration

Technology Evaluation for Environmental Risk Mitigation Principal Center

Final Report and Deliverables

for

National Aeronautics and Space Administration Precision Cleaning of Oxygen Systems and Components Phase II – Oxygen Cleaning Products Preliminary Testing

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- Robert Ruiz of Kennedy Space Center Engineering Directorate ISS Fluids Branch
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- Mike Puskar of Space Suits & EVA (Hamilton Sundstrand)

Executive Summary

In the 1990s and 2000s, NASA and its contractors began replacing ozone depleting chemicals with other, non-ozone depleting substances for cleaning and verification testing of oxygen parts. Current chemicals used or approved by NASA include: isopropyl alcohol, HFE 7100 (methoxy-nonafluorobutane), Vertrel MCA (an azeotrope of HFC-43-10mee and trans-1,2 dichloroethylene), trichloroethylene, perchloroethylene, cyclohexane, and HCFC-225. While most of these alternatives (all except HCFC-225) are not considered ozone depleting, there are additional issues that warrant a search for a more environmentally preferable solution. These issues, which are not necessarily common across the whole group, include: flammability, volatility, solvency/cleanability, oxygen compatibility, environmental persistence, high carbon dioxide equivalency greenhouse gas emitters, and supplier availability/cost. In addition, suitable alternatives for HCFC-225 have not been found for some NASA applications. For these reasons, there continues to be a need for an economically and technically feasible alternative for cleaning oxygen systems that does not increase environmental, safety, or occupational health risks and costs.

ITB developed a test protocol meant to be inclusive of all NASA requirements that would be used in future phases of this effort to demonstrate and validate promising alternatives. Input was sought from potential NASA stakeholders, requirements and technical standards were retrieved from the NASA Tech Standards web site, and assistance was requested from Yale to recommend changes to the procedures.

Work conducted under this effort by Yale University continued to explore the following categories of chemicals as sources of potential alternative cleaning agents for NASA oxygen systems:

- Fluorocarbons
- Surfactants
- Room temperature ionic liquids
- Aqueous solutions
- Supercritical liquids

The following major points can be established from the project:

- NVR testing completed on fluorinated/perfluorinated molecules shows that the ideal alternative will not be an HFC, but may aid in the screening of molecules modeled by COSMO-RS
- Anionic and nonionic aqueous surfactants mixtures showed promise for future fine-tuning and possible viability with the addition of corrosion inhibitors and biocides
- Seven room temperature ionic liquids were purchased from Bioniqs based on COSMO-RS modeling and will be investigated further
- Supercritical carbon dioxide appears to be a promising alternative, though further investigation is necessary to understand the impact of elevated pressure and temperature in representative hardware
- The project will be on hold for the next year while the technical lead is on sabbatical; this break will allow an opportunity to reevaluate risks and requirements, and become better acquainted with affected processes

1. Introduction

The standards of the Department of Defense (DOD), National Aeronautical and Space Administration (NASA), National Fire Protection Agency (NFPA), American Society of Testing and Materials (ASTM) and Society of Automotive Engineers (SAE) all specify that the rigorous removal of organic and particulate contamination from oxygen and oxygen enriched handling equipment is absolutely necessary to prevent a fire hazard. Failure to thoroughly clean oxygen and oxygen enriched handling equipment will and has resulted in catastrophic fires.

The requirements for oxygen cleaning agents include the capability of removing common hydrocarbon soils such as lubricating oils and greases, since the presence of these soils represents an extreme fire hazard. Oxygen cleaning agents must also be capable of removing particulate contamination, since the presence of excessive particulate contamination provides a potential ignition source in oxygen and oxygen-enriched handling equipment. Further, oxygen cleaning agents must be capable of removing halogenated lubricants approved for use with oxygen storage and delivery equipment. Although halogenated lubricants are used in oxygen-enriched handling equipment because they are not flammable, the failure to remove these lubricants during cleaning provides a mechanism for trapping particulate and/or hydrocarbon contamination. The cleaning process in general must not leave trace substances that would increase flammability risk. The oxygen cleaning agent must have an acceptably low toxicity level for both end users and in the event the cleaner is not completely removed during the cleaning process. Finally, the oxygen cleaning agent must be capable of being analyzed for residual total hydrocarbon contamination with a sensitivity of at least 1 part per million (ppm) to permit accurate, certifiable verification of hydrocarbon cleanliness. DOD, NASA, and various commercial standards require oxygen-enriched handling equipment to be certified hydrocarbon clean. The DOD standard (MIL-STD-1330C) certifies hydrocarbon cleanliness when the effluent cleaning agent, that is, the cleaning agent following its use in cleaning the oxygen enriched handling equipment, measures less than 5 ppm total hydrocarbon contamination. A conversion factor is applied to convert the DOD standard to the NASA hydrocarbon cleanliness standard of 1 milligram per square foot.

Two historical oxygen cleaning agents are trichlorotrifluoroethane solvent (also identified as CFC-113) and dichloropentafluoropropane solvent (also identified as HCFC-225). Both of these compounds are ozone depleting substances (ODS), and replacements will become necessary due to the banned production and importation schedules mandated by the Montreal Protocol and Environmental Protection Agency: 1996 for Class I ODS like CFC-113 and 2015 for Class II ODS like HCFC-225. Exceptions exist for some applications such as refrigeration. The NASA Space Shuttle Program (SSP) Shuttle Environmental Assurance Initiative (SEA) identified the obsolescence of Class II ODS as an environmentally driven risk to mission. Specifically, HCFC-225, used to clean contaminated oxygen systems and precision cleaning of components, was targeted. Commercially available alternatives to HCFC-225 exhibit issues such as flammability, volatility, solvency/cleanability, oxygen compatibility, environmental persistence, high carbon dioxide equivalency greenhouse gas emissions, and supplier availability/cost. Given the impact to multiple program elements; potentially the Constellation Program (CxP), International Space Station (ISS); and technology transfer to DOD entities, a Technology Evaluation for

Environmental Risk Mitigation Principal Center (TEERM) project was initiated by NASA Headquarters Environmental Management Division (HQ EMD).

The pursued approach was to engage academia and the green chemistry community to investigate next generation alternatives. The first year of the effort was primarily intended to get the project team members up to speed on the processes involved in cleaning, to conduct a literature search, and to develop a list of candidate chemicals for further investigation. The second year was to build on the progress of the first year by developing a recommended test protocol for future demonstration/validation, and to perform investigation of the candidate chemicals to down-select for the next phase. Another difference in the Phase II effort was that the funding was incremental. Only Task 1 was funded.

Quarterly status reports were prepared and delivered by ITB (with assistance from Yale) throughout the period of performance. These reports were used by ITB to keep NASA HQ EMD apprised of project progress. ITB is pleased to have provided programmatic and project development support services to NASA for the past year.

2. Activities and Results

ITB developed a test protocol meant to be inclusive of all NASA requirements that would be used in future phases of this effort to demonstrate and validate promising alternatives. Assistance was requested from Yale to recommend changes to the procedures. Several of the requirements documents are still being finalized for the Constellation Program, and other traditionally accepted requirements such as the mechanical impact test for assessing oxygen compatibility have been removed or are used less to screen out alternative materials.

The identification and assessment of alternative cleaning chemicals began later than desired due to contracting delays; the Phase II award did not occur until November 14, 2008. Holiday and international travel schedules further impacted the start of Task 1. In December 2008, feedback was received from the CxP Materials & Processes Lead which led to a TEERM effort to contact relevant points of contact to more definitively assess the risk to mission. Table 1 shows who was contacted and gives an overview of the information provided or discovered. The only confirmed users of ozone depleting chemicals within NASA (and beyond SSP) are at Johnson Space Center White Sands Test Facility (WSTF). HCFC-225 is used to clean Bourdon gauges, as noted below:

> *'…Many of these gauges do not have a flow-thru port, and it is common for manufacturers to calibrate them with hydrocarbon oils. From an oxygen fire hazard perspective, this oil poses a problem, and solvents such as HFE 7100 are just not effective enough in this type of application where it is not possible to get good flow rates or use mechanical cleaning.'*

Table 1: Oxygen Cleaning Points of Contact

Program/Center	Contact	Chemical Used	Confirmed alternative?	Test requirements / reference documents?
ISS	Robert Ruiz Dave Wiedemuth Mike Pedley	PERC (Node 2) IPA	Y	ASTM MNL 36 ASTM G127 KSC-C-123H

Program/Center	Contact	Chemical Used	Confirmed alternative?	Test requirements / reference documents?
Orion	Steven Deblasio			
Hamilton Sundstrand (Orion ECLSS)	Mike Puskar	Vetrel MCA & HFE 7100	Y	
Boeing (Orbiter)	Eric Eichinger	HCFC-225 & HFE 7100	Y	SE-S-0073H
WSTF	Sarah Smith Christina Pina	HFE 7100 & Water; some HCFC-225 still	Y	WSTF IR 0134-002-01
JSC	Mike Pedley	HFE 7100 & Water	Y	CxP 70156
J2-X	Mike Kynard	cyclohexane		
Ares Upper Stage	Nikki Lowrey	TCE & aqueous	Y	MSFC-SPEC-164 ASTM-F331
MAF (ET)	Earl Pratz	HCFC-225 / TCE		SE-S-0073H
SSC		HCFC-225		

Communications with Yale were unsuccessful until the first quarterly status report was due (mid January 2009), and a month after the test protocol was due. Further feedback from the CxP Materials & Processes Lead in January 2009 stated that use of HCFC-225 would end with the SSP. HQ EMD expressed the view that CxP was undervaluing the risk, and gave the guidance to press forward during a Program Management Review. As for the test protocol, HQ EMD understood the situation and emphasized that quality outweighed timeliness. Additional feedback from HQ EMD stressed the focus of following the cleaning process from precleaning all the way through cleanliness verification. To increase the quality of the test protocol the focus was expanded to include as many NASA requirements as could be identified. Once communication was established with Yale, numerous teleconferences were scheduled to build momentum and allow more direct interaction with the subject matter experts at WSTF. Cleaning procedures were requested from WSTF, though were unavailable due to snags with Export Control. Teleconferences were generally well-attended until Yale began asking about funding for Task 2 (mid March 2009). The ITB effort to collect requirements continued as CxP released its initial Fluid Procurement and Use Control Specification in mid April 2009. The SEA team reported acceptance of the obsolescence risk in late April 2009, due in large part to the 2010 scheduled retirement of the SSP. NASA TEERM management requested a progress report and clear future direction of the testing from Yale before they would provide a determination on funding. In June 2009, a progress report was received, along with confirmation that the technical lead from Yale would be taking a year-long sabbatical. The progress report is included as Appendices A and B. Appendix C is the final statement of work and Appendix D lists all of the deliverables. Within days after Yale's submittal, WSTF provided supplemental information to describe representative cleaning processes.

