REMOVAL OF PERFLUORINATED GREASE COMPONENTS FROM NTO OXIDIZER*

Mark B. McClure
Ben Greene
Honeywell Technical Solutions Inc.
NASA Johnson Space Center
White Sands Test Facility
Las Cruces, New Mexico

Harry T. Johnson
NASA Johnson Space Center
White Sands Test Facility
Las Cruces, New Mexico

ABSTRACT

Perfluorinated greases are typically used as a thread lubricant in the assembly of non-welded nitrogen tetroxide (NTO) oxidizer systems. These greases, typically a perfluoroalkylether, with suspended polytetrafluoroethylene (PTFE) micro-powder, have attractive lubricating properties toward threaded components and are relatively chemically inert toward NTO oxidizers. A major drawback, however, is that perfluoroalkylether greases are soluble or dispersible in NTO oxidizers and can contaminate the propellant. The result is propellant that fails the non-volatile residue (NVR) specification analyses and that may have negative effects on test hardware performance and lifetime. Consequently, removal of the grease contaminants from NTO may be highly desirable. Methods for the removal of perfluorinated grease components from NTO oxidizers including distillation, adsorption, filtration, and adjustment of temperature are investigated and reported in this work. Solubility or dispersibility data for the perfluoroalkylether oil (Krytox®* 143 AC) component of a perfluorinated grease (Krytox 240 AC) and for Krytox 240 AC in NTO were determined and are reported.

INTRODUCTION

Perfluorinated greases, such as Krytox 240 AC, are typically used as a thread lubricant in the assembly of valves and threaded components for use in NTO oxidizer components and systems. Perfluorinated greases are typically composed of a grease component (such as a perfluoroalkylether) and suspended micro-particles of PTFE. Perfluorinated greases work satisfactorily for their intended purpose because their lubricating properties minimize galling of threaded components and they are relatively chemically inert toward NTO oxidizers. These greases are widely used at the NASA JSC White Sands Test Facility (WSTF). Over time, however, excess grease that contacts NTO dissolves or disperses and contaminates the propellant. This problem is exacerbated when propellant is circulated or transferred between storage units and test stands, resulting in widespread contamination. Contamination can also occur when propellant is introduced into a system that contains exposed grease that was used in the assembly of hardware including sampling containers, valves, and connectors. The resulting contaminated propellant can fail the NVR requirement of various specification analyses, and may have negative effects on test hardware performance and lifetime. Although it is recognized that prevention of contamination is the preferred solution, there remains a large volume of perfluorinated grease-contaminated propellant at WSTF. The WSTF Propellants Laboratory investigated methods for the removal of perfluorinated grease components from NTO oxidizers.

Krytox 240 AC is a mixture of a perfluoroalkylether (73 to 82 percent Krytox 143 AC oil) and PTFE (18 to 27 percent). The size distribution of the PTFE component in Krytox 240 AC is about 0.2 to 0.4 micron (μm), although agglomeration may produce particulate that is larger.

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* Krytox® is a registered trademark of E. I. Du Pont de Nemours and Company, Wilmington, Delaware.

The WSTF investigators acknowledge they did not fully understand the speciation or physical state of the perfluorinated grease components in NTO. It was nominally accepted that the particulate components were suspended, and that the oil components were soluble, dispersed, precipitated, or in any combination of these states. While methods exist for the determination of aqueous solubility, they did not seem applicable to this work and were not investigated.[1]

BACKGROUND

Experience at WSTF over the years has shown that PTFE particulate matter is effectively filtered using a 0.2-μm PTFE filter. During the sampling process, the NTO is filtered through a 0.2-μm filter. This filter would be expected to retain any particulate material, including suspended PTFE that was larger than 0.2 μm. The current WSTF particulate characterization process (optical microscopy) is capable of seeing particles as small as 3 to 4 μm, provided they have sufficient contrast against the white background of a filter. This process is unable to see small, white PTFE particles in less than silting quantities. Consequently, the relative composition of the Krytox 240 AC contaminants (Krytox 143 AC and PTFE) in WSTF NVRs is not entirely characterized. However, it has been observed during numerous NTO analyses that the NVR of 0.2-μm filtered NTO has no visible particulate matter other than what appears to be iron oxides. This suggests that the 0.2-μm filter is capable of filtering the PTFE to some degree, an occurrence that is consistent with the estimated size distribution of agglomerated PTFE (0.2 to 0.4 μm). For this reason, few experiments were performed with grease-containing particulate matter in order to simplify the experimental matrix.

