Naval Research Laboratory
Washington, DC 20375-5320

NRL/MR/6180--11-9352

Assessment of the Effectiveness of Post-Refinery Antioxidant Additions to Jet A Fuel

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October 14, 2011

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
14-10-2011

2. REPORT TYPE
Memorandum Report

3. DATES COVERED *(From - To)*
3 March - 20 July 2011

4. TITLE AND SUBTITLE

Assessment of the Effectiveness of Post-Refinery Antioxidant
Additions to Jet A Fuel

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
61-9251-E-0-5

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375-5342

8. PERFORMING ORGANIZATION REPORT NUMBER

NRL/MR/6180--11-9352

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Defense Logistics Agency Energy QT
8725 John J. Kingman Road
Fort Belvoir, VA 22060

10. SPONSOR / MONITOR'S ACRONYM(S)
DLA-E

11. SPONSOR / MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
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14. ABSTRACT

This study was conducted in support of the Air Force Jet A initiative to deploy commercial Jet A as a “drop in” replacement for MIL-SPEC JP-8 fuel. The effectiveness of antioxidant additives when added to additive-free Jet A fuel at either point of use or at delivery was evaluated through thermal stressing of hydrotreated Jet A fuels at 90 °C under 100 psig oxygen for up to 96 hours in accordance with ASTM D5304 (low pressure reactor, LPR). Hydroperoxide concentrations did not exceed the limit of 8 ppm (1 meq/kg) in two hydrotreated Jet A fuels and 14 CONUS Jet A fuels after 16 hours of LPR stress. This was taken as an indication that these fuels would be stable in ambient storage for at least two years without added antioxidants. The findings also indicated that there may be some decrease in storage and possibly thermal stability with the addition of the JP-8 additive package, consisting of a corrosion inhibitor, antistatic additive and the fuel system icing inhibitor, to Jet A fuel. While these results indicate that Jet A fuels can be stored without antioxidants, it was recommended that antioxidant-free fuels in storage be periodically checked for hydroperoxide formation.

15. SUBJECT TERMS

Jet A	Antioxidant	Air Force Jet A Initiative
JP-8	Storage Stability	

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Robert E. Morris
a. REPORT Unclassified	**b. ABSTRACT** Unclassified	**c. THIS PAGE** Unclassified	UU	46	**19b. TELEPHONE NUMBER** *(include area code)* (202) 767-3845

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

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ABBREVIATIONS

AFPET	Air Force Petroleum Office
AO	antioxidant
ASTM	American Society for Testing and Materials
CI	Corrosion inhibitor
CRC	Coordinating Research Council
DiEGME	Diethyleneglycol monomethyl ether
DLA-E	Defense Logistics Agency-Energy
DTBP	2,6-di-t-butyl phenol
DTBMP	2.6-di-t-butyl-4-methyl phenol
GC-MS	Gas chromatography with mass selective detection
HT	Hydrotreated
IAD	Dulles International Airport
JFTOT	Jet Fuel Thermal Oxidation Test
LPR	Low pressure reactor
MDL	Method detection limit
meq/kg	milliequivalents per kilogram
MQL	Method quantitation limit
NFPM	Navy Fuel Property Monitor
NRL	Naval Research Laboratory
PPM	parts per million (milligrams per liter)
PSI	pounds per square inch
ROOH	hydroperoxide
SDA	Static dissipater additive
SIM	Selected Ion Monitoring
SNR	signal-to-noise ratio
STP	Special Technical Publication
SwRI	Southwest Research Institute
TBP	2-t-butyl phenol
TIC	Total Ion Chromatogram
TTBP	2,4,6-tri-t-butyl phenol
ULSD	ultra-low sulfur diesel

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1.0 OBJECTIVE

The objective of this proposed study is to determine if Jet A fuel stability can be mediated appropriately by adding an approved antioxidant (AO) to purchased product downstream in the supply chain. The success of late additive addition will depend on the effectiveness of the antioxidant to suppress ongoing autoxidation and the impact of oxidation that may have occurred during transport and storage before the antioxidant was introduced. This is critical for deployment of commercial Jet A as a "drop in" replacement for MIL-Spec JP-8 fuel in military tactical platforms.

Since commercial Jet-A fuel does not require an approved antioxidant additive (AO), it is necessary to establish whether or not acceptable stability can be ensured by adding AO after receipt or storage. The objective of this study is to resolve the following two issues:

1) The extent to which antioxidant-free Jet-A fuels tend to undergo autoxidative degradation in the supply chain, and the response of these fuels to addition of an approved antioxidant at the point of use.

2) The relative effectiveness of adding approved antioxidants to a reactive Jet fuel at the refinery vs. adding the antioxidant after the fuel has undergone autoxidative degradation in the supply chain.

2.0 BACKGROUND

Fuel Autoxidation. Fuel stability is defined as the resistance of a fuel to undergo chemical processes that lead to either undesirable changes in properties or the formation of insoluble reaction products such as gums and sediments. Two types of stability, low-temperature storage and high-temperature thermal oxidation, are of concern. It is widely accepted that free-radical autoxidation is the predominant chemical mechanism that affects fuel stability during storage and use. A generalized mechanism for hydrocarbon autoxidation is shown in Scheme 1. Autoxidative degradation involves chemical changes that lead to oxidation of fuel molecules to form a variety of oxygenated species, often resulting in the accumulation of hydroperoxides (ROOH), as shown in equation 4. Hydroperoxides have been known to attack elastomers in the fuel system, particularly in the fuel control lines. Hydroperoxides can also play a key role in the degradation processes of aviation fuels by initiating a variety of free-radical reactions. Heteroatomic (i.e., nitrogen, sulfur, and oxygen) bearing species are particularly subject to involvement in these types of reactions.

Manuscript approved August 2, 2011.

Initiation:

$$2RH + O_2 \rightarrow 2R^{\bullet} + H_2O_2 \qquad (1)$$

$$RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet} \qquad (2)$$

Propagation:

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \qquad (3)$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \qquad (4)$$

Chain Branching:

$$2ROOH \rightarrow ROO^{\bullet} + H_2O + RO^{\bullet} \qquad (5)$$

$$ROOH \rightarrow RO^{\bullet} + HO^{\bullet} \qquad (6)$$

Termination:

$$2ROO^{\bullet} \rightarrow \text{alcohols, ketones} \qquad (7)$$

$$ROO^{\bullet} + R^{\bullet} \rightarrow ROOR \qquad (8)$$

$$2R^{\bullet} \rightarrow R\text{-}R \qquad (9)$$

Scheme 1. Generalized hydrocarbon free-radical autoxidation mechanism.

Antioxidant additives have thus been developed and are used to inhibit this free-radical process by donating a hydrogen radical, which serves to terminate the radical chains, as shown in Scheme 2. These antioxidants are generally phenolic and are often hindered at the 2- and 5-positions to sterically stabilize the resulting phenoxy radical. A common antioxidant is 2,5-di-t-butyl-4-methylphenol, where the electron donating character of the 4-methyl group further stabilizes the phenoxy radical. However, electron delocalization can occur to produce the 4-methyl radical, which can further react in accordance with equations 11 – 13. It has been shown[1] that two 2,5-di-t-butyl-phenol-4-methyl radicals can react with oxygen to form an oxygen bridged adduct (eq. 14) which has been reported[2] to be stable up to temperatures between 60 – 150°C (eq. 15) .

Since hydrotreatment tends to remove naturally occurring phenols and thiols that can act to inhibit autoxidation, these fuels tend to more readily undergo autoxidation and can be unstable without the aid of antioxidants. Previous examinations of additive behavior on diesel fuel storage stability at elevated temperatures have produced mixed results. At 100 °C and 100 psig of oxygen, reductions in insolubles and hydroperoxides were reported by Nixon[3] in the presence of two different hindered phenols, whereas these same antioxidants were ineffective in ASTM D4625 long-term storage tests[4] at atmospheric pressure at 43°C.

Inhibition:

$$ROO^{\bullet} + InH \rightarrow In^{\bullet} + ROOH \qquad (10)$$

$$ROO^{\bullet} + In^{\bullet} \rightarrow In\text{-}OOR \qquad (11)$$

$$R^{\bullet} + In^{\bullet} \rightarrow In\text{-}R \qquad (12)$$

$$2In^{\bullet} \rightarrow In\text{-}In \qquad (13)$$

Reactions with oxygen:

$$R^{\bullet} + O_2 \rightarrow In\text{-}O\text{-}O\text{-}In \qquad (14)$$

$$In\text{-}O\text{-}O\text{-}In \rightarrow 2In^{\bullet} + O_2 \qquad (15)$$

Disproportionation:

$$In\text{-}OOR \rightarrow In^{\bullet} + O_2 + R^{\bullet} \qquad (16)$$

$$In\text{-}R \rightarrow In^{\bullet} + R^{\bullet} \qquad (17)$$

Scheme 2. Free-radical inhibition by hydrogen atom donation (In = inhibitor).

The effectiveness of phenolic antioxidants is related to the structure and concentration of the additive as well as the age and composition of the fuel. In addition, the nature of the test employed to assess thermal stability has often influenced the behavior of the antioxidants. While phenolic antioxidants have been used with varying degrees of success, evidence suggests that they are more effective[5,6] when added at the refinery, or shortly thereafter.