Work conducted under this effort by Yale University continued to explore the following categories of chemicals as sources of potential alternative cleaning agents for NASA oxygen systems:

- Fluorocarbons
- Surfactants

- Room temperature ionic liquids
- Aqueous solutions
- Supercritical liquids

The following major points summarize findings from Yale:

- NVR testing completed on fluorinated/perfluorinated molecules shows that the ideal alternative will not be an HFC, but may aid in the screening of molecules modeled by COSMO-RS
- Anionic and nonionic aqueous surfactants mixtures showed promise for future fine-tuning and possible viability with the addition of corrosion inhibitors and biocides
- Seven room temperature ionic liquids were purchased from Bioniqs based on COSMO-RS modeling and will be investigated further
- Supercritical carbon dioxide appears to be a promising alternative, though further investigation is necessary to understand the impact of elevated pressure and temperature in representative hardware

3. Conclusions and Recommendations

The recent developments have left a looming question regarding how to proceed. Below several recommendations are offered based on the current and anticipated regulatory environment. There is a strong possibility that a renewed interest in cleaning alternatives will surface due to concerns over greenhouse gas emissions. Many of the commercially available products have higher global warming potential (GWP) relative to carbon dioxide.

Table 2: Global Warming Potential of commercially available cleaners

Cleaning solvent	GWP	Source
Vertrel MCA	806	http://www2.dupont.com/Vertrel/en_US/assets/downloads/pdf/k04169.pdf
HFE 7100	320	http://www.galladechem.com/msds/hfe-7100.pdf
perchloroethylene	9	http://www.eurochlor.org/facts
isopropyl alcohol	not found	
Cyclohexane	not found	
trichloroethylene	much less than 9	http://www.eurochlor.org/facts

Per the decision made on July 27, 2009 at an ITB-NASA meeting, the project will be on hold for the next year while the technical lead is on sabbatical; this break will allow an opportunity to reevaluate risks and requirements, and become better acquainted with affected processes. After the sabbatical has concluded a decision to restart will be made based on stakeholder support and definition of scope. ITB offers these additional recommendations at this time:

- Explore feasibility of providing Oxygen Systems class to Yale team
- Schedule visit by Project Manager to Wiltech cleaning facilities at KSC
- Keep abreast of fluids requirements and baseline changes of Constellation Program

APPENDIX A – Yale Progress Report (November 08 – June 09)

Oxygen Cleaning Products Preliminary Testing

Progress Report, Spring 2009

SUMMARY

Recent Progress

- Given the lack of reproducible results due to coupon to coupon variability, recommendations were submitted for test protocol modifications. The most significant proposed change to the method in support of this goal is to characterize the surface roughness of the test coupon such that the observed NVR results can be normalized to surface conditions. This is based on inconsistent results between test coupons of identical material. Furthermore, based on the findings in the JTR, we propose a shift back towards SEM to verify soil removal as the mass difference method and visual examination are not sensitive enough to detect slight, or even moderate, differences in residue when evaluating alternatives that may not perform as well as the standard case.

- Immersion testing of plates using fluorinated and perfluorinated solutions. A matrix of chemical structures has been started to determine the optimum structure for cleaning and de-greasing purposes. Efforts were made to evaluate the degree of fluorination necessary to render these compounds non-flammable, while still providing high levels of cleanliness and minimizing environmental persistence. Work was done with chain lengths of five to seven carbons, as this excludes compounds with boiling points that are too low and compounds with unacceptably long persistence. These cha in lengths also allow easy distillation of the solvents at temperatures less than 150ºC, making solvent recycling more feasible, which will further reduce environmental impacts. Preliminary findings indicate that the fluorine atoms on these molecules are primarily related to flammability and not to cleaning efficacy as 1-fluoroheptane performed as well as perfluoroheptane when evaluated for NVR.

- Compilation of related literature. A review of literature pertaining to cleaning and de-greasing, oxygen systems cleaning, ozone-depleting chemical alternatives, and the environmental and toxicological effects of the alternatives is on going.

Milestones

- Completed JTR NVR testing of fluorinated and perfluorinated molecules based on five to seven carbons.
- Completed JTR NVR testing of anionic and nonionic surfactants with varying non-polar and polar molecular structures to determine desirable

characteristics for surfactants candidates in a aqueous formulation.

- Completed modeling of various alternative solvents in COSMO-THERM to identify hydrophobic ionic liquid candidates for testing.

Near-Term Goals

- Complete testing of ionic liquids candidates identified through COSMO-THERM modeling.
- Determine statistical significance of structure variations on solvent performance for anionic and nonionic surfactants being considered as potential alternatives.
- Complete literature review on state of the science for precision cleaning of oxygen systems and potential alternatives to include aqueous surfactant systems, supercritical fluids, ionic liquids, and perfluorinated compounds.
- Complete purchase of a supercritical fluid extractor system to begin testing on near critical and supercritical water and carbon dioxide as alternatives. Also, begin literature review of potential co-solvents or surfactants for use in these near or supercritical systems.

BACKGROUND

Historically, solvents such as 1,1,2-trichloro-1,2,2-trifluoroethane and 1,1,1-trichloroethane have been the chemicals of choice for NASA, the Department of Defense and the aerospace industry in cleaning aviation oxygen systems and components. The U.S. Environmental Protection Agency classified and regulated these chemicals as Class I (most harmful) ozone depleting substances. In the mid 1990's, in response to the U.S. Clean Air Act and Montreal Protocol, aerospace organizations began replacing these Class I ozone depleting chemicals with less harmful hydrochlorofluorocarbons (HCFC), which are still ozone depleting substances (Class II). Two common HCFCs are 1,1-dichloro-1-fluoroethane (HCFC-141b) and 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC 225g). The Class II solvents provide only a temporary solution, however, because the Clean Air Act and Montreal Protocol have set finite caps and phase-out dates for their manufacture. Other qualified solvents, such as hydrofluoroethers, are not ozone depleting but are limited in the applications in which they can be used.

INTRODUCTION

This progress report is update on work conducted under the call to define the necessary testing and reporting to validate potential chemical alternatives for environmentally friendly oxygen systems and component cleaning identified during the initial year (2008) phase study. Testing procedures were evaluated and suggested modifications were made by the Center for Green Chemistry and Green Engineering at Yale (CGCGEY) based on the tests and procedures outlined in the Joint Test Protocol (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).

A full discussion of the test protocol evaluations and suggested modifications are included in Appendix B. The key learning points are included and evaluated below:

1. Coupon-to-coupon variability should be addressed. Normalizing observed cleaning efficiency behavior to coupon surface roughness should be explored a primary mechanism.
    a. Surface roughness could be evaluated by a contact-based stylus instrument or by SEM with optical recognition software.
2. The amount of contaminant and thickness of the contaminant applied should be normalized as variations in observed cleaning efficiency may be related to variable amounts of contaminant to be removed.
3. Based on current results, it may be possible to limiting testing to XXX and XXX as these contaminants are the most resistant to variety of alternative cleaners currently under evaluation.

Coupon-to-coupon variability

The test procedure currently does not provide a mechanism to address variation in cleaning performance from coupon to coupon. While this is not an issue at or near 100% cleaning efficiency, it poses a significant challenge for alternatives with reduced cleaning performance. While it recognized that any successful alternative cleaning agent must perform at or near 100% efficiency, there is much knowledge and insight to be gained from lesser performing agen ts including trends in molecular structure-activity relationships.

Currently, cleaning efficiency (% clean) is a compound value that is based three gravimetric measurements, so that following error propagation formulations can approximate the final error. Initial measurements revealed inconsistent results for baselining measurements with Sebacate as the contaminant and HCFC-225 as the cleaning solvent. Scale repeatability tests (10 measurements) on a single uncontaminated coupon revealed a repeatability of approximately 0.4 mg for a 2 gram uncontaminated coupon. The average contaminant weight for Mil-H-5606 was 13.5 mg for 1.5 square inch coupons. As such, an error of 0.4 mg per measurement represents a significant error. Using larger coupons is recommended because this would decrease the relative error and potentially allow for more consistency between coupons. The disadvantage, of course, of using larger coupons is a reduction in the number of alternatives that can be evaluated in a given time period.

Another pathway to addressing the observed variability between coupons is to characterize the surface roughness of the individual coupons. This perhaps, normalizes the observed cleaning efficiency behavior to this characteristic of the individual coupons. To evaluate this approach, a contact-based portable stylus instrument was obtained and measurements were performed in the middle of the coupon or across a significant scratch if one was present. However, measurements in different locations on the same coupon typically lead to significantly different results as the roughness is not uniform across the coupon. For instance, 10 measurements in the same location on coupon 01 of the Mil-H-5606 trial (without lifting the profilometer) yielded an average roughness of 0.38 um (Ra) with a standard deviation of 0.04 um while 10 measurements across the same coupon yielded an average roughness of 0.63 um (Ra) with a standard deviation of 0.25 um. In comparison the average roughness across all 60 coupons used in the Mil-H-5606 trial was 0.66 um (Ra) with a standard deviation of 0.44 um. From this, it is clear that this characteristic of the coupon should be characterized as it may be significantly impacting observed cleaning efficiency but that a contact-based may not be the most appropriate.

Contaminant thickness variability

Since cleaning efficiency is calculated as percent clean:

[(post cleaning weight – uncontaminated weight) / contaminated weight] x 100%

It is potentially sensitive to the amount of contaminant applied. Applying a fixed amount of contaminant and aiming for consistent thickness of the contaminant across the coupon could also help to reduce variability observed in replicate tests.

ALTERNATIVES EVALUATION

The second year testing for Phase II, Oxygen Cleaning Products Preliminary Testing was based upon the Phase I study final report. In that report, CGCGEY identified potential solvents and solvent blends for further testing. Requirements for the statement of work underlying this work include:

- Hydrofluorocarbons (Task 1)
- Aqueous Cleaning Solutions (Task 2)
- Surfactant behavior and concentration levels (Task 2)
- Ionic Liquids (Task 2)

Hydrofluorocarbons

Preliminary testing with monofluorinated aliphatic hydrocarbons has shown promising results in cleaning tests (see Figure 1). Immersion tests performed with 1-fluoroheptane show cleaning efficiency of 94% or greater for both single contaminants and contaminant mixtures. Limited immersion testi ng conducted with monofluorinated compounds with carbon chain lengths between nine and twelve also shows promising cleaning results (see Figure 2). These fluorocarbons, however, suffer from a number of limitations including flammability concerns [1].