Routine specification analyses of NTO oxidizers at WSTF have also led to the observation that 0.2-μm PTFE filters accumulate globules of perfluorinated oil and grease. It has also been observed that filtration is effective until the filter becomes sufficiently wetted that oil components pass through the membrane. This suggests PTFE (100 μm) as a candidate adsorbent material. Other candidate adsorbent materials were chosen based on anticipated adsorptive properties, inert chemical properties with NTO, and physical characteristics including ability to flow through and resistance to mechanical degradation.

Earlier work at WSTF showed that the solubility of Krytox 240 AC in NTO was temperature dependent. Krytox 240 AC-saturated NTO was prepared at room temperature (22 °C) by adding approximately 25 g of Krytox 240 AC to 360 mL of NTO. The mixture was allowed to stand for 1 week. The NVR obtained from the 0.2-μm filtered fluid at room temperature was reported to be 310 ±38 mg/L at 22 °C. In another experiment, the same fluid as above saturated with Krytox 240 AC at room temperature was chilled to 0 °C, then filtered through a 0.2-μm filter and the NVR obtained. This NVR at 0 °C was reported to be 100 ±24 mg/L. Although the fate of the Krytox when chilled was not known, it was possible that the Krytox 240 AC oil component came out of solution, agglomerated to a size that allowed it to be filtered, or adhered to the vessel walls when chilled.

OBJECTIVE

The objective of this work is to characterize the solubility or dispersibility of perfluoroalkylether oil in NTO and to investigate laboratory bench methods for the removal of perfluoroalkylether grease components from NTO oxidizer.

EXPERIMENTAL

REAGENTS

1,1,2-trichloro-1,2,2-trifluoroethane was obtained as 99.9+% from Aldrich, and was distilled prior to use. All NTO used in these experiments was MON-3 grade obtained from WSTF and met the NVR requirements of MIL-PRF-26539E and NASA SE-S-0073.[2,3] The iron content of the NTO met the requirements of NASA SE-S-0073 (1 ppm maximum).[3] HFE-7100 was obtained from 3M.
Krytox 143 AC, the perfluoroalkylether oil constituent of Krytox 240 AC, was obtained from Dupont.

Dryfilm GT, a PTFE powder with a primary particle size in the 0.2-µm range, was obtained from Dupont. Aluminum oxide, activated, acidic, Brockmann I, standard grade ~150 mesh, 58Å, was obtained from Aldrich. Hyflo Super Cel diatomaceous earth and PTFE (100 µm) were also obtained from Aldrich.

PROCEDURES

Hoke Cylinder NVR Determination

The Hoke®† cylinder samplers were 3 L in volume, constructed of 304 stainless steel, and fitted with Anderson Greenwood H1 valves. The H1 valves were constructed of 316 stainless steel and PTFE seat and packing soft goods. Hoke cylinder serial number (S/N) 65A914 and valves had been disassembled and cleaned to level 50A for gaseous oxygen (GOX) service, then reassembled. Krytox 240 AC had been applied during the reassembly process. Hoke cylinder S/N 65A645 and valves had been initially cleaned like S/N 65A914, but after having been placed in NTO service had been flow-cleaned with deionized water to level 100 between NTO samples.

The interior of a Hoke cylinder and its associated valves were rinsed with 1,1,2-trichloro-1,2,2-trifluoroethane as follows. Both valves were opened and the AN caps were removed; 200 mL of 1,1,2-trichloro-1,2,2-trifluoroethane were added through a clean glass funnel connected with short lengths of polytetrafluoroethane, stainless steel tubing, and stainless steel connectors to the Hoke cylinder. The funnel and connectors were then removed and the AN caps were replaced and securely tightened. The Hoke cylinder was placed in a vertical position and the valve at the low end of the Hoke cylinder was fully closed then opened five times. The Hoke cylinder was then inverted again and the valve actuation process was repeated. The Hoke cylinder was then agitated to maximize exposure of inner surfaces to fluid. After 15 min of exposure to 1,1,2-trichloro-1,2,2-trifluoroethane, the Hoke cylinder was placed in a horizontal position, the AN caps were carefully removed, and the fluid was drained into a clean, round-bottom flask.