Jet Fuel Storage Stability. Jet fuel storage stability is generally not an issue due to the fact that jet fuels contain fewer reactive constituents, e.g., aromatics, unsaturated compounds, acids, nitrogen- and oxygen-bearing constituents, all of which can impact stability in storage. The Coordinating Research Council Group on Oxidation Stability of Jet Fuels[7] agreed in 1980 to form a panel that would develop a procedure to determine the hydroperoxide potential of jet fuels. Three round robins and 12 participating laboratories worked towards this goal. Temperatures ranging from 43°C to 100°C and stress periods of 3, 7, 24, 48, 72, 96 and 168 hours and 14, 21, 35 and 56 days were investigated. Sample sizes varied between 250 mL to 400 mL, and aliquots were removed and analyzed at the various stress times. The outcome of this program was a proposed Go/No-Go test conducted with 400 mL samples stressed at 65°C for 1, 2, 3, 4 and 6 weeks.

ASTM D4625 is a widely accepted method to predict the storage stability of middle distillate diesel fuels. This method entails stressing 400 mL of filtered fuel for specified periods ranging from 4 to 24 weeks at 43°C in vented borosilicate bottles. After cooling, the test samples are filtered and total insolubles are gravimetrically measured. This method was cited in two papers as part of an ASTM Special Technical Publication (STP) on distillate fuel cleanliness[8,9] as showing good correlation with long-term ambient storage. In the STP paper by Garner and White it was stated that one week of accelerated storage at 43°C yields essentially the same quantities of total insolubles in diesel fuels as one month of storage at ambient conditions.

Pande, et al.[10] had concluded that stressing jet fuels with the NRL Low Pressure Reactor (LPR) at 100°C and 50 psig of air for up to 48 hours was adequate in assessing long-term storage stability of jet fuels. In 1999, the Coordinating Research Council (CRC) sponsored a joint program[11] to develop a test for hydroperoxide potential and antioxidant effectiveness of aviation fuels. Participating laboratories were Southwest Research Institute (SwRI), the Naval Research Laboratory (NRL), Naval Air Warfare Center (NAWC, now NAVAIR at Patuxent River NAS), and the National Institute of Petroleum and Energy Research (NIPER). Three test regimens were examined. The 43°C bottle test (ASTM D4625), a SwRI 65°C bottle test, and the NRL low pressure reactor (LPR) at 50 psig air at 100°C, which later formed the basis for ASTM D5304 at 100 psig oxygen and 90°C. A variety of antioxidants were examined in two hydrocracked blending stocks and blends with light cycle oil. Correlations with antioxidant structure, stress regimen and fuel quality were obtained. At the conclusion of this study, it was recommended that the LPR should be used at a minimum of 24, 48 and 96 hours to evaluate the effectiveness of antioxidants for use in jet fuels as an alternative to the 12 weeks required for the 43°C test.

The LPR test conditions for hydroperoxide potential measurements as recommended in the CRC report were based on data from flask oxidation tests conducted by Hardy and Black[12] with four different jet fuels stressed at 50, 100 and 120°C in air at atmospheric pressure. Since the 50°C tests had not been completed at that time, they extrapolated the data to estimate how long it would have taken for the most reactive fuel to reach 8 ppm hydroperoxides. Additionally, they used data from earlier work with a different fuel from the same refinery at 100°C to obtain that data point. Using these data, they obtained a linear Arrhenius plot of the rate of hydroperoxidation to reach 8 ppm vs temperature. From this, they obtained an estimate of the activation energy and frequency factor for that process, which agreed with other published values. This validated the use of these data to predict hydroperoxidation rates. Using this, they developed a correlation between the LPR test conditions and ambient storage times, which later became part of ASTM D5304.

However, extrapolation of these data from heated flasks that are open to the atmosphere to the thermal stress conducted under high pressures of oxygen or air in the LPR, assumes that the autoxidation mechanisms remain unchanged and it is only the rates of these processes that are accelerated. It is beyond the scope of this investigation to test that hypothesis to either validate or derive new relationships between LPR stress and ambient storage times of aviation fuels.

In this study, in order to evaluate the effectiveness of hindered phenolic antioxidants, the fuels were stressed in accordance with ASTM D5304, i.e., 90°C at 100 psig oxygen. In the absence of a definitive link between the LPR and ambient storage of jet fuels, the criterion of ASTM D5304, i.e., 1 meq/kg (8 ppm active oxygen) at 16 hrs stress in the LPR was used as an indicator of ambient storage stability for 1 - 2 years.

3.0 EXPERIMENTAL

3.1 Supply Chain Analysis

An in-depth analysis was conducted by the Defense Logistics Agency-Energy (DLA-E) of the JP-8 Supply Chain from procurement (refinery) to Defense Fuel Supply Point to Service activity issuing product to end user. This was intended to provide information about the range of expected fuel residence times from procurement to issue to end user. The findings of this analysis were used to put into perspective the potential for risk of fuel autoxidation in the supply chain.

3.2 Fuel Samples

A total of 22 fuel samples were provided for this study by Southwest Research Institute **(**SwRI) and the Air Force Petroleum Office (AFPET). These fuels are shown in Table 1.

Hydrotreated Jet A fuels. Two baseline hydrotreated (HT) Jet A fuels (#10-1, #10-2) were obtained by SwRI from two different refineries, one with the antioxidant package and one without. SwRI prepared JP-8 simulant fuels (#10-3, #10-4) from each of these two Jet A fuels by adding the "JP-8 package", which consisted of a static dissipater additive (SDA, 1 mg/L), corrosion inhibitor (DCI-4A, 15 mg/L) and fuel system icing inhibitor (dielethyleneglycol monomethylether, DiEGME, 1500 mg/L). The JP-8 additive package was added to the additive-free Jet A (#10-02), and the AO-37 antioxidant additive package was added to both of these samples, to allow direct comparison of the impact of the antioxidants on the same fuels. This was necessary since the differences in reactivity between the two base fuels were greater than the impact of the antioxidant on each fuel. The fuel blending scheme is summarized in Figure 1.

The two HT Jet A fuels were also stressed by SwRI at 43°C in accordance with ASTM D4625 and aliquots of these fuels (#10-19, 10-20) were provided to NRL for testing and analysis. The SwRI test program also included assessment of thermal stability of these test fuels in accordance[13] with ASTM D3241. In addition, an Australian jet fuel (#10-17) and a Jet A fuel from a local airport (#10-18) were obtained.

Into-Plane JP-8 Fuels. Since the initial findings of this study were based on only two selected hydrotreated Jet A fuels, it was necessary to include an evaluation of representative Jet A fuels to assure that the results obtained were representative of the variance in fuels that would be encountered in practice. The Air Force Petroleum Office (AFPET) provided the 14 into-plane Jet A fuel samples shown in Table 1.

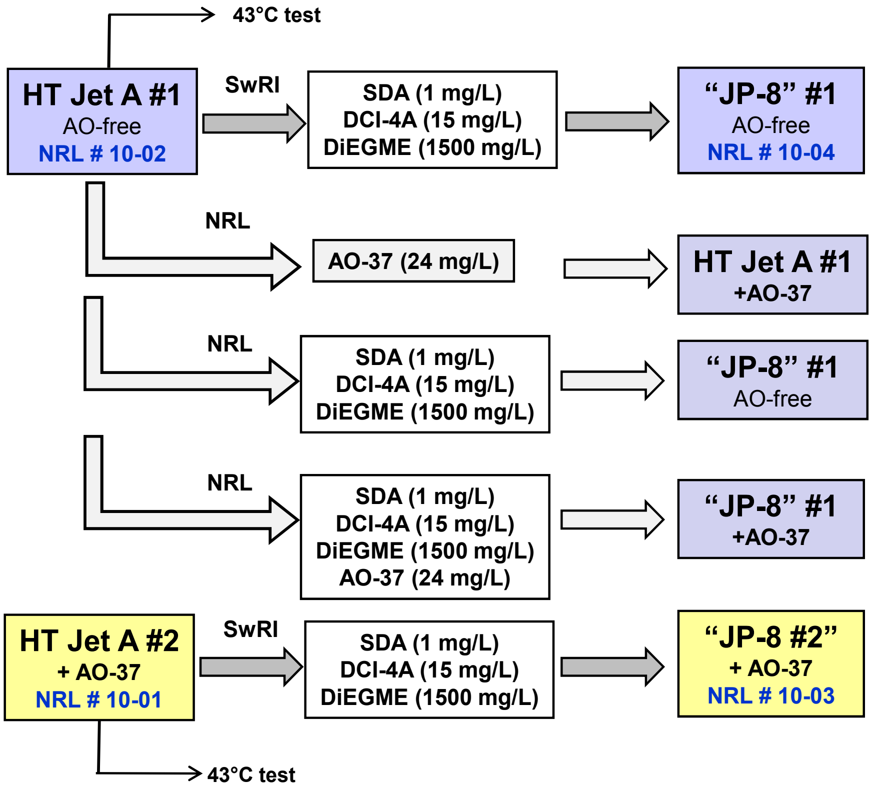

Figure 1. Summary of test fuels provided by Southwest Research Institute and samples derived from them by addition of various additives.

3.3 Additives

The AO-37 additive package was obtained from Innospec and used as received. Diethyleneglycol monomethyl ether, Stadis 450 antistatic additive and the DCI-4A corrosion inhibitor additive were provided by NAVAIR.

Table 1. Fuel samples used in the test program.