One of the advantages of fully fluorinated (perfluorinated) compounds is their non-flammable nature [1]. Conversely, monofluorinated compounds are highly flammable, and thus may not be suitable for use in an oxygen environment. Unfortunately, perfluorinated compounds have been to have environmental persistence concerns [2], due to the very strong bond that forms between carbon and fluorine atoms. The persistence of these compounds is also affected by the carbon chain length such that persistence increases as chain length increases [3]. However, if chain lengths are too short, the compounds have boiling points that are below room temperature impeding their application as solvents. One additional limitation of using fluorinated hydrocarbons is that the toxicological properties of these compounds are generally not well understood and require additional investigation.

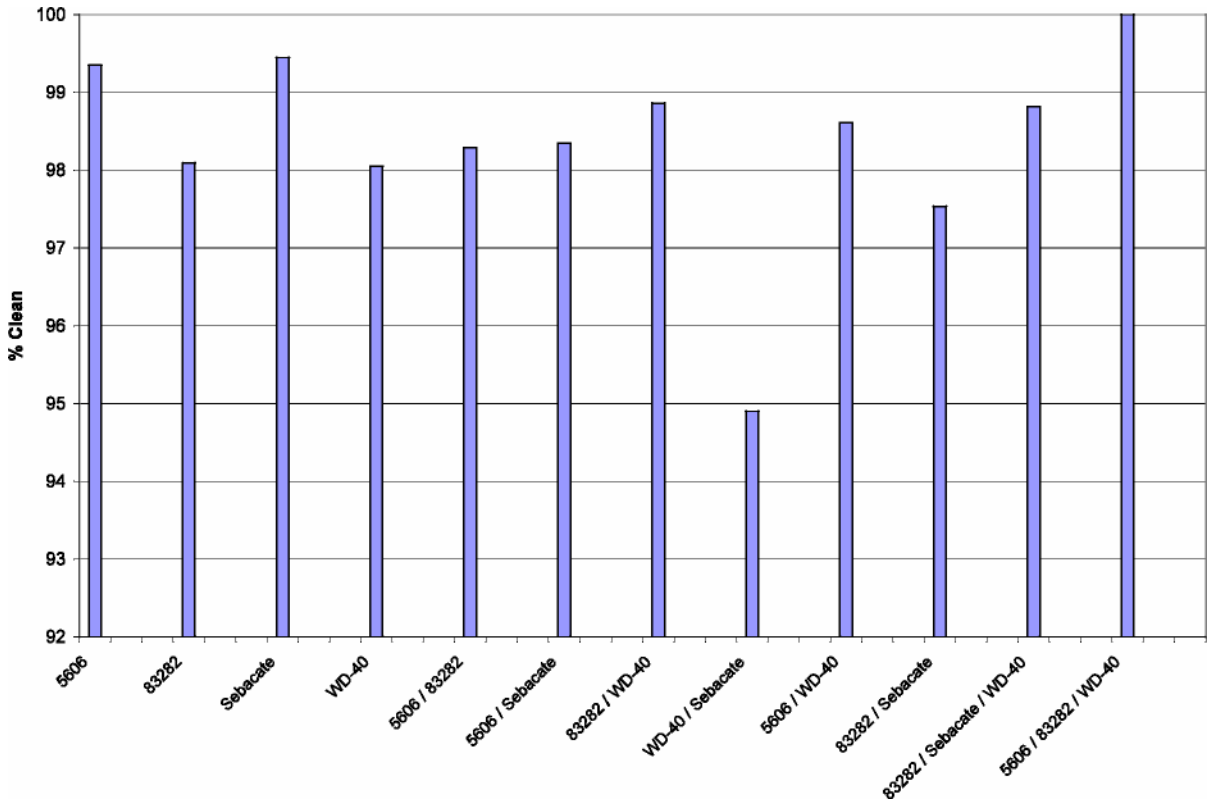

Figure 1: Immersion test results with 1-fluoroheptane. Contaminants are Mil-Spec-H-5606 (5606). Mil-H-83282B (83282), Di-2-ethylhexyl sebacate (Sebacate), and WD-40.

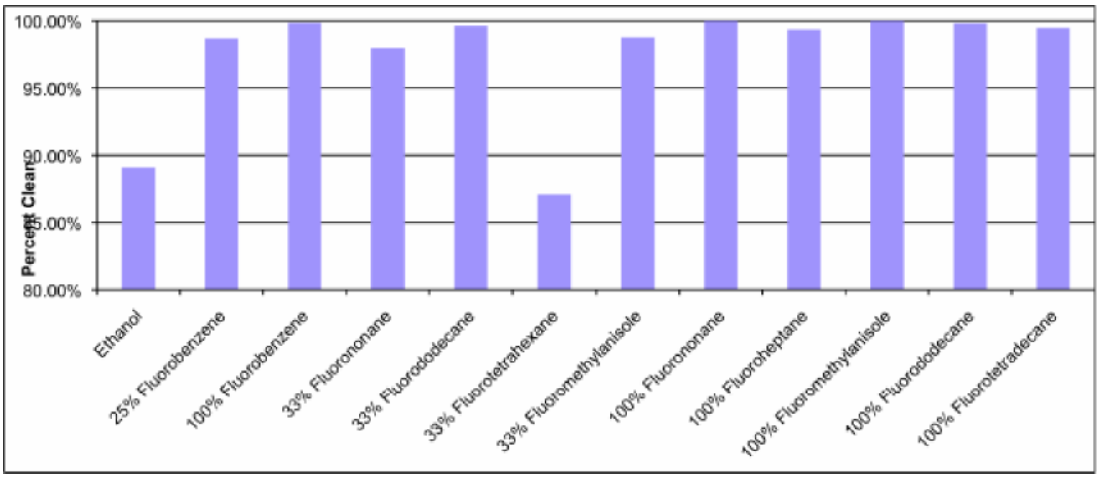

Figure 2: Immersion test results with Mil-H-5606 across a range of hydrofluorocarbons (HFCs) of varying degrees of fluorination. The HFCs were tested neat where appropriate and dissolved in ethanol where necessary.

Hydrofluorocarbon (HFC) work in this effort focused on finding the degree of fluorination necessary to render these compounds non-flammable, while still providing high levels of cleanliness and minimizing environmental persistence. Work was done with chain lengths of five to seven carbons (see Figure 3 as an example), as this excludes compounds with boiling points that are too low and compounds with unacceptably long persistence. These chain lengths also allow easy distillation of the solvents at temperatures less than 150°C, making solvent recycling more feasible, which will further reduce environmental impacts.

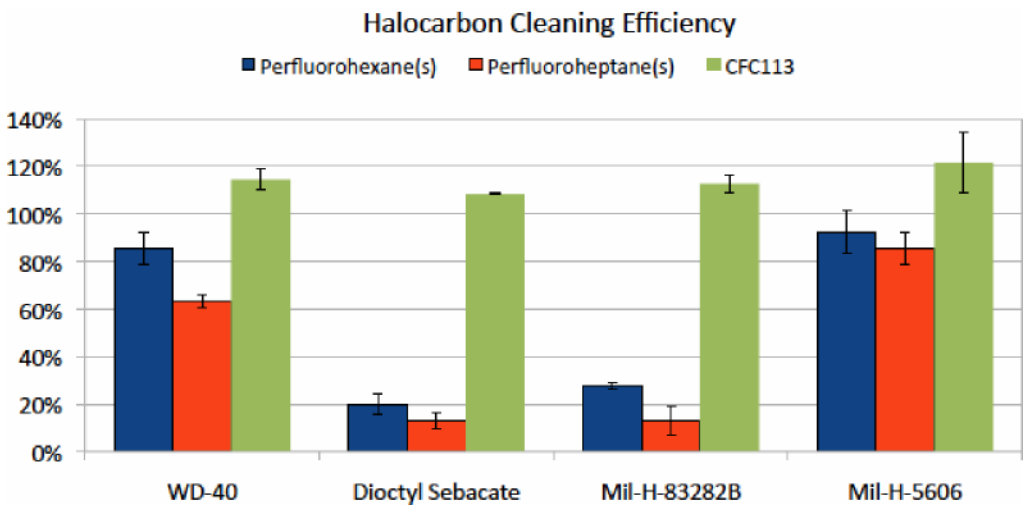

Figure 3: Immersion testing results for the four individual contaminants comparing perfluorohexane to perfluoroheptane. Note that CFC1 13 observed cleaning efficiency above 100% is likely due to incomplete pretest cleaning by HCFC225.

From these results, it can be concluded that perfluoroheptane is less, albeit slightly, effective than perfluorohexane. While the ideal alternative candidate would not be an HFC, using this information will provide valuable insight and knowledge of the optimum HFC characteristics for the molecular design efforts proposed as future work (see Molecular Design section).

Aqueous surfactant solutions

In addition to hydrofluorocarbons, aqueous cleaning solutions are of interest, as water is both environmentally benign and compatible in an oxygen environment. Surfactants have long been utilized to increase the solvency of oils in aqueous systems as well as being used in a variety of degreasing applications [4,5]. Surfactants also offer the advantage of being highly customizable. Surfactant behavior can be modified via such properties as surfactant concentration, temperature, and pH [4,5] as well as the type and str ucture of the surfactant. This offers the opportunity to fine tune surfactant solutions for optimal cleaning performance.

Surfactants do come with several potential issues regarding their use including the deposition of surfactant residues on the surface being cleaned. This may necessitate the use of greater volumes of solvent for a secondary rinse stage. Furthermore, the use of surfactant may limit the ease with which cleaning solutions can be recycled.

Work was conducted to determine the effectiveness of several types of surfactants including anionic (negatively charged) and non-ionic (neutrally charged) compounds. The goal is to evaluate the optimum structure of the surfactant components and the minimum surfactant concentration needed to provide acceptable cleanliness, as minimizing surfactant concentration should limit residue and recycling issues. While these particular surfactants may not be included in a final formulation for oxygen cleaning, the information gained about their structure -activi ty in terms of removing these contaminants from this material will be valuable in moving forward with formulation activities. Additionally, a final formulation may include a combination of anionic and nonionic surfactants and will need to include additional components to the surfactants such as corrosion inhibitors and biocides.

The following surfactants were tested in this time period:

Anionic: sodium dodecyl sulfate (SDS)

Nonionic: a range of linear alcohol ethoxylates (LAE), recognized as excellent wetting agents, emulsifiers and detergents with ease of handling and formulation:

$$R\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$$

where R is a hydrocarbon chain and n represents the number of ethoxylate (EO) groups. Shorter R chains and more EO groups lead to increased polarity. The range of hydrocarbon chain length evaluated was 9 to 15 and the range in the number of EO groups was 2 to 13. The individual surfactants were evaluated at concentrations of 1 % w/w and 5% w/w. Three replicates at each concentration were conducted for each of the contaminants.