The NVR of the fluid was then determined by distilling the bulk of the test fluid from a round-bottom flask using a hot-water bath, rinsing the remaining liquid into a tarred aluminum weigh boat with 1,1,2-trichloro-1,2,2-trifluoroethane, and drying at approximately 105 °C. The weigh boat was then equilibrated to room temperature before obtaining its final weight, which was the difference between before and after. The NVR of a 200 mL aliquot of the 1,1,2-trichloro-1,2,2-trifluoroethane was also obtained as a blank.

An aliquot of the NVR from each of the Hoke cylinder 1,1,2-trichloro-1,2,2-trifluoroethane rinses was smeared on a potassium bromide (KBr) window and its infrared spectrum was obtained using a Nicolet®‡ Magna 750 infrared spectrometer. The KBr background spectrum was subtracted from the sample spectrum by the instrument software.

Solubility/Dispersibility Experiments

Several experiments were initially performed to characterize the solubility or dispersibility of Krytox 240 AC and Krytox 143 AC in NTO. Unless otherwise specified, NVR determinations were made in triplicate using the standard platinum crucible method described in MIL-PRF-26539E.

† Hoke® is a registered trademark of Hoke Incorporated, Spartanburg, South Carolina.
‡ Nicolet® is a registered trademark of the Nicolet Instrument Corporation, Madison, Wisconsin.

Krytox 240 AC in NTO A Fisher Porter bottle containing 360 mL of NTO was spiked with approximately 3 g of Krytox 240 AC and agitated periodically for 3 h. The fluid was subsequently filtered through a 0.2-μm PTFE filter and the NVRs of replicate aliquots were determined (the result of the third aliquot of the 3-h sample was discarded because the sample was overheated). NVRs of the contents of the same Fisher Porter bottle were similarly determined after 4 days.

Krytox 143 AC in NTO A Fisher Porter bottle containing 360 mL of NTO was spiked with approximately 3 g of Krytox 143 AC and allowed to equilibrate by standing with occasional agitation. The fluid was subsequently filtered after 5 days through a 0.2-μm PTFE filter and the NVRs of replicate aliquots were determined.

A solution of 18,000 mg/L Krytox 143 AC in 1,1,2-trifluoro-1,2,2-trichloroethane was prepared in a volumetric flask. One mL of this solution was added to an empty Fisher Porter bottle and the solvent was allowed to evaporate. The subsequent addition of 360 mL of NTO to the Fisher Porter bottle produced NTO spiked with 50 mg/L of Krytox 143 AC (the initial NVR of the NTO was 5 mg/L). The Fisher Porter bottle was agitated, then two 50 mL aliquots were removed sequentially within 1 h without filtration into a glass graduated cylinder, then transferred to a platinum crucible for NVR determinations.

A Fisher Porter bottle equipped with an eductor tube containing 360 mL of NTO was spiked with approximately 3 g of Krytox 143 AC and magnetically stirred for 4 h. NTO was obtained gravimetrically by flowing without filtration into tarred platinum crucibles to avoid intermediate transfer with volumetric glassware (and potential loss to the glass surface). NVRs of the contents were subsequently determined.

Krytox 143 AC in NTO at 0 °C A Fisher Porter bottle containing 360 mL of NTO was spiked with approximately 3 g of Krytox 143 AC. The contents were magnetically stirred overnight at room temperature then allowed to settle for 6 h in an ice bath at 0 °C. Three 50-mL aliquots were decanted into platinum crucibles without filtration and the NVRs were determined.

Column Adsorption Experiments

Glass-barreled, acrylic-jacketed glass columns with PTFE jacket end fittings and 20-μm porosity PTFE bed supports were obtained from Kimble Kontes. Adsorbent, 10-μm PTFE membranes obtained from Millipore Corporation were installed above the downstream 20-μm bed supports for all experiments except the Dryfilm GT, which used a 0.2-μm PTFE membrane. The columns had an inner diameter of 1 cm, a length of 30 cm, and an internal volume of 24 mL. Stainless steel compression fittings (0.125 in. (0.32 cm) external diameter, 316 series) were attached to the PTFE end fittings to allow introduction of NTO and metering of flow. The wetted parts of the columns were PTFE, glass, and stainless steel.