NRL I.D.	Sampling Date	Description	Source
10-1	--	HT Jet A #2 + AO	SwRI
10-2	--	HT Jet A #1	SwRI
10-3	--	HT Jet A #2 + AO + JP-8 additives	SwRI
10-4	--	HT Jet A #1 + JP-8 additives	SwRI
10-17	--	Australian Jet A fuel identified as unstable	Australian MRL
10-18	--	Jet A	Local Airport
10-19	--	HT Jet A #1 after 8-week 43°C stress	SwRI
10-20	--	HT Jet A #2 + AO after 8-week 43°C stress	SwRI
11-11	04 Feb 2011	Into-Plane from Fairfield AFB, WA #29802	AFPET
11-12	16 Feb 2011	Into-Plane from Charleston, SC #29984	AFPET
11-13	15 Feb 2011	Into-Plane from Columbus, IN #30010	AFPET
11-14	16 Feb 2011	Into-Plane from Amarillo, TX #30035	AFPET
11-15	15 Feb 2011	Into-Plane from Ozark, AL #30041	AFPET
11-16	27 Jan 2011	Into-Plane from Brady, TX #30042	AFPET
11-17	14 Feb 2011	Into-Plane from Morgantown, WV #30043	AFPET
11-18	17 Feb 2011	Into-Plane from Tulsa, OK #30046	AFPET
11-19	16 Feb 2011	Into-Plane from Farmingdale, NY #30068	AFPET
11-20	17 Feb 2011	Into-Plane from Norman, OK #30099	AFPET
11-21	14 Feb 2011	Into-Plane from Tyler, TX #30100	AFPET
11-23	17 Feb 2011	Into-Plane from Fayetteville, AR #30109	AFPET
11-25	17 Feb 2011	Into-Plane from Frankfort, KY #30036	AFPET
11-26	14 Jan 2011	Into-Plane from Windsor Locks, CT #30017	AFPET

Table 2. Estimated properties of provided test fuels from NFPM analysis.

Characteristic	Units	Spec	HT Jet A #1		HT Jet A #2	
			Jet A + AO	JP-8 + AO	Jet A neat	JP-8 neat
			10-01	10-03	10-02	10-04
Flash Point	°C	> 38	52.8	56.1	65.7	68.9
Density (15 °C)	Kg/L	0.788 - 0.845	0.807	0.808	0.816	0.818
Viscosity (-20 °C)	mm2/sec	<8.5	4.9	5.1	5.8	6.2
FSII	Vol%	0.10 - 0.15	-0.03	0.09	-0.02	0.08
Freeze Point	°C	<-46	-46.9	-46.8	-46.9	-46.7
Aromatics	Vol%	<25	17.8	18.3	14.8	15.4
Naphthalenes	Vol%	N/A	1.7	2.0	2.5	2.7
Saturates	Vol%	N/A	80.0	79.9	83.7	83.3
Pour Point	°C	N/A	-67.3	-66.4	-65.1	-64.1
Dist. IBP	°C	N/A	137.3	141.5	140.3	148.6
Dist. 10%	°C	< 185	168.5	166.9	170.3	173.7
Dist. 20%	°C	N/A	179.0	178.3	181.4	184.5
Dist. 50%	°C	N/A	209.1	209.4	212.0	215.2
Dist. 90%	°C	N/A	249.4	252.2	247.4	251.3
Dist. FBP	°C	< 330	268.7	271.9	262.0	266.0

3.4 Laboratory Studies

Fuel Sample Characterization. The fuels obtained from SwRI were analyzed with the Navy Fuel Property Monitor[14] (NFPM), which is an automated fuel analyzer based on chemometric modeling of near-infrared spectra. The NFPM is designed to identify a fuel sample and provide estimates in real-time of a range of critical specification properties for that grade of fuel. From the results shown in Table 2, it is evident that the two hydrotreated Jet A fuels were obtained from different refineries, one containing AO-37 and one without the antioxidant package

Fuel Stressing Procedure. To simulate long-term ambient storage, the low pressure reactor (LPR) was used to stress the fuels in accordance with ASTM D5304[15]. This is an accepted method to simulate long-term storage of diesel fuels. The stress regime used in this study was 90°C under 100 psig oxygen for time periods of 24, 48 and 96 hours. For each fuel sample, three bottles of fuel were stressed: two bottles for insoluble products determination in duplicate, and one bottle for hydroperoxides, antioxidant concentration, and GC-MS analysis. The AO-37 antioxidant package was added to the fuels at the maximum allowable concentration (24 mg/L), per MIL-DTL-83133F[16].

Jet fuels don't generally form measureable quantities of filterable particulates in storage or in accelerated stability testing, and this was confirmed in this study. We therefore based our assessment of autoxidation and antioxidant effectiveness on hydroperoxide formation.

In order to compare the impact of temperature and oxygen vs air the initial 4 test fuels from SwRI, the Australian fuel, and the fuel obtained from a local airport were stressed at both LPR test conditions. In Table 3, the times required to attain the limit of 1 meq/kg (8 ppm) hydroperoxides in the LPR at 90°C under 100 psig O_2, and at 100°C under 50 psig air are compared. What is evident from Table 3, is that under both sets of test conditions, there is no consistent trend between LPR testing at 90°C and 100°C. HT Jet A#1 was more susceptible to oxygen content, whereas HT Jet A #2 seemed to respond more to the higher temperature. The JP-8 additive package also seemed to exert the same deleterious impact on hydroperoxidation at both test conditions. It is interesting to note that in the stable Jet A fuel from the local airport, the different test conditions had no significant impact on hydroperoxidation.

Table 3. Impact of LPR test conditions on the time required for each of the test fuels to accumulate 1 meq/kg (8 ppm) hydroperoxides from autoxidation.

NRL #	Description	Hours, 100°C, 50 Psi Air (CRC)	Hours, 90°C, 100 Psi O_2 (NRL)
10-02	HT Jet A #1	160	104
10-01	HT Jet A #2 + AO	67	106
10-04	HT Jet A #1 + JP-8 additives	65	36
10-17	Australian Jet A	74	113
10-18	Jet A from local airport	204	208

Based on the comparative data from the two LPR conditions, while there are some fuel dependent differences in response, it is evident that even at the higher temperature, all the base fuels were stable for up to at least 65 hrs, which would be equivalent to up to at least 2 years of ambient storage, in accordance with ASTM D5304.

Hydroperoxide Concentrations. Hydroperoxides were measured by indirect iodometry in accordance with ASTM method[17] D3703, using potentiometric endpoint detection. Results were expressed in milliequivalents per kilogram (meq/kg) and averages of the replicate determinations were converted to PPM active oxygen by multiplying by eight. A Mettler DL-20 automatic titrator with a platinum ring combination electrode was used. Distilled water was boiled each day in order to remove any dissolved carbon dioxide gas present prior to testing. Thiosulfate titrant (0.01 N) was standardized with a minimum of two replicates using potassium dichromate. After standardization, the absence of free iodine in the potassium iodide reagent was ensured by obtaining a solvent blank ≤ 0.005 meq/kg. All hydroperoxide determinations were conducted in replicate, using approximately 8 grams of fuel per titration. In order to preserve the samples until the titrations could be completed, the stressed fuels were stored in a freezer and then brought to room temperature before analysis.

Antioxidant Concentrations. An in-house method was developed to monitor all the constituents in the AO-37 additive package during simulated storage. This method was based on gas chromatography-mass spectrometry (GC-MS) with selective ion monitoring (SIM), however, some of the constituents had interferences caused by the co-elution of the fuel. One additive component, 2,4,6-tri-tert-butylphenol (TTBP), eluted separately and was quantifiable. By knowing the percentage of TTBP in the AO-37 additive package, the consumption rates of the AO-37 could be estimated. Most jet fuels encountered were found to contain trace levels of antioxidant, presumably acquired from contact with wetted surfaces in the fuel handling system that have been exposed to other fuels containing antioxidants. This was verified to indeed be the case and not an artifact of the analytical procedure. The GC-MS SIM method for antioxidant quantification in jet fuels is described in Appendix A.

4.0 RESULTS AND DISCUSSION

4.1 Supply Chain Analysis

DLA-E provided an analysis of typical Department of Defense JP-8 jet fuel storage residence times in the U.S. as shown in Table 4. Tank residence times were calculated as the quotient of the maximum storage capacity by the average monthly fuel deliveries in gallons. The data in Table 4 indicate that the average storage time for JP-8 was three months over all reported locations, with no locations storing jet fuel longer than 11 months. The percentage of total storage capacity that is turned over per month can be estimated by dividing the average monthly quantities by the system maximum storage capacity. While the actual residence time of a particular fuel in a given tank will depend on the extent of mixing, it still seems reasonable to assume that in the cases given in Table 4, the maximum jet fuel storage time after receipt would be on the order of one year, with most locations turning over their supplies in less time.

4.2 Initial Fuel Survey

Filterable Insolubles. The initial fuel survey was conducted with the five test fuels received from SwRI. Samples were stressed in the LPR and total insolubles gravimetrically determined in accordance with ASTM D5304 under 100 psig oxygen at 90°C for 24, 48 and 96 hours. The results of the LPR testing are shown in Table 5. The low levels of insolubles (filterable particulates + adherent gum) produced after 96 hours of LPR stress, revealed that despite the fact that these jet fuels were purportedly severely hydrotreated, they exhibited excellent storage stability in this test. Therefore, it was not deemed necessary to conduct further gravimetric measurements of insoluble products. Subsequent experiments were thus focused on liquid-phase analysis to monitor antioxidant consumption and hydroperoxide formation which could serve as an indication of autoxidation that could affect resultant thermal stability.

Table 4. Military JP-8 Jet fuel turnover rates (source: Defense Logistics Agency Energy).