The following present the results from these tests: SDS (Figure 4), LAE with an average R chain length of 9-11 (R9-11) and an average of 2.5 EO groups (EO2.5) (Figure 5), LAE R9-11 EO6 (Figure 6), LAE R9-11 EO8 (Figure 7), LAE R12-13 EO3 (Figure 8), LAE R12-13 EO5 (Figure 9), LAE R12-15 EO7 (Figure 10), LAE R12-15 EO9 (Figure 11), LAE R14-15 EO7 (Figure 12), and LAE R14-15 EO13 (Figure 13).

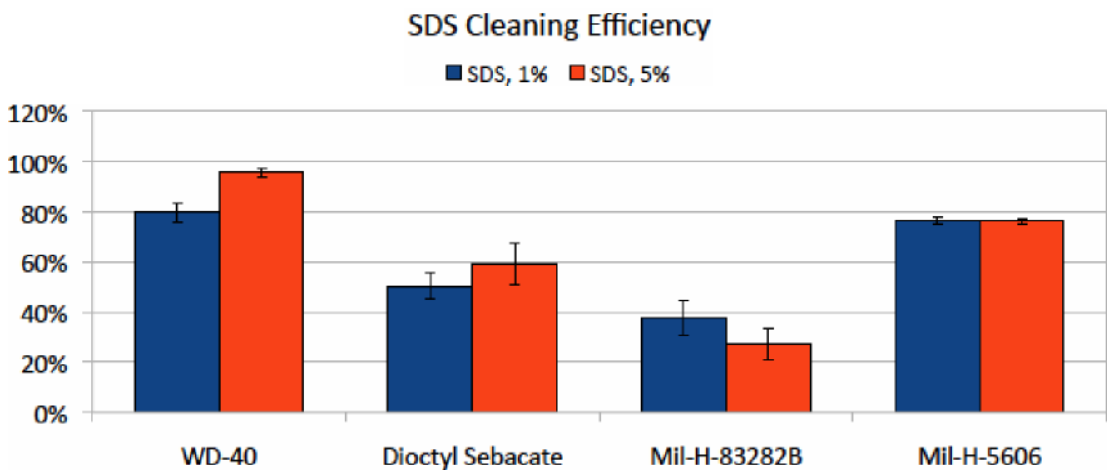

Figure 4: Immersion testing results for the sodium dodecyl sulfate (SDS) at 1% w/w and 5% w/w concentration for four individual contaminants.

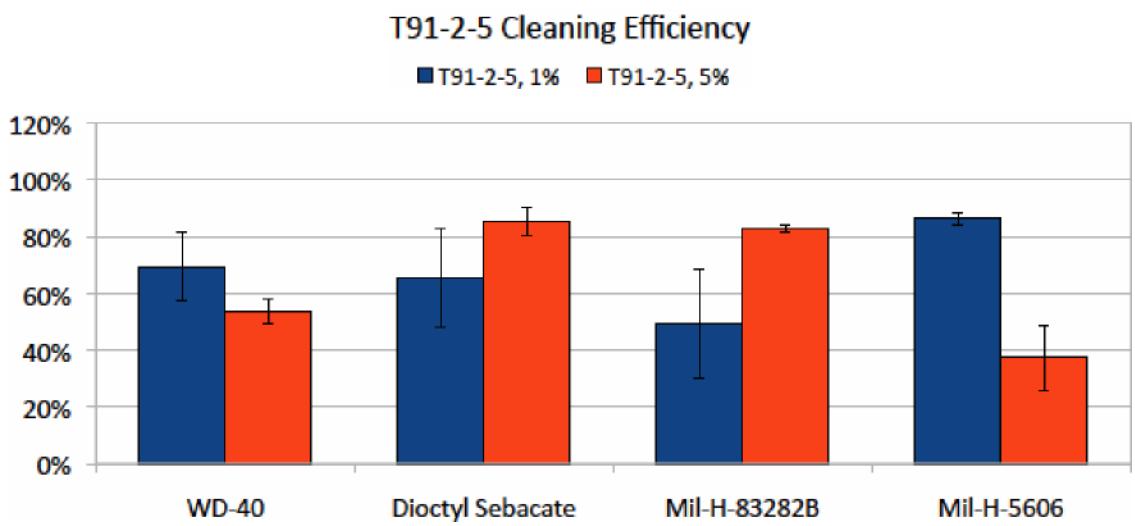

Figure 5: Immersion testing results for a linear alcohol ethoxylate with an average R chain length between 9 and 11 carbons and an average of 2.5 ethoxylate groups at 1% w/w and 5% w/w concentration for four individual contaminants.

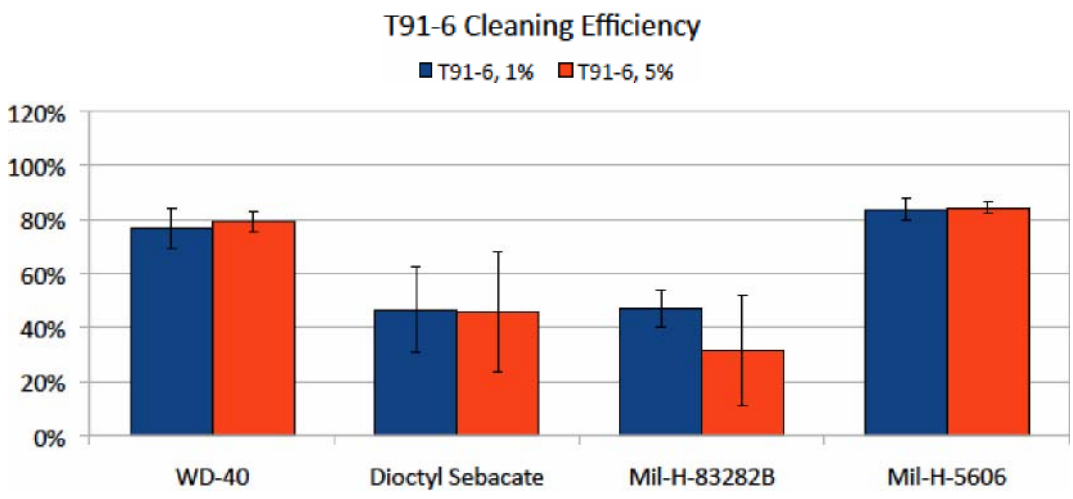

Figure 6: Immersion testing results for a linear alcohol ethoxylate with an average R chain length between 11 and 12 carbons and an average of 6 ethoxylate groups at 1% w/w and 5% w/w concentration for four individual contaminants.

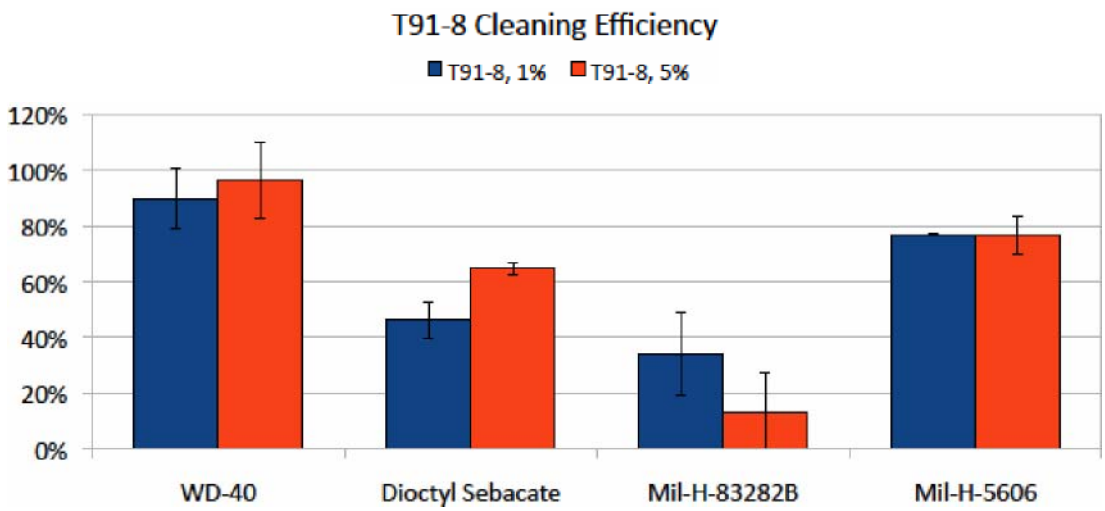

Figure 7: Immersion testing results for a linear alcohol ethoxylate with an average R chain length between 9 and 11 carbons and an average of 8 ethoxylate groups at 1% w/w and 5% w/w concentration for four individual contaminants.

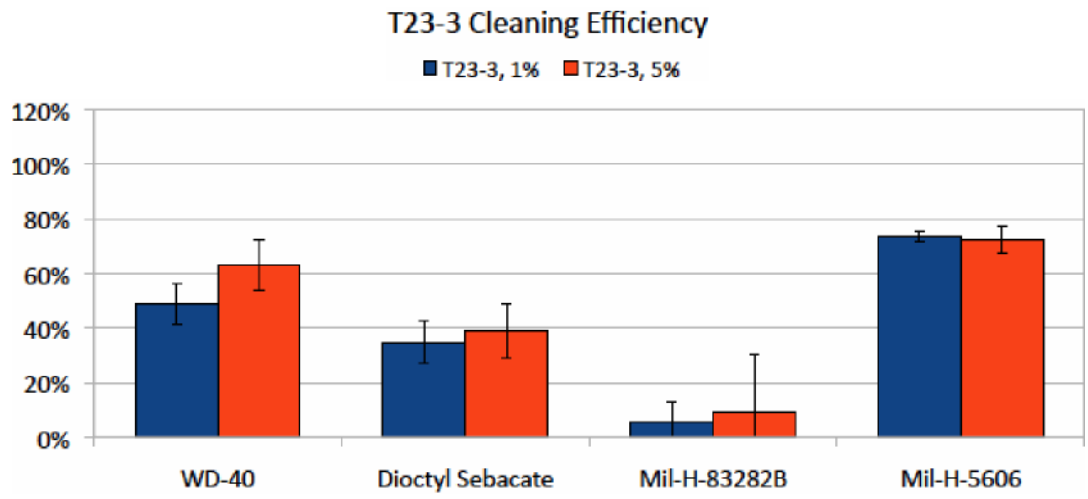

Figure 8: Immersion testing results for a linear alcohol ethoxylate with an average R chain length between 12 and 13 carbons and an average of 3 ethoxylate groups at 1% w/w and 5% w/w concentration for four individual contaminants.