Columns were packed with adsorbent material (Dryfilm GT, aluminum oxide, diatomaceous earth, and PTFE (100 μm)) by adding through a funnel while tapping lightly to minimize void spaces. Packed columns were connected to a Fisher Porter bottle containing Krytox 143 AC-saturated NTO. Each Fisher Porter bottle had approximately 3 g of Krytox 143 AC oil and 360 mL of NTO; the mixture having been magnetically stirred for hours, typically overnight, and then allowed to settle for at least 3 to 4 h prior to use. An eductor tube was immersed in the Fisher Porter bottle to a height of approximately 1 in. (2.54 cm) above the nondissolved oil level. The connections between the Fisher Porter bottle and the column were made with 1/8-in. external diameter stainless steel. NTO flow rates through the columns were adjusted using metering valves.

Because the column effluent aliquots were collected at ambient temperature (approximately 25 °C unless otherwise noted), there was evaporative loss of NTO from each aliquot collected. Reported NVR results were corrected for evaporative loss based on the time (min) required to collect each aliquot and the total evaporative loss for that experiment ((volume delivered – volume collected)/min). This calculation did not include the amount of NTO remaining on the column as it was deemed constant for each aliquot collected and small compared to the total volume lost to evaporation. Unless otherwise specified, the total volume of NTO flowed through each column was 266 or 256 mL, depending if 10 mL was withdrawn for waste, respectively.

At the beginning of each experiment a 50 mL aliquot of NTO was collected from the Fisher Porter bottle through the eductor tube. The 50 mL aliquots were collected for analysis to determine the initial NVR of the NTO. Fractions of NTO eluting from the columns were collected in 50 mL aliquots (approximately 2 bed volumes) in tarred Erlenmeyer flasks. The NVR of the collected fractions was subsequently determined after evaporation of the NTO and drying.

Dryfilm GT Dryfilm GT was packed into a column and tested as is without any solvent washing.

Aluminum Oxide Aluminum oxide was packed into a column and tested as is without any solvent washing.

Diatomaceous Earth Diatomaceous earth was washed with HFE-7100 and dried prior to column experiments.

PTFE PTFE (100 μm) was first packed into a column, flow-cleaned with HFE-7100, then dried with gaseous nitrogen prior to use. An initial 10 mL aliquot of NTO was withdrawn for waste.

PTFE at 2 °C PTFE (100 μm) was first packed into a column, flow cleaned with HFE-7100, then dried with gaseous nitrogen prior to use. Krytox 143 AC oil-saturated NTO was flowed through a jacketed column while the temperature measured at the column jacket was maintained at approximately 2 °C (1.6 to 2.1 °C) with a recirculating pump and bath. An initial 10 mL aliquot of NTO was withdrawn for waste.

Distillation Experiment

A Fisher Porter bottle containing 360 mL of NTO saturated with Krytox 143 AC was prepared as described in the column experiments. With the Fisher Porter bottle valve closed, it was connected to an evacuated Fisher Porter bottle using 0.25-in. (0.66-cm) internal diameter PTFE tubing after the line was flushed with NTO vapor. The first cylinder was equilibrated to 0 °C in an ice bath; the second cylinder was immersed in liquid nitrogen in a metal Dewar. The valves of both Fisher Porter bottles were opened and the NTO was allowed to distill. After distillation was complete the NVR of the distilled fluid was determined in triplicate using the standard platinum crucible method described in MIL-PRF-26539E. A swab sample of the NVR was collected and smeared on a KBr window and its infrared spectrum was obtained using a Nicolet Magna 750 infrared spectrometer. The KBr background spectrum was subtracted from the sample spectrum by the instrument software.

RESULTS AND DISCUSSION

PROCEDURES

Hoke Cylinder NVR Determination

The NVRs obtained from each Hoke cylinder had the visual appearance of colorless oil. The NVR weights of the blank and the Hoke cylinders are shown in Table 1.