Location	Average Monthly Use (USG)	System Max Storage (USG)	Storage Time (Months)	%Storage Capacity per Month
NAS Pensacola, FL	695,236	7,581,000	10.9	9%
Pearl Harbor, HI	5,788,544	55,188,000	9.5	10%
JRB Fort Worth, TX	510,746	4,762,800	9.3	11%
NAS Meridian, MS	628,365	3,003,000	4.8	21%
NAS Kingsville, TX	541,817	2,423,400	4.5	22%
MCAS Yuma, AZ	1,207,117	5,359,200	4.4	23%
CBC Gulfport, MS	3,487	12,600	3.6	28%
NAS New Orleans, LA	427,924	1,512,000	3.5	28%
MCAS Kaneohe Pearl Harbor, HI	863,620	2,431,800	2.8	36%
MCAF Camp Pendleton, CA	1,577	4,200	2.7	38%
CAMP Lejeune, NC	109,906	289,800	2.6	38%
Naval Base Ventura, CA	481,815	1,150,800	2.4	42%
NALF Orange Grove, TX	40,183	75,600	1.9	53%
NAS Whidbey Island, WA	2,061,803	3,393,600	1.6	61%
NAS Whiting Field, Milton, FL	292,874	415,800	1.4	70%
NAF El Centro	1,205,474	1,675,800	1.4	72%
NAS Fallon	2,421,649	2,969,400	1.2	82%
MCMWTC Pickle Meadows, Bridgeport, CA	11,932	12,600	1.1	95%
MCAF Quantico, VA	141,036	142,800	1.0	99%
NAS Patuxent River, MD	99,970	84,000	0.8	119%
NWC China Lake, CA	675,307	378,000	0.6	179%
NAS Corpus Christi, TX	32,028	16,800	0.5	191%
MCB 29 Palms, CA	162,923	58,800	0.4	277%
MCLB Albany, GA	16,443	4,200	0.3	392%
NAWC Lakehurst, NJ	21,495	4,200	0.2	512%

Table 5. Total insolubles measured in fuels as received after LPR stress.

NRL I.D.	Fuel	Filterable Insolubles (mg/100 mL)		
		24 h	**48 h**	**96 h**
10-01	Jet A#2 + AO	0.0	0.1	0.0
10-02	Jet A#1	0.0	0.5	0.3
10-03	Jet A #2 + JP-8 additives + AO	0.0	0.2	0.0
10-04	Jet A #1 + JP-8 additives	0.2	0.3	1.0
10-17	Jet A	0.2	0.1	0.1

Hydroperoxide concentrations. The hydroperoxides measured in the original test fuels shown in Table 6, indicate that only those HT Jet A fuels containing the JP-8 additive package produced hydroperoxides at levels of more than 8 ppm active oxygen. Comparison of the levels of hydroperoxides reached in the HT Jet A fuel samples #10-1 and #10-2, further indicate that these two fuels had different reactivities and thus could not be used interchangeably to compare the impact of adding antioxidant.

Table 6. Hydroperoxides developed in the SwRI fuels during D5304 stress.

NRL I.D.	Fuel Sample	Hydroperoxides, ppm Active Oxygen			
		0 hrs	**24 hrs**	**48 hrs**	**96 hrs**
10-1	HT Jet A#2 + AO	<0.1	2.2	1.4	7.2
10-3	HT Jet A#2 + JP-8 additives + AO	0.2	1.0	**8.4**	**16.9**
10-2	HT Jet A#1	1.3	3.3	3.5	5.0
10-4	HT Jet A#1 + JP-8 additives	1.0	4.9	**8.5**	**9.1**
10-17	Australian Jet	0.8	3.8	0.9	7.2

4.3 Antioxidant Effectiveness

Ultra Low Sulfur Diesel. To illustrate how AO-37 performs to suppress autoxidation in a highly peroxidizing fuel during D5304 LPR stress, an ultra-low sulfur diesel (ULSD) fuel was stressed for up to 96 hrs. Sulfur is removed from diesel fuels to produce ultra-low sulfur diesel fuels (ULSD) by hydrotreatment. This process also serves to remove other constituents, including indigenous phenols and thiols that can also inhibit autoxidation. As a consequence, many ULSD fuels will readily hydroperoxide in storage or under D5304 stress. As shown in Figure 2, this particular ULSD passed the requirements of D5304 at 16 hrs, but rapidly began to undergo autoxidation after 20 hrs to produce over 300 meq/kg hydroperoxides (2400 ppm active O) at 96 hrs. Addition of 24 mg/L of AO-37 served to suppress autoxidation below the 1 meq/kg (8 ppm) limit for 64 hrs, well within the 16 hour standard for 3 years of ambient storage.

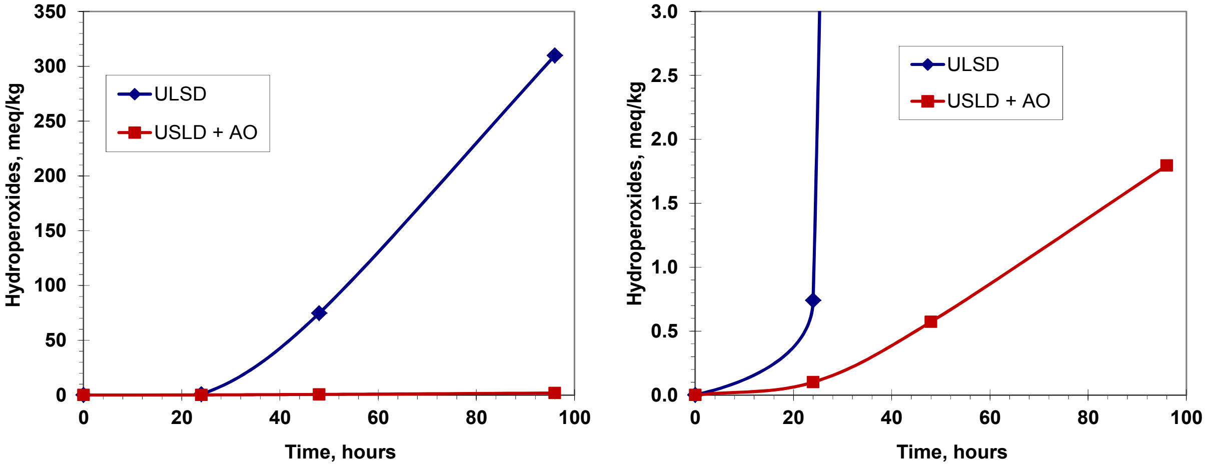

Figure 2. Oxidation of a reactive ultra-low sulfur diesel (ULSD) in the LPR. Ordinate scale is expanded in the plot on right to show formation of up to 3.0 meq/kg hydroperoxides.

JP-8 Additives. The "JP-8" fuels provided by SwRI were produced (Figure 1) from the Jet A fuels by the addition of the JP-8 additive package, which consisted of a static dissipater additive (SDA), corrosion inhibitor (CI) and fuel system icing inhibitor (FSII). Comparison of Figure 3, for the AO-free Jet A fuel (#10-02), with Figure 4, for the same fuel with the JP-8 additive package (#10-04), indicates that the JP-8 additive package reduced the stability of the fuel during LPR stress. The ROOH concentrations and the AO levels, as tri-t-butylphenol (TTBP) are shown. Note that there is a residual amount of TTBP in this fuel, which is typically present in all Jet A fuels that have been examined thus far, presumably acquired during transit through the supply system. It is clearly evident that in the presence of the JP-8 additive package, the fuels oxidized to a greater extent and thus consumed the AO at a greater rate than the additive-free Jet A fuels. These results suggest that in the absence of other variables, the higher reactivity of the JP-8 is most likely attributable to one or more of the components of the JP-8 additive package.

The impact of AO on formation of hydroperoxides in Jet A #10-02 and that fuel with the JP-8 additive package is shown in figures 5 and 6, respectively. While the AO was not effective in significantly reducing hydroperoxidation in these fuels, neither fuel exceeded the 1 meq/kg level for ROOH after 16 hrs of stress. However, comparison of these two figures illustrates the increase in autoxidation during LPR stress, due to the JP-8 additive package.

In an attempt to determine which of the three JP-8 additives (antistatic additive, corrosion inhibitor, fuel system icing inhibitor) had a detrimental effect on the stability of the Jet A fuel, each additive was mixed with the AO free Jet A (#10-02), individually and in combination and stressed in the LPR. A fourth sample was also stressed in the LPR, which contained the JP-8 package with the antioxidant, to replicate the sample (#10-03) provided by SwRI. The results of these tests are summarized in Figures 7 through 10. In all cases, there was a detrimental effect with the addition of each additive, but as mentioned previously, none of the samples exceeded the pass/fail criterion of 1 meq/kg ROOH (8 ppm) at the 16 hr limit. These findings suggest that the additive package currently used in JP-8 may act to actually decrease storage stability, when evaluated by the LPR method (ASTM D5304). While beyond the scope of this study, it is recommended that this investigation be extended to determine if the apparent delieterious impact of the JP-8 additive package in the LPR is relevant to ambient storage, or unique to high temperature stress under oxygen overpressure.