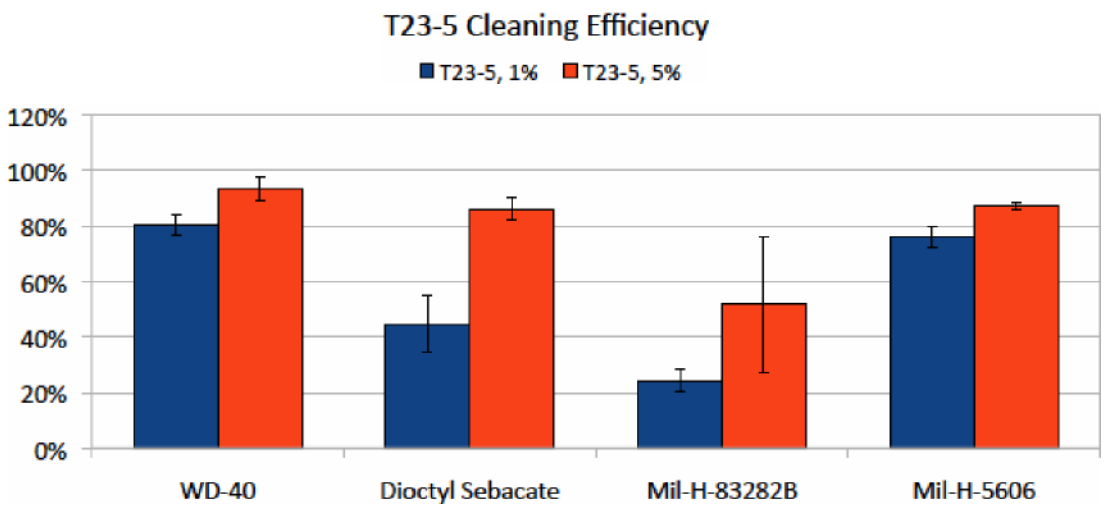

Figure 9: Immersion testing results for a linear alcohol ethoxylate with an average R chain length between 12 and 13 carbons and an average of 5 ethoxylate groups at 1% w/w and 5% w/w concentration for four individual contaminants.

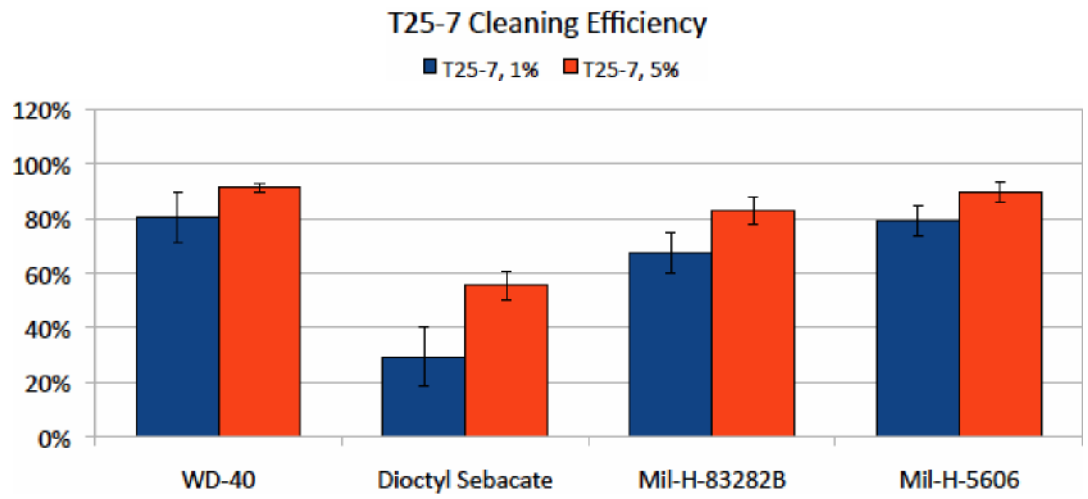

Figure 10: Immersion testing results for a linear alcohol ethoxylate with an average R chain length between 12 and 15 carbons and an average of 7 ethoxylate groups at 1% w/w and 5% w/w concentration for four individual contaminants.

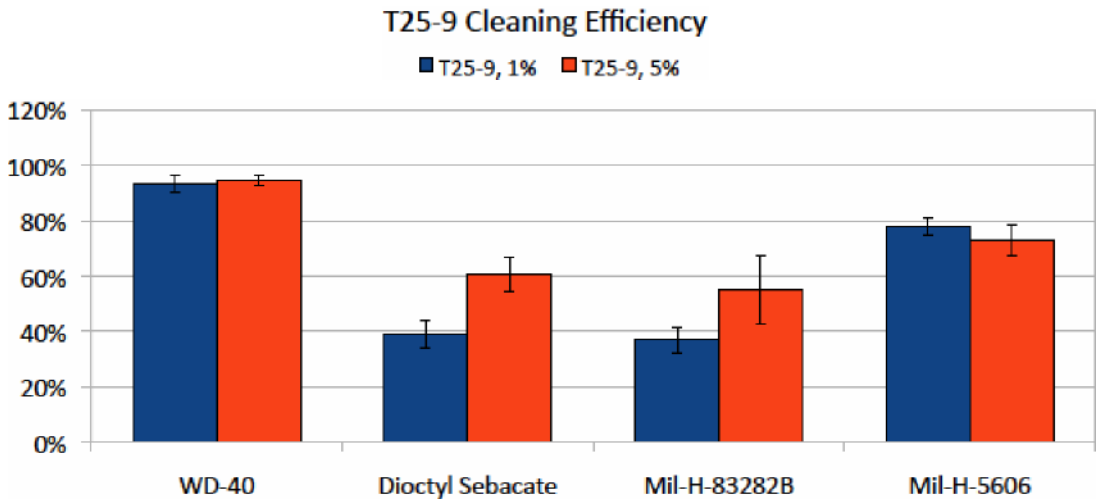

Figure 11: Immersion testing results for a linear alcohol ethoxylate with an average R chain length between 12 and 15 carbons and an average of 9 ethoxylate groups at 1% w/w and 5% w/w concentration for four individual contaminants.

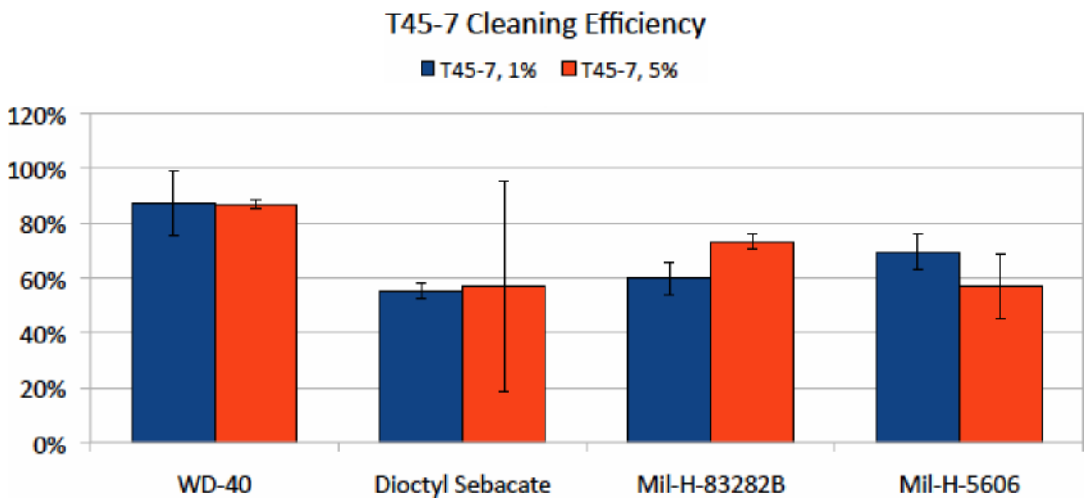

Figure 12: Immersion testing results for a linear alcohol ethoxylate with an average R chain length between 14 and 15 carbons and an average of 7 ethoxylate groups at 1% w/w and 5% w/w concentration for four individual contaminants.

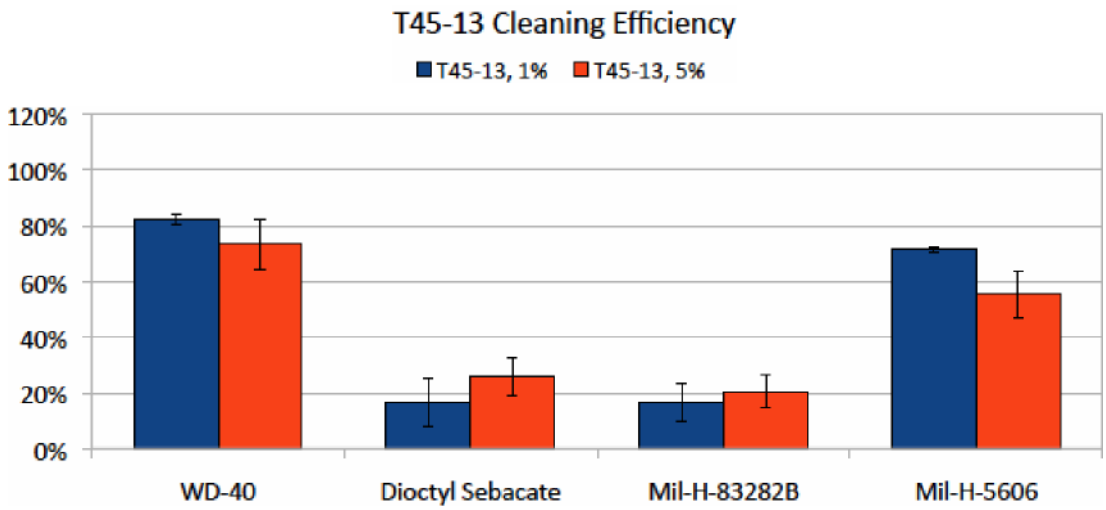

Figure 13: Immersion testing results for a linear alcohol ethoxylate with an average R chain length between 14 and 15 carbons and an average of 13 ethoxylate groups at 1% w/w and 5% w/w concentration for four individual contaminants.

These tests demonstrate that WD40 and Mil-H05606 were more effectively and consistently removed by the 10 surfactants evaluated. They were each cleaned with an average of at least 80% efficiency under these conditions, which were not optimized. It is also noted that there is little difference observed for an increase in surfactant concentration from 1% w/w to 5% w/w. Dioctyl Sebacate and Mil-H-8328B were less effectively and evenly removed. This may suggest that aqueous cleaning tests can focus on these two contaminants rather than the enter suite of four contaminants. Surprisingly, clear consistent trends by head or tail length of the surfactant are not apparent. This suggests that additional work

needs to be done to evaluate the optimum surfactant structure to yield in maximized cleaning efficiencies for all of the contaminants tested.
The results from these tests were also plotted by contaminant to further elucidate the trends and observations reported above (see Figures 14-17).