Table 1. Hoke Cylinder NVR Results

Sample	NVR (mg)
Blank (200 mL 1,1,2-trichloro-1,2,2-trifluoroethane)	0.0
Hoke 65A914 (GOX service)	6.1
Hoke 65A645 (NTO service)	2.7

The infrared spectra of the NVR from each Hoke gave a good match with a perfluorinated alkyl ether. The specification for an A-level cleanliness is 1mg/ft^2.[4] The NVRs obtained from each of the Hoke cylinders would have caused them to fail an A-level test because the interior surface area of each cylinder is approximately 1.7 ft^2 and the equivalent NVR mass that would cause them to fail the A-level test is 1.7 mg (excluding valve internal surface areas). Since Krytox 240 AC was the lubricant used in the assembly of the two Hoke cylinders that were selected at random, the results indicate the ubiquitous presence of Krytox 240 AC in quantities that would normally cause those Hoke cylinders to fail an A-level cleanliness test. Use of less lubricant or improved lubrication procedures might be appropriate to mitigate this situation. An earlier proposal was to evaluate the application of lubricant by a spray process. Currently, electropolishing of metal surfaces is being investigated as a potential alternative to use of lubricants.

Solubility/Dispersibility Experiments

Krytox 240 AC in NTO The NVRs of Krytox 240 AC-spiked NTO (after filtration through a 0.2-µm PTFE filter) taken at 2 times after spiking were:

3 h	29 ±1 mg/L
4 days	200 ±20 mg/L

These results indicate the solubility or dispersion of Krytox 240 AC in NTO is time-dependent. Since the NVR determined after 3 h was from a mixture that was periodically agitated and the NVR after 4 days was from the same mixture that had not been periodically agitated, agitation could be expected to increase the rate of dissolution or dispersion.

Krytox 143 AC in NTO The mean NVR result of the 3 aliquots was 600 ±170 mg/L. The NVRs of Krytox 143 AC-spiked NTO that were equilibrated 5 days, then filtered through a 0.2-µm PTFE filter and determined sequentially were:

Aliquot 1	490 mg/L
Aliquot 2	530 mg/L
Aliquot 3	800 mg/L

The 0.2-µm PTFE filter membrane, initially clean, was observed to be totally wetted with oil after Aliquot 3 was filtered and the membrane was visually examined. The sequentially and dramatically increasing NVR results coupled with the observation of the PTFE filter membrane suggest the Krytox 143 AC was initially adsorbed or physically trapped by the membrane, but flowed through with time after the membrane was sufficiently wetted or saturated. This may have interesting implications in the analytical determination of NVRs of perfluoroalkylether-contaminated NTO when the fluid is first flowed through a PTFE filter because the PTFE filter clearly captures some quantity of Krytox 143 AC and the final NVR result may be artificially low due to this phenomenon. Conversely, an NTO sample relatively free of Krytox 143 AC may appear to be contaminated due to breakthrough from a PTFE filter used earlier with a Krytox 143 AC-contaminated sample.

The two NVRs of NTO spiked with 50 mg of Krytox 143 AC (solvent evaporation) determined sequentially were 11 ±1.7 mg/L and 35 ±2.9 mg/L, respectively. The glass graduated cylinder that the fluid was initially transferred to before delivery to the platinum crucible was observed to have beads of oil adhering to it. Since the background NVR of the NTO was 5 mg/L, 100 percent recovery of the NVR components would have yielded a result of 55 mg/L for each determination. These low recovery values suggest the Krytox 143 AC was not completely soluble, was not homogeneously dispersed throughout the NTO, and that some adhered to the glass graduated cylinder.

Krytox 143 AC in NTO at 0 °C The NVR determined in the three aliquots decanted from the 0 °C NTO/Krytox 143 AC-mixture was 100 ±14 mg/L. This value compared well to the 100 ±24 mg/L previously determined at WSTF and described in the Introduction.

Column Adsorption Experiments

Dryfilm GT The fluid was observed to channel severely through the column in addition to separation of the media into irregular and discontinuous bands. Flow of NTO through the media was minimal and although nitrogen dioxide (NO_2) gas was observed in the collection vessel, no effluent fluid could be obtained. It was evident that the flow characteristics were inadequate and it appeared that the filter plugged, prohibiting liquid flow through the column. This experiment was terminated with no NVR results obtained.

Aluminum Oxide The fluid flowed evenly through the column proceeded by a brown NO_2 gas front. The flow rate was maintained at approximately 3 to 4 mL/min (0.1 to 0.2 bed volumes/min); 3 to 50 mL fractions and 1 to 24 mL fractions were collected. The results are shown in Table 2.

Krytox 143 AC was partially removed from NTO on the aluminum oxide column. The data indicate that removal increased with time. A possible explanation is that accumulation of Krytox 143 AC on the aluminum oxide increases the column affinity for adsorption of additional Krytox 143 AC.