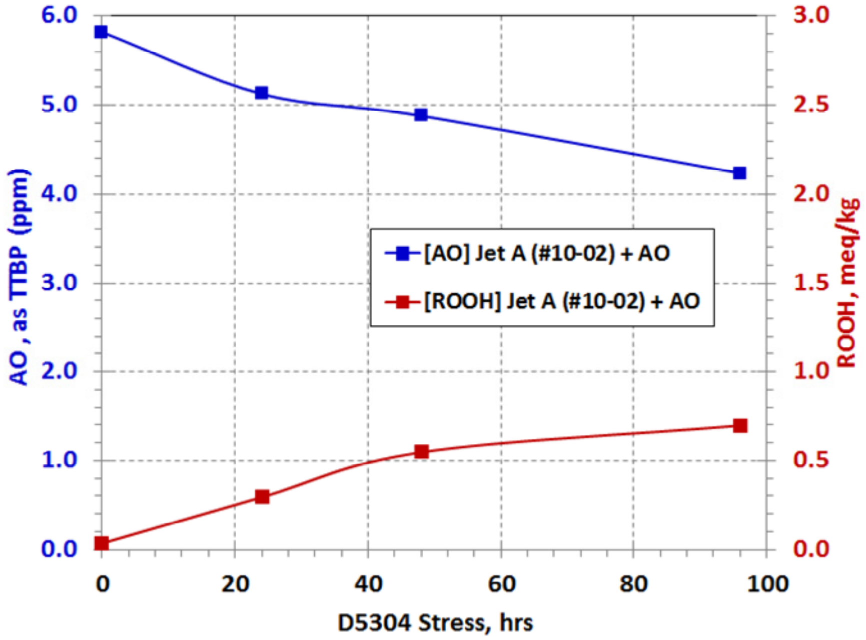

Figure 3. Hydroperoxides produced with concurrent antioxidant depletion during LPR stress of the Jet A fuel, initially containing 24 mg/L AO-37.

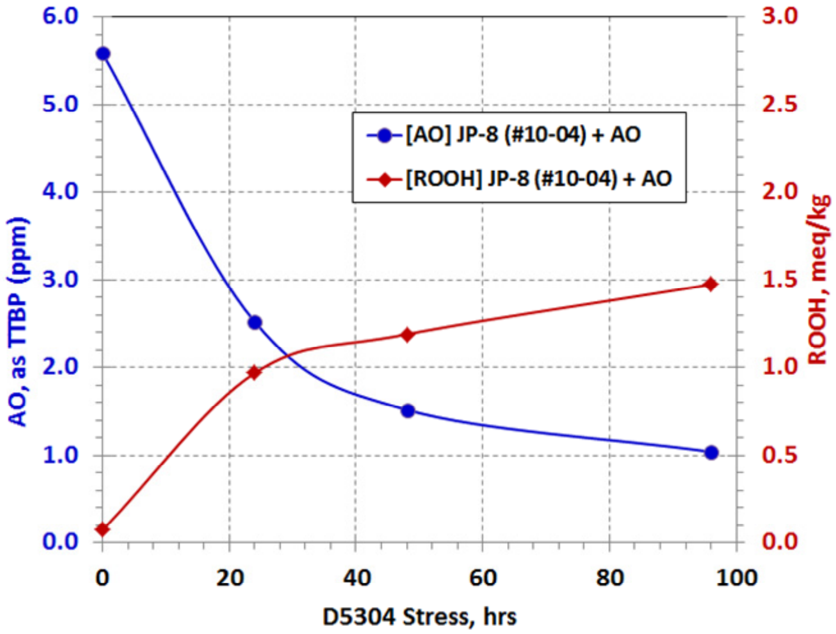

Figure 4. Hydroperoxides produced with concurrent antioxidant depletion during LPR stress of the Jet A fuel #10-04 with the JP-8 additives, initially containing 24 mg/L AO-37.

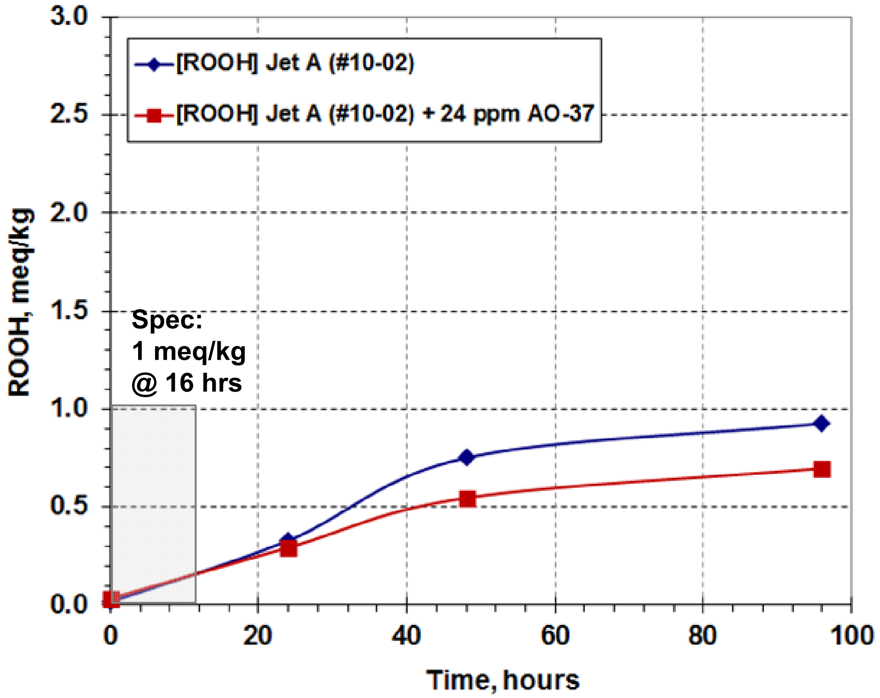

Figure 5. Antioxidant effectiveness in suppressing hydroperoxide formation from autoxidation in the antioxidant-free Jet A fuel #10-02.

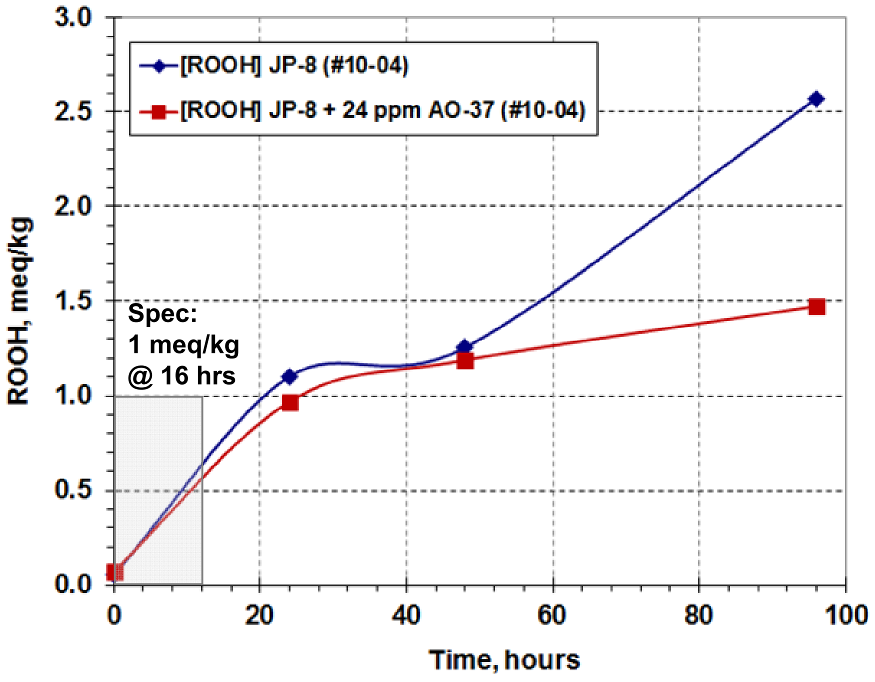

Figure 6. Antioxidant effectiveness in suppressing hydroperoxide formation from autoxidation in the antioxidant-free Jet A fuel #10-04 containing the JP-8 additives.

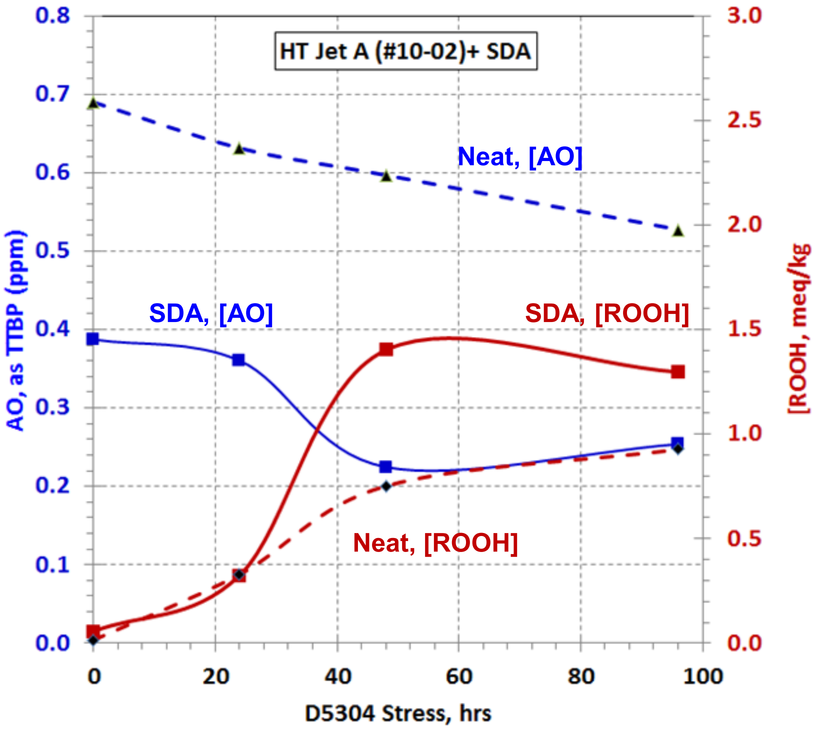

Figure 7. ROOH and AO concentration variations in HT Jet A #10-02 containing the static dissipater additive.