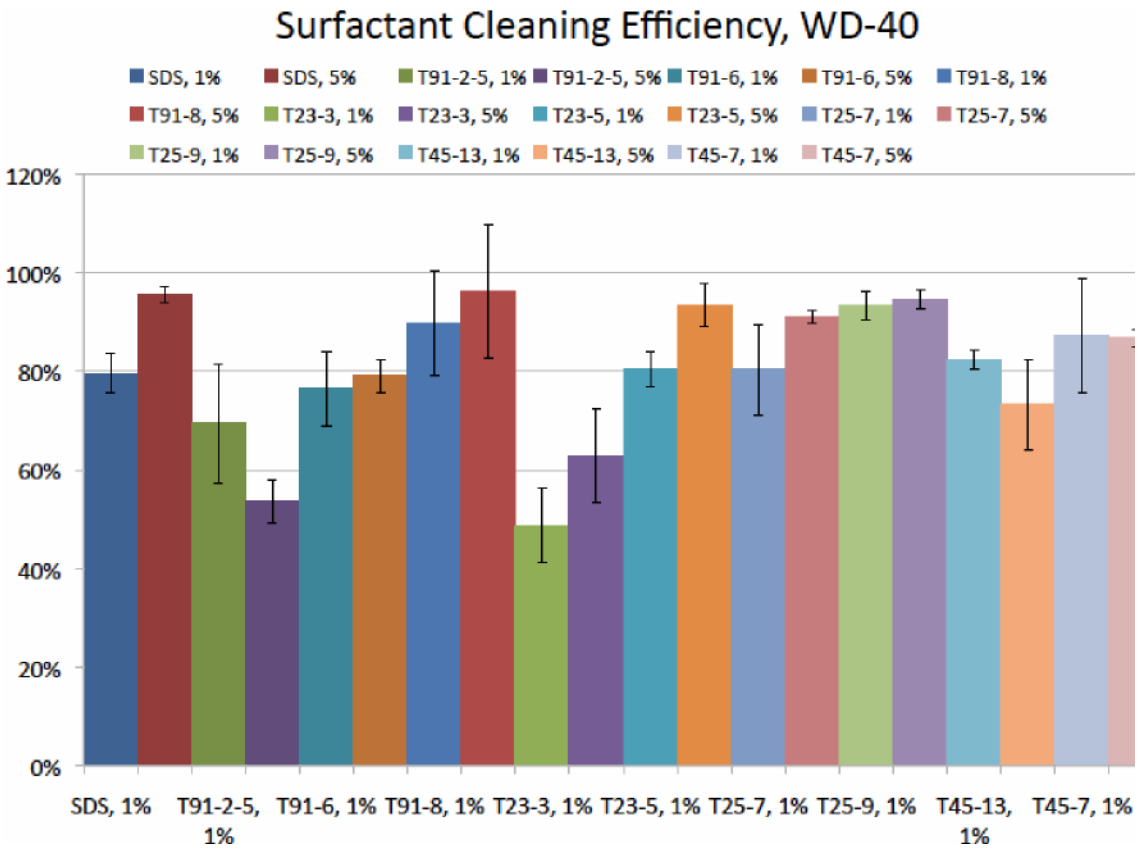

Figure 14: Immersion testing results for all surfactants evaluated for the contaminant WD40. Surfactant concentrations were 1% w/w.

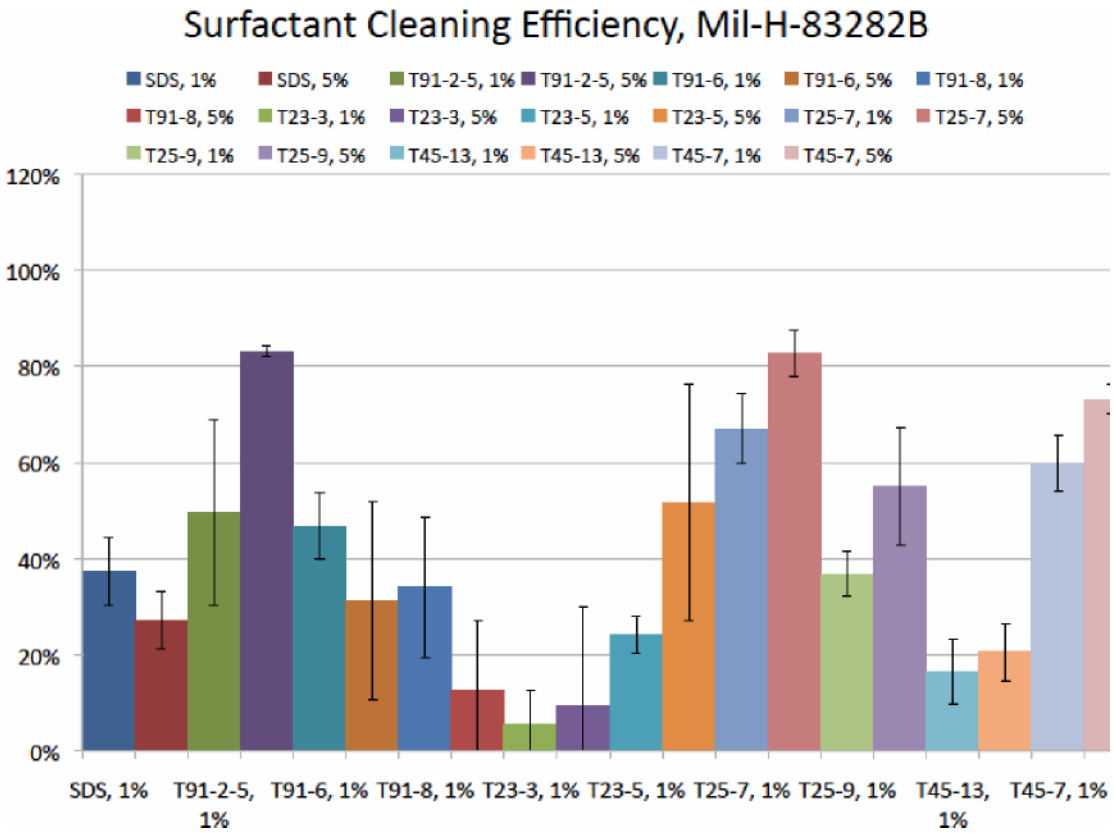

Figure 15: Immersion testing results for all surfactants evaluated for the contaminant Mil-H-83282B. Surfactant concentrations were 1% w/w.

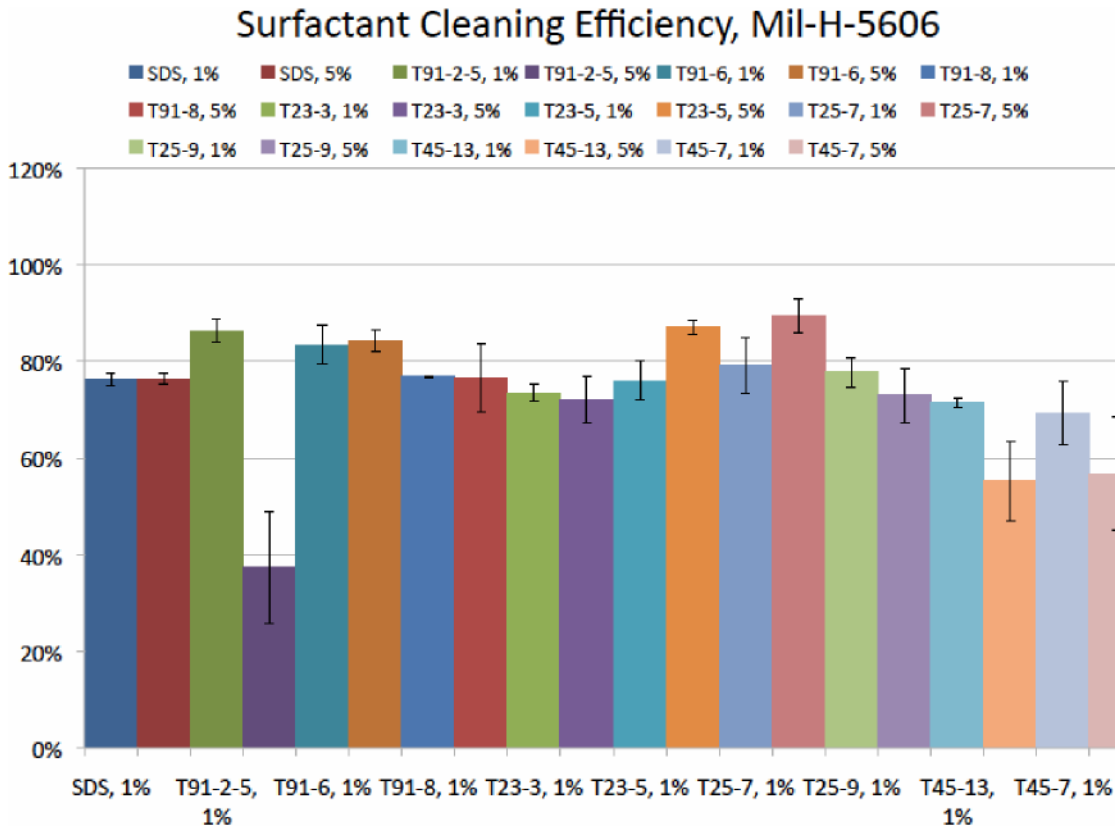

Figure 16: Immersion testing results for all surfactants evaluated for the contaminant Mil-H-5606. Surfactant concentrations were 1% w/w.