Diatomaceous Earth The column compressed about 1 in. (2.54 cm) as liquid was first introduced. Severe channeling was observed throughout the test and it could be seen that large voids between the sides of the column and the packing, and within the packing, allowed liquid to flow with a minimum of contact with the packing. Flow rate through the column was maintained at approximately 2 mL/min (~0.1 bed volume/min), and four 50-mL aliquots and one 46-mL aliquot were collected. By the end of the experiment the column height had compressed by 2 in. (5.08 cm). Results of Krytox 143 AC removal are shown in Table 3.

Table 2. Removal of Krytox 143 AC from NTO on an Aluminum Oxide Column

Fraction Number	NVR (mg/L)	% Removal
0 (initial fluid sample)	350	NA (initial sample)
1 (50 mL)	280	20
2 (50 mL)	240	30
3 (50 mL)	230	34
4 (24 mL)	220	35

Table 3. Removal of Krytox 143 AC from NTO on a Diatomaceous Earth Column

Fraction Number	NVR (mg/L)	% Removal
0 (initial fluid sample)	Sample was compromised* (330)	NA (initial sample)
1 (50 mL)	210	NC**
2 (50 mL)	230	NC**
3 (50 mL)	200	NC**
4 (46 mL)	210	NC**
* Excess lubrication (tungsten disulfide) from a valve contaminated this sample. ** Not calculated because the initial NVR was not known.		

The NVRs of the post-column aliquots were 210 ±11 mg/L and were fairly constant. There was no apparent trend in the data to indicate whether adsorption of Krytox 143 AC occurred. The initial NVR was not known because the sample was compromised; as a result these data could not be evaluated any further.

PTFE No channeling was observed throughout the test and the flow rate was maintained at about 1 mL/min (~0.04 bed volume/min). Three 50-mL aliquots and one 40-mL aliquot were collected. No attempts were made to change the flow rate through the column. Results of Krytox 143 AC removal are shown in Table 4.

The NVRs of the post-column aliquots were 180 ±9.5 mg/L and were fairly constant. The data showed that 38 ±3.3 percent Krytox 143 AC was removed from each aliquot of NTO on the PTFE column.

PTFE at 2 °C No channeling was observed throughout the test and the flow rate was maintained at about 2 mL/min (~0.08 bed volume/min). Four 50-mL aliquots and one 19-mL aliquot were collected. After the first two aliquots were collected, no attempts were made to change the flow rate through the column. There was less evaporative loss of NTO because the column bed was chilled. Results of Krytox 143 AC removal are shown in Table 5.

The NVRs of the post-column aliquots were 19 ±5.6 mg/L and were fairly constant. The exception was the first aliquot, in which the NVR nearly met the specification limit of 10 mg/L.[2, 3] Although the trend in these data was the same as the room temperature PTFE experiment above, 92 ±2.5 percent Krytox 143 AC was removed from each aliquot of NTO at the lower temperature. The collective results of this experiment suggest the following:

- Lowering the temperature of the column reduced the solubility of the Krytox 143 AC on the column (the NVR was 102 mg/L as reported above)
- PTFE has an affinity for Krytox 143 AC (as reported in the PTFE column experiment above)

Combinations of these suggested factors are likely contributors to the success of this experiment.

Table 4. Removal of Krytox 143 AC from NTO on a PTFE Column

Fraction Number	NVR (mg/L)	% Removal
0 (initial fluid sample)	280	NA (initial sample)
1 (50 mL)	170	41
2 (50 mL)	170	39
3 (50 mL)	190	33
4 (40 mL)	180	37

Table 5. Removal of Krytox 143 AC from NTO on a PTFE Column at 2 °C

Fraction Number	NVR (mg/L)	% Removal
0 (initial fluid sample)	230	NA (initial sample)
1 (50 mL)	11	95
2 (50 mL)	19	92
3 (50 mL)	23	90
4 (50 mL)	22	90
5 (19 mL)	24	89

Distillation Experiment

The NVR of the distilled NTO was 11 ±8.2 mg/L. The individual NVRs determined sequentially were 20, 10, and 4 mg/L, respectively. There was insufficient fluid to allow an initial NVR determination. A reddish-brown stain typically characteristic of iron residues was visible in each of the platinum crucibles. The swab sample gave infrared absorbance bands characteristic of a perfluoroalklyether lubricant barely discernable above the background.