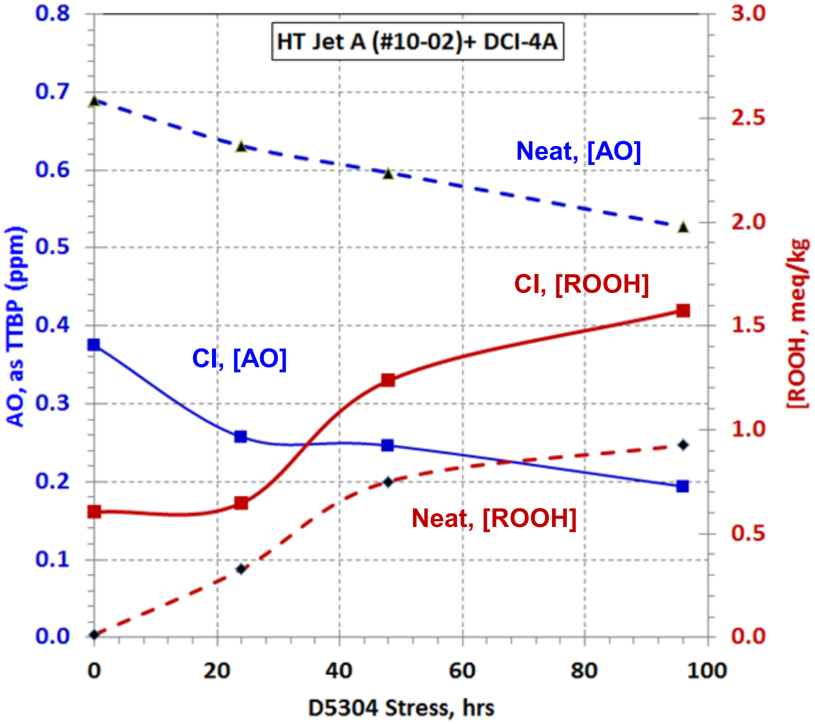

Figure 8. ROOH and AO concentration variations in HT Jet A #10-02 when and corrosion inhibitor was added.

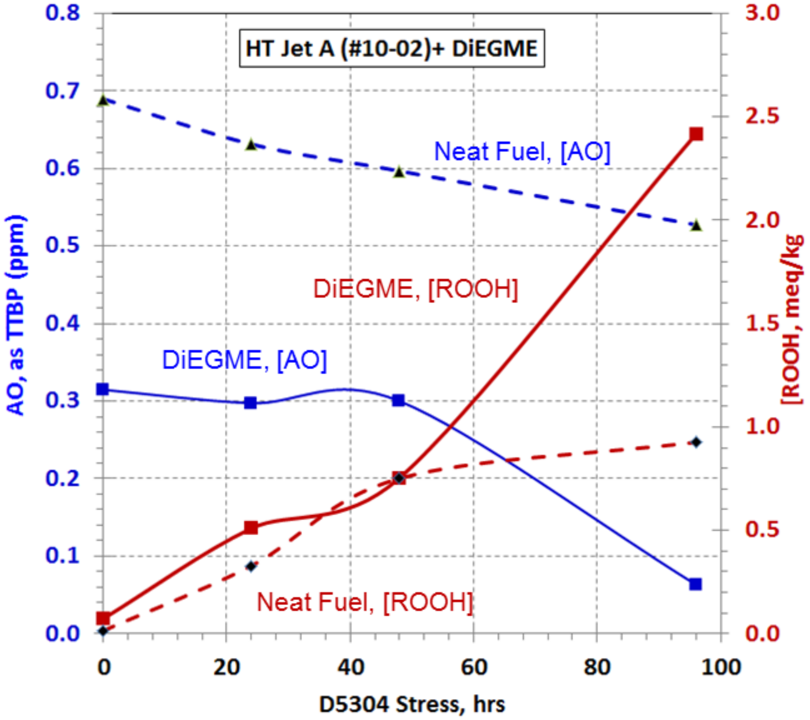

Figure 9. ROOH and AO concentration variations in HT Jet A #10-02 when the fuel system icing inhibitor was added.

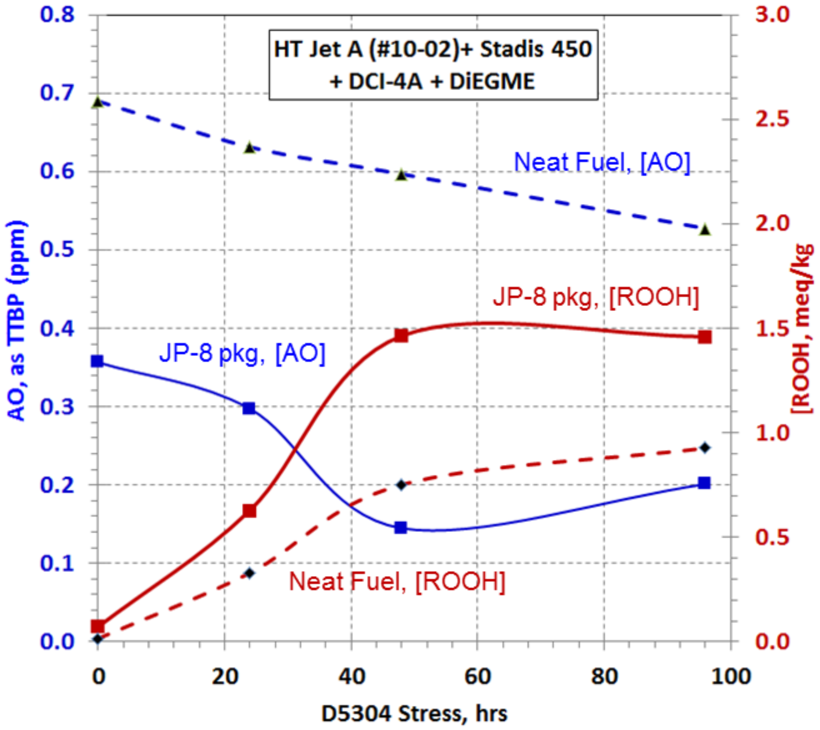

Figure 10. ROOH and AO concentration variations in HT Jet A #10-02 when all three JP-8 additives were added.

Impact of Copper Contamination. It has been shown[18] that in most fuels, the presence of 30 – 50 µg/kg (ppb) of dissolved copper will act to decrease the thermal stability of jet fuels. This is of particular concern to the US Navy, since JP-5 fuels on board Navy ships have been found[19] to typically contain from 150 – 350 µg/kg (ppb) of dissolved copper, acquired from the Cu-Ni alloys used in shipboard fuel systems.

A Jet A fuel was obtained from a fuel supplier at a local airport (Dulles International Airport, IAD) and found to be stable, as shown in Figure 11. It is not known if this fuel was hydrotreated, but it is clear that with such high storage stability, the impact of antioxidant was minimal and not needed in this instance.

An experiment was conducted with this stable Jet A fuel to illustrate the impact of dissolved copper on stability of jet fuel in the LPR and to explore the relevance of adding AO to copper-contaminated fuels. As expected, from the results shown in Figure 12, the presence of copper initiated rapid autoxidation, exceeding 1 meq/kg well within the 16 hr test time, with concurrent

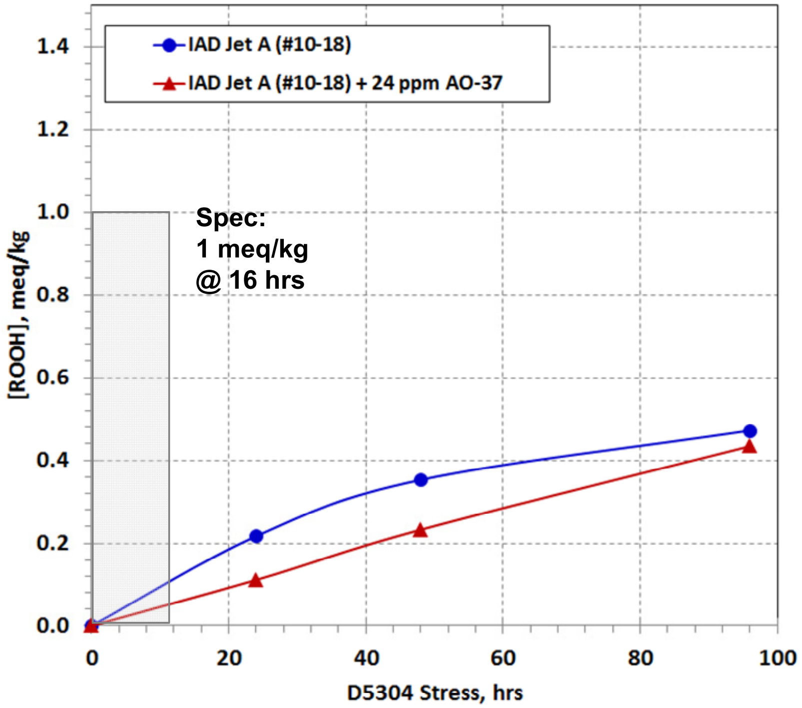

Figure 11. Antioxidant effectiveness in suppressing hydroperoxidation from autoxidation in an AO-free Jet A fuel obtained from a local airport.