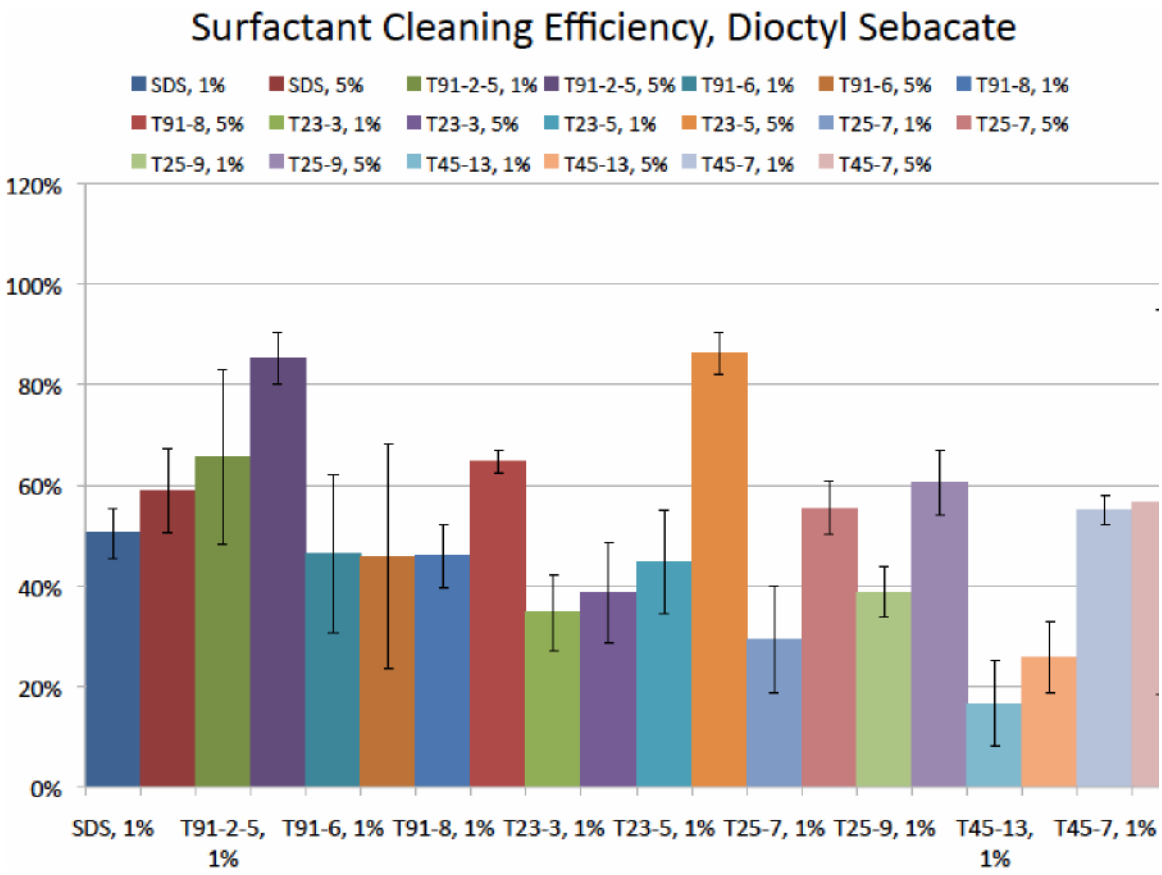

Figure 17: Immersion testing results for all surfactants evaluated for the contaminant Dioctyl Sebacate. Surfactant concentrations were 1% w/w.

Room temperature ionic liquids

Room temperature ionic liquids (RTILs) are organic salts with melting points less than 100°C. Although first synthesized in 1914, these compounds rose to prominence along with the rise the of the green chemistry/engineering movement. Due to their non-volatility and thermal stability over a wide range of temperatures, they have been touted as a potential replacement for the volatile organic compounds (VOCs) that are widely used as reaction mediums and cleaning fluids in industry. It is estimated that roughly 10^{18} RTILs are accessible from combinations of known cations and anions. Such a variety of compounds offers the opportunity to tune RTIL structure to best suit a particular application.

RTILs do come with a number of limitations. They generally have high viscosities (between 10 to 1000 times that of water), which presents difficulties in removing RTIL residue after cleaning has been completed [6]. The environmental effects of these compounds have not been yet been well studied.

It maybe possible to mitigate these undesirable characteristics either by emulsifying hydrophobic RTILs in aqueous solutions or blending hydroscopic RTILs with water. To advance this effort, RTILs specially formulated for solubilization of hydrophobic contaminants were purchased from Bioniqs as further described in the Molecular Design section. The arrival of seven candidate RTILs is expected in the next two weeks. Upon arrival of these chemicals, testing will immediately commence and results will be reported as soon as available.

Supercritical carbon dioxide

Another promising green solvent alternative is supercritical carbon dioxide. This system is based on increasing the temperature and pressure on carbon dioxide gas until it undergoes a phase change and takes on the nature and characteristics of liquid organic solvent. Preliminary tests for this type of system are promising and a system has been procured by the CGCGEY for use on this project as well as other endeavors. There are remaining questions about the impact the pressure in this system will have on components being cleaned will need to be explored.

MOLECULAR DESIGN

The current selection process for new solvents to test is not as strategic as would be desirable. Solvents were selected largely based on their availability, approximated “greenness”, and past application although little research has been conducted on the performance of these solvents in oxygen environments. While this has indeed generated some promising results, devising a method of screening solvents prior to full scale testing is highly desirable. One current means of comparing solvents and their behavior is the solubility parameter, which is a function of the energy density of the solvent. Equation 1 shows how the solubility parameter for a compound is calculated by:

$$\delta = \sqrt{c} = \left[\frac{\Delta H - RT}{V_M}\right]^{1/2} \qquad \text{Eq. 1}$$

where δ = solubility parameter ($kPa^{-1/2}$);
c = cohesive energy density (kPa);
ΔH = enthalpy of vaporization (kJ/mol);
R = gas constant (kJ/mol-K);
T = temperature (K);
And V_M = molar volume (m^3).

Solvents with similar solubility parameters will generally dissolve the same types of compounds.

Fluorinating compounds are known to change the properties of the non-fluorinated compound in unpredictable ways [7]. Such properties changes can also exhibit a non-linear response to the degree of fluorination. Such changes make predicting the properties of fluorinating compounds a challenge.

RTILs are another challenge to model. As these compounds have only starting to be intensely studied over the last fifteen years, there are no widely applicable models to predict the behavior of specific cation and anion combinations. Physical property data for RTILs is also lacking.

Molecular design of a solvent for precision cleaning of oxygen systems is a challenging task, and the software tools available are only applicable to portions of this task at best. It is important to make a distinction between virtual screening and reverse search methods. In the context of cleaning, virtual screening methods require candidate solvents to be provided by the user and then utilize property prediction methods to assess which of the candidate solvents would provide better removal of a particular contaminant. True molecular design is the reverse of property prediction and in the context of cleaning would allow the prediction of the molecular structure of a solvent from the molecular structure of a particular contaminant or set of contaminants.

Although more limited than molecular design, if the results of virtual screening software are sufficiently close to experimental results, virtual screening can be very useful because it is potentially less expensive and faster than laboratory tests. However, cleaning ability is a complex property for which robust prediction does not appear to be readily available, and generally literature articles remain the best source of candidate solvents. Property prediction methods which rely on group contribution methods based on experimental data can be very accurate within limited ranges. However, sufficient experimental data is frequently lacking. in which case ab initio methods are required.

COSMO-RS is an ab initio thermodynamic property prediction software tool that has had some limited success in some solvent screening applications. It utilizes quantum-mechanical and statistical mechanical calculations combined with some simplifying assumptions for the solute/solvent interface. It is able to predict liquid-liquid equilibrium in some cases for fluorocarbons and ionic liquids, but liquid-solid equilibrium requires additional experimental data, and COSMO-RS is not able to handle surfactants or supercritical systems well at present.
Bioniqs, (www.bioniqs.com) a company in the UK, claims to have a proprietary database which they claim allows them to “evaluate both commercially available molecular and ionic solvents to quickly identify the optimal green solvent“ for a particular task, including cleaning applications. The accuracy and utility of

bioniqs solvent selection service utilizing their proprietary database does not appear to have been evaluated in a peer reviewed journal so far.

Such means of estimating solubility behavior do not, however, take into account the environmental impacts of a solvent. To facilitate future research into green solvents, both for oxygen cleaning applications and other uses, a ranking system that combines solvent efficiency with environmental information would be helpful. Such a system should include information on environmental persistence and human health issues such as bioaccumulation and toxicity. These factors can be predicted through a variety of modeling systems based on physical properties and structures present in the solvent. One such model is the EPA's EPI (Estimation Programs Interface) Suite™. This model uses chemical structures to estimate the physical properties of a compound as well as the likely eventual environmental fate of these compounds.

Any potential solvent is limited by the fact that it needs to be employed cleaning a system that is operated under an oxygen environment. Once a list of potential solvents has been developed, the solvents will undergo oxygen compatibility testing as specified in the JTR in collaboration with White Sands Laboratory.

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APPENDIX B – Protocol Evaluation and Suggested Modifications

Engineering performance for off-aircraft oxygen line cleaning (i.e., cleaning contaminated oxygen lines removed from the aircraft) was identified by a joint group led by JG-PP and consisting of technical representatives from NAVAIR, OC-ALC, NASA, B-1, B-2, and Northrop/Grumman in 2002. This group then reached consensus on tests with procedures, methodologies and acceptance criteria to qualify alternatives against these critical technical and performance requirements.

All engineering and test requirements identified by the JG-PP participants for validating alternatives to CFC-113 and HCFC-141b used for off-aircraft oxygen line cleaning were presented in the Joint Test Report J-99-CL-015-R1 (JTR). The four primary tests include:

- Non-volatile Residue
- Soil removal
- Particle count
- Moisture content

Based on experiments conducted using the proposed non-volatile residue (NVR) test and a review of the ASTM standards that support the other three tests, it is our suggestion to modify the NVR as described below. These modifications are recommended based on optimized experimental conditions that strengthen confidence and consistency in the data over a wide range of individual tests.

The most significant proposed change to the method in support of this goal is to characterize the surface roughness of the test coupon such that the observed NVR results can be normalized to surface conditions. This is based on inconsistent results between test coupons of identical material. Furthermore, based on the findings in the JTR, we propose a shift back towards SEM to verify soil removal as the mass difference method and visual examination are not sensitive enough to detect slight, or even moderate, differences in residue when evaluating alternatives that may not perform as well as the standard case. While this is undesirable, it may be the case the most viable alternative solvents will require energy additions in the form of agitation, increased flow rate, or temperature or some combination thereof. In addition, the JTR findings that particle count was not an accurate indicator of cleanliness suggested to us that this was not a valuable test and should be removed from the protocol. This was not independently verified in our laboratory as we are not working with solid particle contaminants such as Arizona Road dust. Finally, we do not propose any modifications to the moisture content test but would suggest that there may be a need to consider higher water content alternative systems if environmental considerations continue to increase in importance and role in a final solvent design for oxygen cleaning systems.

The following are proposed modifications to the NVR test for a no-flow (or immersion) test to screen the candidate solvent's performance at removing individual or combination contaminants. This enables of quicker and more consistent qualitative measure of a solvent's potential performance without adding additional energy to the system. This approach seems more appropriate for offline oxygen cleaning. In addition, some of the alternative solvents being evaluated will be readily evaporated making the

current test protocol difficult to implement. Reducing vapor pressure of the solvent will prevent the solvent from contributing to air emissions and ozone depleting potential.

Modified NVR Testing Protocol

Storage
Cleaned coupons are stored in a glass container filled with HCFC 225.

Test Procedure

1. Remove coupons from storage container. Dry for 30 minutes at 60 to 70 °C.
2. Determine surface roughness of coupon using SEM and optical recognition software or using a contact-based portable stylus instrument
3. Weigh coupons. Record uncontaminated weight.
4. Apply contaminant to coupon using a cotton swab or similar applicator.
5. Suspend coupons vertically to allow excess oil to drip off coupon. It may be necessary to pat excess oil off using a KIM wipe.
6. Weigh contaminated coupons. Record contaminated weight.
7. Immerse coupons in test solvent. Coupon should be fully immersed. (Our tests use approximately 50 mL of solvent which results in the coupon being approximately 1/2 inch below the surface of the solvent) Immersion time is 10 minutes.
8. Remove coupons from solvent. Hold coupons horizontally to allow solvent to drip off.
9. Dry coupons in oven at 60 to 70 °C. Drying time for aqueous solvents is 3 hours. Drying time for organic solvents is 30 minutes.
10. Weigh coupons. Record post-cleaning weight.
11. Clean coupons using the Post Test Cleaning described below.