These results, however, suggest that the distillation experiment was successful at removing most of the oil contaminant from Krytox 143 AC-saturated NTO. However, the ubiquitous presence of pefluoroalkylether lubricant WSTF hardware, such as fittings and the receiving vessel used in this experiment, may have contributed to its presence in the NVR.

SUMMARY OF SOLUBILITY/DISPERSIBILITY DATA

Table 6 provides a summary of solubility/dispersibility data collected during this work and elsewhere at WSTF. The data shows a wide range of NVRs, suggesting the dissolution/dispersion process is highly dependent on relative fluid and grease or oil quantities, contact time, agitation, temperature, and filtration.

Table 6. Summary of Solubility/Dispersibility Data

Perfluorinated Lubricant/ Component	Solubility/Dispersibility*	Notes
Krytox 240 AC	310 ±38 mg/L after 1 week	25 g in 360 mL NTO; 0.2-µm PTFE filter
Krytox 240 AC	100 ±24 mg/L at 0 °C after 1 week	25 g in 360 mL NTO; 0.2-µm PTFE filter
Krytox 240 AC	29 ±1 mg/L after 3 h	3 g in 360 mL NTO; 0.2-µm PTFE filter
Krytox 240 AC	200 ±20 mg/L after 4 days	3 g in 360 mL NTO; 0.2-µm PTFE filter
Krytox 143 AC	600 ±170 mg/L after 5 days	3 g in 360 mL NTO; 0.2-µm PTFE filter
Krytox 143 AC	11 ±1.7 mg/L within 1 h	50 mg/L spiked NTO; not filtered
Krytox 143 AC	35 ±2.9 mg/L within 1 h	50 mg/L spiked NTO; not filtered (determined sequentially after the above determination)
Krytox 143 AC	350 mg/L after 3 h	3 g in 360 mL NTO; 10-µm PTFE filter; from t = 0 aluminum oxide column experiment (single determination)
Krytox 143 AC	280 mg/L after 3 h	3 g in 360 mL NTO; 10-µm PTFE filter; from t = 0 PTFE column experiment (single determination)
Krytox 143 AC	230 mg/L after 3 h	3 g in 360 mL NTO; 10-µm PTFE filter; from t = 0 PTFE 2 °C column experiment (sample obtained from room temperature NTO supply; single determination)
Krytox 143 AC	100 ±14 mg/L at 0 °C after 18 h	3 g in 360 mL NTO; not filtered
*Room temperature unless otherwise specified.		

CONCLUSIONS

Perfluorinated grease components were found to be ubiquitous contaminants in WSTF hardware as evidenced by NVR determinations of two precision-cleaned Hoke cylinders.

The solubility or dispersibility of the Krytox 143 AC, the oil component of Krytox 240 AC, was found to be temperature dependent in NTO. Column adsorption with aluminum oxide removed approximately 30 percent of the spiked Krytox 143 AC NVR. Column adsorption with diatomaceous earth did not yield a calculated percent removal because the initial, baseline sample was compromised. Column adsorption with PTFE (100 μm) removed approximately 38 percent of spiked Krytox 143 AC. Column adsorption with PTFE (100 μm) at 2 °C removed approximately 92 percent of spiked Krytox 143 AC. This suggests that a combination of reducing the oil's solubility or dispersibility and flowing, oil-contaminated NTO through an oil-adsorbing column has potential as a column adsorption technique. However, resistance to flow was the limiting factor with the use of PTFE adsorbents and particle size is critical to flow. This was evidenced by a column with Dryfilm GT PTFE micro-powder that would not support flow. Channeling, column compression, and difficulty in maintaining or increasing flow rates are problems with column adsorption techniques, in addition to column regeneration or replacement activities that will produce waste materials. Columns and temperature control could in theory, however, be used to remove Krytox 143 AC from NTO tank and piping systems.

Distillation did not remove Krytox 143 AC and all other contributing components from Krytox 143 AC- saturated NTO to below the NVR specification limit.[2,3] Distillation, however, has advantages over column adsorption for several reasons including its applicability to flow-through and stationary systems. A portable or permanent distillation unit could be installed at test facilities to remove Krytox 143 AC from NTO as needed or continuously.

The collective results of this work suggest the solubility/dispersibility of perfluoralkylether grease components in NTO is not well understood.

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