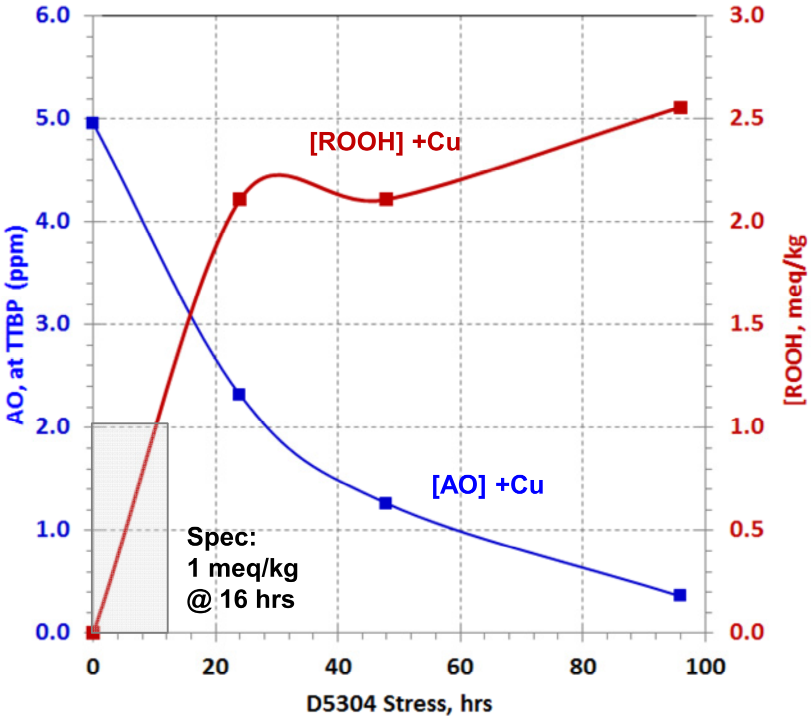

Figure 12. Impact of 24 ppm AO-37 in the presence of 300 ppb dissolved copper on autoxidation of Jet A fuel from local airport during LPR stress.

consumption of the antioxidant. It is also evident that even though the AO was rapidly consumed, at 24 ppm the AO-37 package was not sufficient to effectively counteract the impact of the dissolved copper on fuel autoxidation. This is consistent with the known mechanism of copper to not only accelerate free-radical autoxidation, but to catalyze the disproportionation of the hydroperoxides to branch and lengthen the free-radical chains. Thus, the antioxidant was rapidly consumed, allowing the autoxidation of the fuel to proceed.

The impact exerted on the stability of the baseline hydrotreated Jet A fuel (#10-02) by addition of the AO, the JP-8 additives and copper is summarized in Figure 13. As discussed above, these data also illustrate that the addition of the JP-8 additive package resulted in higher levels of hydroperoxides, which indicates that the autoxidation rates were higher. Addition of the AO-37 antioxidant package to both the neat fuel and the fuel with the JP-8 additives provided minimal benefits. The impact of AO to mediate copper-initiated autoxidation was also minimal, so it was omitted from this figure.

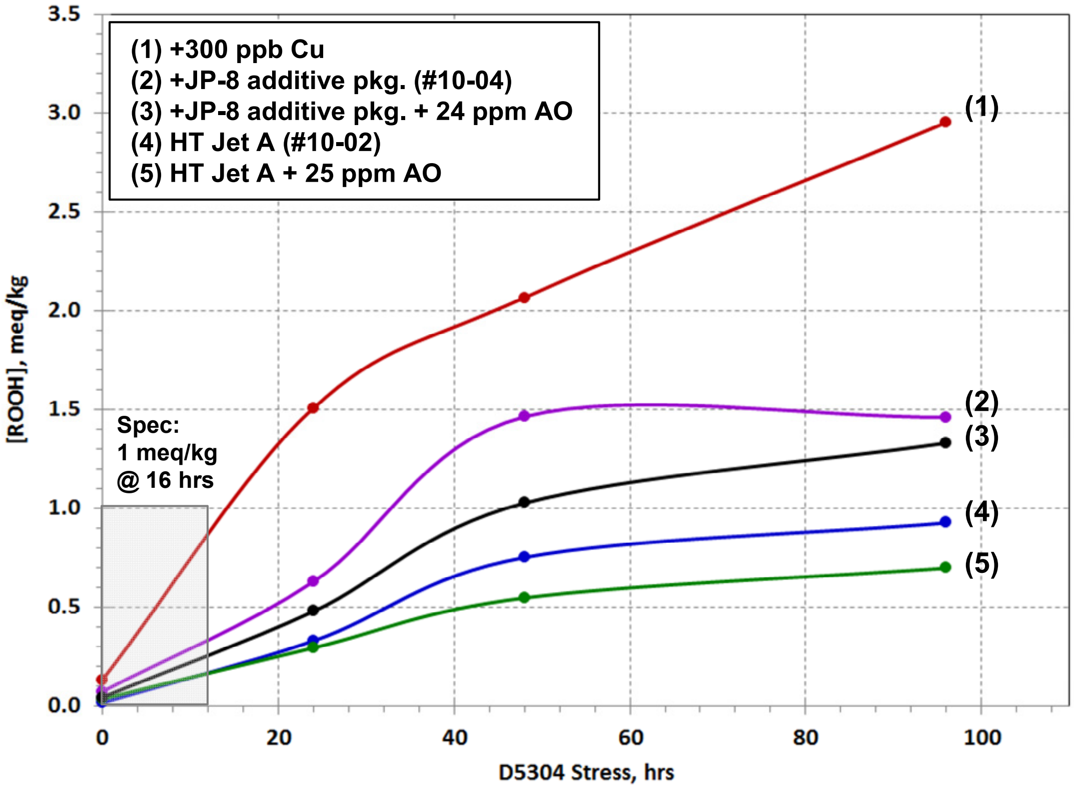

Figure 13. Summary of impact exerted by copper, the JP-8 additive package and antioxidant on hydroperoxidation of the hydrotreated Jet A fuel during LPR stress.

4.4 Antioxidant Effectiveness in Aged Fuels

The objective of these experiments was to simulate a worst-case scenario where the procuring authority adds an approved antioxidant to a fuel that has already undergone autoxidative degradation in the supply system. This was simulated in the laboratory by conducting LPR stress of a reactive fuel to produce a reasonable level of oxidation products, then adding the AO. For this experiment, the AO-free JP-8 fuel (#10-04) produced from the AO-free hydrotreated Jet A fuel (#10-02) was stressed in the LPR for 24 hours, then 24 mg/L of the AO-37 antioxidant was added, and returned to the LPR for further stress. Initial hydroperoxide and AO concentrations were measured as described above for all samples. Experiments were conducted with and without the addition of the antioxidant. Figure 14 shows the hydroperoxide and antioxidant (as 2,4,6-TTBP) concentrations during LPR stress for up to 96 hours in the neat fuel without the addition of the antioxidant.

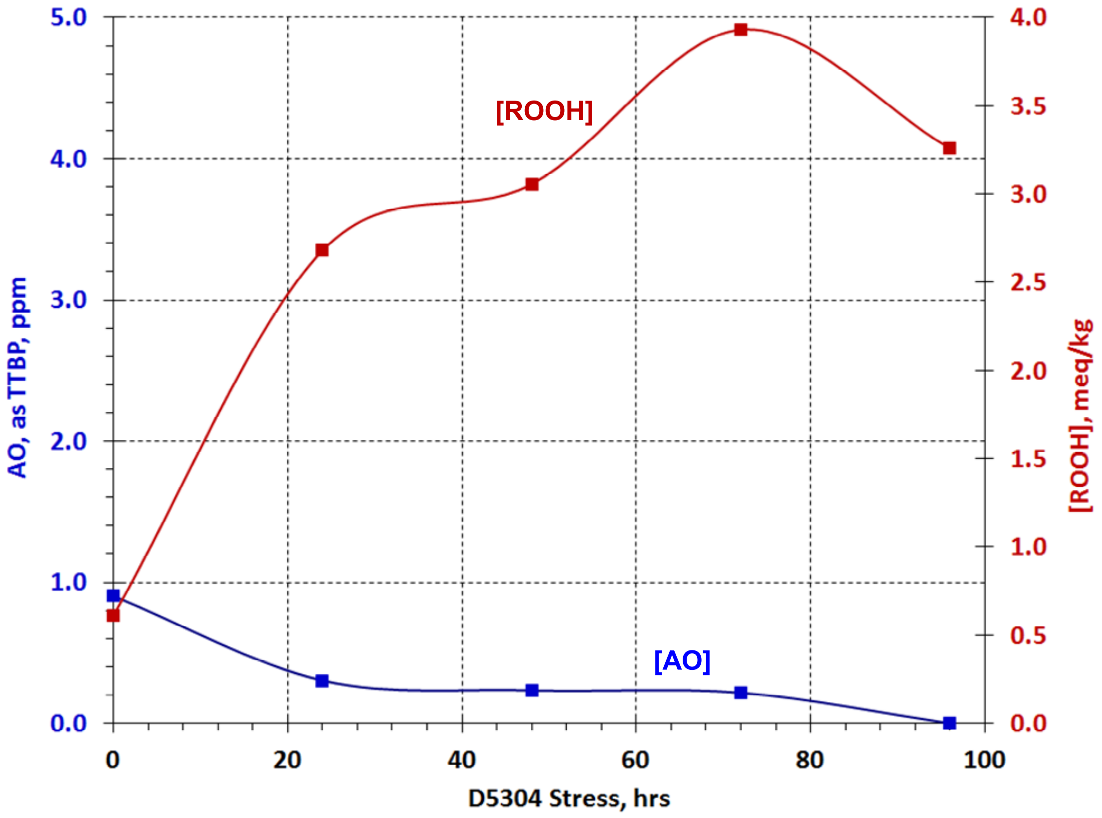

Figure 14. Oxidation behavior in the LPR for the AO-free HT JP-8 (#10-04), derived from HT Jet A (#10-02) by addition of the JP-8 additive package.