Post Test Cleaning
After testing is completed, coupons are cleaned using HCFC 225. The coupons are immersed in the solvent and the solvent is agitated. Cleaning time is 30 minutes.

Statement of Work

For

Delivery Order #027
Titled

Precision Cleaning of Oxygen Systems and Components Phase II
Oxygen Cleaning Products Preliminary Testing

Under NASA Contract Number NNH06CC40C with ITB, Inc.

PR4200267431

August 22, 2008

Statement of Work
for
The Center for Green Chemistry and Green Engineering at Yale University
for
Precision Cleaning of Oxygen Systems and Components Phase II
Oxygen Cleaning Products Preliminary Testing

1. PURPOSE

The services procured under this Statement of Work (SOW) are to provide experimental testing and evaluation of the performance of potential chemical alternatives for environmentally friendly oxygen systems and component cleaning. This project constitutes the second phase of efforts to develop and test one or more "green" alternatives to existing Class II Ozone-Depleting Substances (ODS). If a viable green alternative is found, it will be incorporated into a future demonstration/validation project.

2. SCOPE

This SOW defines the necessary testing and reporting to validate potential chemical alternatives for environmentally friendly oxygen systems and component cleaning. Testing procedures will be identified by Yale University's Green Chemistry Center and NASA will incorporate at least some of the tests and procedures outlined in the Joint Test Protocol (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).

3. REQUIREMENTS

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

3.1 General Requirements

3.1.1 Security

Access to classified information is not required.

3.1.2 Travel

Travel will include one representative from Yale's Green Chemistry Department to attend up to two (2) meetings, conferences, or other technical exchange forums approved by NASA.

3.2 Specific Requirements

This second year (Phase II) testing effort of oxygen cleaning products preliminary testing will leverage off of earlier Phase I study and final report. In that report, Yale University's Green

Chemistry Department identified potential solvents and solvent blends for further testing. The Phase II work will explore:

- Perfluorinated Compounds
- Aqueous Cleaning Solutions
- Surfactant behavior and concentration levels
- Ionic Liquids
- Super Critical Carbon Dioxide

Detailed testing requirements will be included in the project test plan to be published 30 days after contract award.

Funding for Phase II will be incrementally funded for TASK 1 and for TASK 2. Contractor may not exceed the funding limitation for the task or may start task prior to funding release.

TASK 1 (September 2008 – January 2009)

Preliminary testing with monofluorinated aliphatic hydrocarbons has shown promising results in cleaning tests (see Figure 1). Immersion tests performed with 1-fluoroheptane sow cleaning efficiency of 94% or greater for both single contaminants and contaminant mixtures. Limited immersion testing conducted with monofluorinated compounds with carbon chain lengths between nine and twelve also shows promising results. These fluorocarbons, however, suffer from a number of limitation including flammability concerns[1].

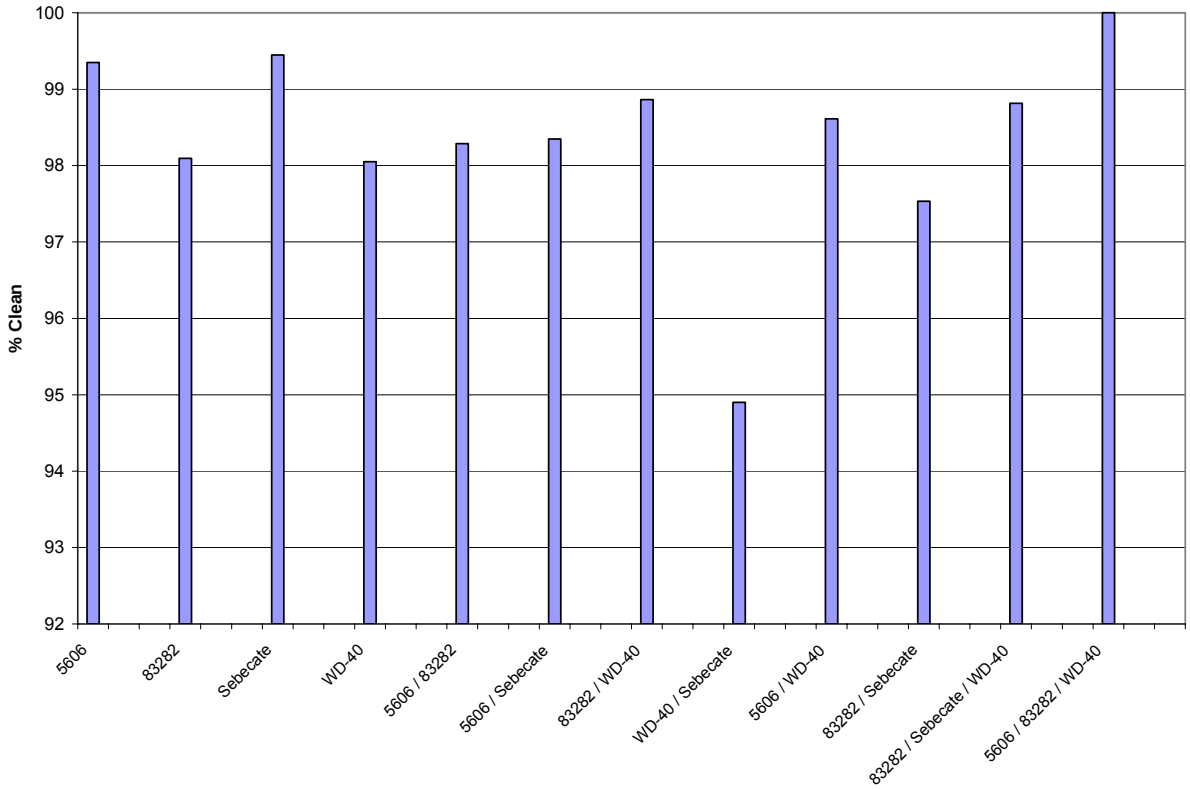

Figure 1: Immersion test results with 1-fluoroheptane.

One of the advantages of fully fluorinated (perfluorinated) compounds is their non-flammable nature [1]. Conversely, monofluorinated compounds are highly flammable, and thus may not be

suitable for use in an oxygen environment. Unfortunately, perfluorinated compounds have been known to have environmental persistence concerns [2], due to the very strong bond that forms between carbon and fluorine atoms. The persistence of these compounds is also affected by the carbon chain length such that persistence increases as chain length increases [3]. However, if chain lengths are too short, the compounds have boiling points that are below room temperature impeding their application as solvents. One additional limitation of using fluorinated hydrocarbons is that the toxicological properties of these compounds are generally not well understood and require additional investigation.

Future work with fluorocarbons will focus on finding the degree of fluorination necessary to render these compounds non-flammable, while still providing high levels of cleanliness and minimizing environmental persistence. Work will be done with chain lengths of five to seven carbons, as this excludes compounds with boiling points that are too low and compounds with unacceptably long persistence. These chain lengths also allow easy distillation of the solvents at temperatures less than 150°C, making solvent recycling more feasible, which will further reduce environmental impacts.

TASK 2 (February 2009 – September 2009):

In addition to these perfluorinated compounds, aqueous cleaning solutions are of interest, as water is both environmentally benign and compatible in an oxygen environment. Surfactants have long been utilized to increase the solvency of oils in aqueous systems as well as being used in a variety of degreasing applications [4, 5]. Surfactants also offer the advantage of being highly customizable. Surfactant behavior can be modified via such properties as surfactant concentration, temperature, and pH [4, 5]. This offers the opportunity to fine tune surfactant solutions for optimal cleaning performance.

Surfactants do come with several potential issues regarding their use including the deposition of surfactant residues on the surface being cleaned. This may necessitate the use of greater volumes of solvent for a secondary rinse stage. Furthermore, the use of surfactant may limit the ease with which cleaning solutions can be recycled.

Work will examine the effectiveness of several types of surfactants, including anionic, cationic, and non-ionic compounds. The goal will be to find the minimum surfactant concentration needed to provide acceptable cleanliness, as minimizing surfactant concentration should limit residue and recycling issues.

Room temperature ionic liquids (RTILs) are organic salts with melting points less than 100°C. Although first synthesized in 1914, these compounds rose to prominence along with the rise the of the green chemistry/engineering movement. Due to their non-volatility and thermal stability over a wide range of temperatures, they have been touted as a potential replacement for the volatile organic compounds (VOCs) that are widely used as reaction mediums and cleaning fluids in industry. It is estimated that roughly 1018 RTILs are accessible from combinations of known cations and anions. Such a variety of compounds offers the opportunity to tune RTIL structure to best suit a particular application.

RTILs do come with a number of limitations. They generally have high viscosities (between 10 to 1000 times that of water), which presents difficulties in removing RTIL residue after cleaning has been completed [6]. The environmental effects of these compounds have not been yet been well studied.

4. REFERENCES

[1] MSDS

[2] Wallington, T.J., and O.J. Nielsen, Atmospheric chemistry and environmental impact of hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs), in: Neilson, A.H. (Ed.), *The Handbook of Environmental Chemistry*, vol. 3, Springer-Verlag, Berlin, 2002, 85-102

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5. MANAGEMENT, REPORTING, AND REVIEW

The Contractor shall attend periodic progress conference calls, as directed, to provide updates on the project status. The contractor will provide quarterly progress status updatesin accordance with an approved template.

The Contractor shall draft a test protocol that identifies the test criteria necessary to demonstrate and validate the most promising chemistry products. The test protocol will describe tests necessary for recommended alternative solvents to demonstrate cleaning ability and compatibility for oxygen systems and components. Some of the tests and procedures are outlined in the Joint Test Protocol (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). Other tests shall be identified by the contractor and reviewed by NASA as they may be specific to recommended alternatives.

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.

6. PERIOD OF PERFORMANCE

The expected period of performance is October 2008 through September 2009.

7. DELIVERABLES

Item	**Delivery Schedule**
Test Protocol	30 days after contract award
Quarterly Progress Status Report	90 days after contract award, and every 90 days thereafter, except if delivery falls within 45 days of the draft or final report
Draft Final Report	35 days prior to end of period of performance
Final Report	Final day of period of performance

The Contractor shall provide these documents and any attachments or appendices in an electronic format.

8. POINTS OF CONTACT

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APPENDIX D – Deliverables

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

D1. Nov 08 – Jan 09 Quarterly Progress Status Report
D2. Feb 09 – Apr 09 Quarterly Progress Status Report
D3. Draft Test Protocol
D4. Draft Final Report