Figure 15 shows the effect of adding the antioxidant to this same fuel after it had been stressed in the LPR for 24 hours. It is clear that the added AO was rapidly consumed, with a concurrent decrease in further ROOH accumulation. The constant hydroperoxide levels after AO addition, indicates that the antioxidant was indeed effective in suppressing further oxidation. Since phenolic antioxidants do not function as hydroperoxide decomposers, the addition of an antioxidant would not be expected to reduce the hydroperoxide content of a previously oxidized fuel. The action of the phenolic AO to suppress further autoxidation in a fuel that has undergone prior oxidation, supports the conclusion that it would be necessary to continue the practice of adding an approved antioxidant to Jet A fuels. However, an AO will not remediate high hydroperoxide levels attained in a reactive fuel, so periodic inspections that include hydroperoxide determinations are also strongly recommended.

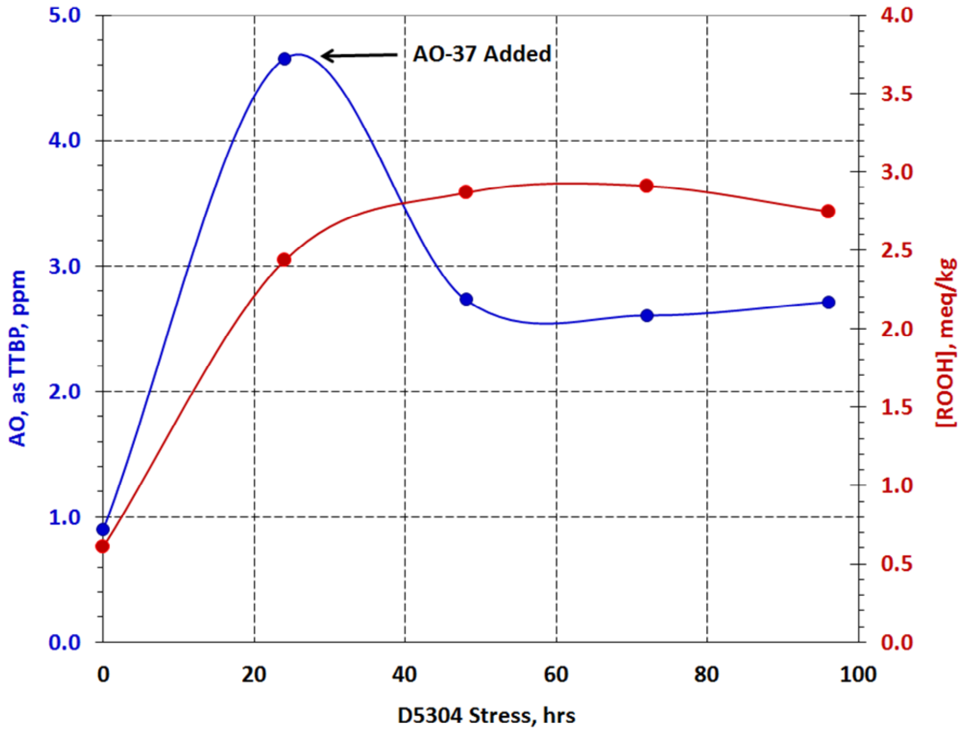

Figure 15. Results of the most reactive fuel, HT JP-8 made from HT Jet A #2 with the addition of antioxidant, AO-37 at 24 hours.

4.5 SwRI Bulk Storage Data

As part of the test program conducted by SwRI, large tank samples of the test fuels were periodically monitored for hydroperoxide concentration, on a monthly basis. The test fuels were stored in outside tanks at ambient conditions. The results[20], summarized in Figure 16, indicate that 1 year storage stability of HT Jet A is well within the 1 meq/kg (8 ppm active oxygen) limit.

These results are in qualitative agreement with the NRL accelerated LPR stability testing performed in accordance with ASTM D5304.

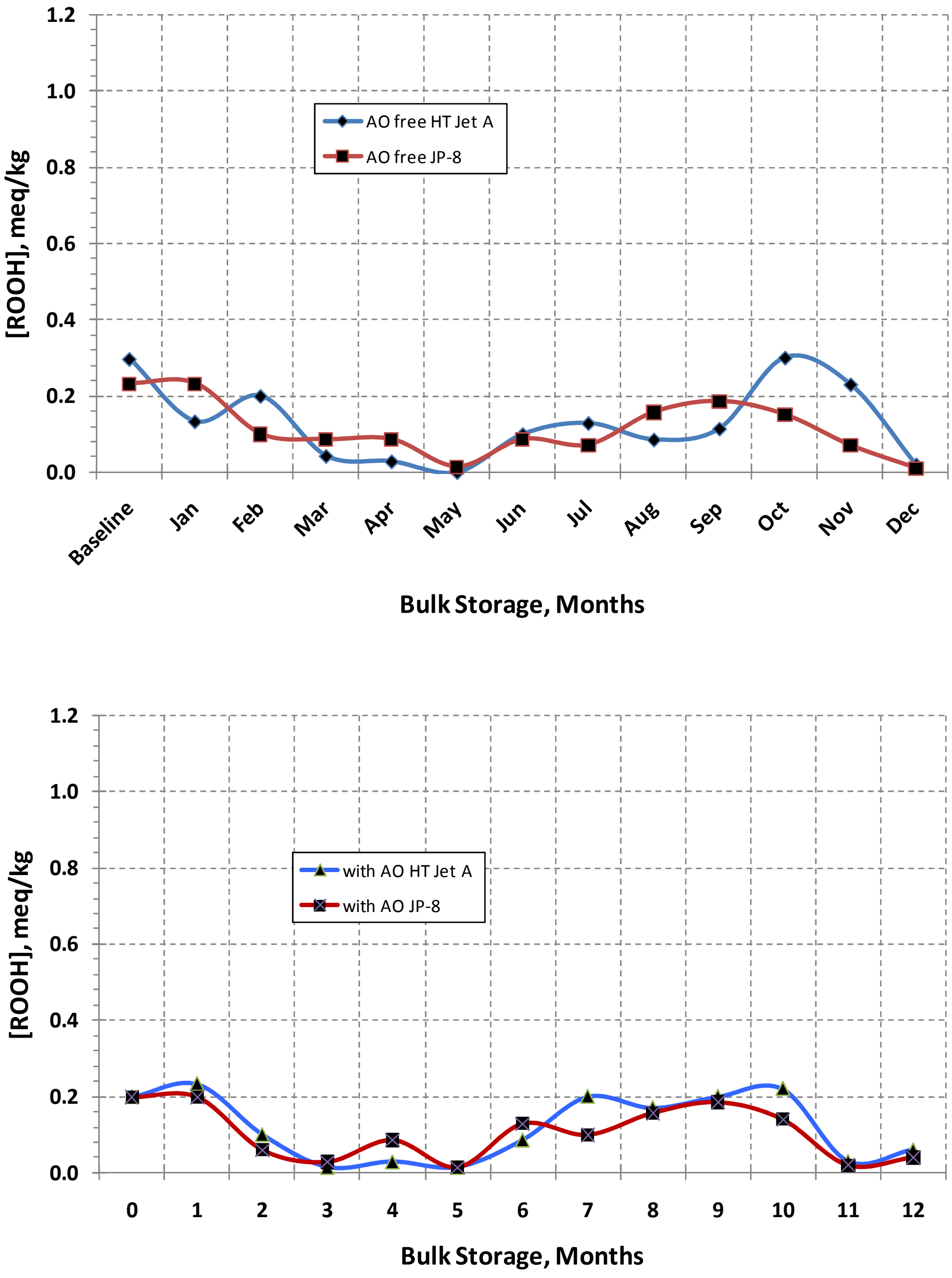

Figure 16. Hydroperoxides accumulated in bulk tank storage under ambient conditions of the hydrotreated Jet A and Jet A + the JP-8 additive package, without antioxidants (upper) and the other hydrotreated Jet A with the JP-8 additives and antioxidants (lower). (Data provided by Southwest Research Institute).

4.6 Comparison with Air Force Into-Plane Jet A Fuels

The into-plane Jet A fuels were provided by AFPET to help ensure that the findings from the limited set of fuel samples initially provided by SwRI, were generally applicable to fuels likely to be encountered in use. This was necessary to provide the appropriate guidance in establishing the viability of deploying additives to commercial Jet A downstream of the point of manufacture. Hydroperoxide and antioxidant concentration in these fuels were measured before and after stressing in the LPR after stress times of 0, 24, 48 and 96 hrs, to coincide with previous work with the original two SwRI fuels.

Hydroperoxides. Autoxidation of all the test samples during D5304 stress was monitored by measuring the hydroperoxides that accumulated during thermal stress. Table 7 summarizes the hydroperoxide measurements from the original SwRI test fuels and the AFPET into-plane samples, which is an indication of the extent of autoxidation. Hydroperoxide levels at 16 hours of LPR stress were extrapolated from the initial and 24 hour data, assuming linearity over this interval. All the fuels were initially in compliance with the 1 meq/kg (8 ppm active oxygen) limit. However, AFPET Jet A #11-16 was essentially at the limit. Only one of the AFPET fuels contained 24 ppm of AO-37, while the antioxidant levels in the other fuels were either undetectable or present at trace levels. The hydroperoxide levels reached as a function of LPR stress time are shown in Figures 17 – 21, comparing the 14 AFPET Jet A fuels with the original fuel sample set. These measurements indicate that the accelerated storage stabilities of the AFPET into-plane Jet A fuels provided were not substantially different from the stabilities of the hydrotreated SwRI fuels. This supports the applicability of the SwRI fuels as a predictor of what could be expected in actual use, assuming that the AFPET fuel sampling represented the range of Jet A fuels likely to be encountered.

Antioxidants. Antioxidant levels were determined as 2,4,6-TTBP, using the GC-MS-SIM method described in Appendix A. The measured antioxidant concentrations indicate that fuel samples 11-11, 11-14, and 11-23 contained a phenolic antioxidant, with sample 11-14 containing 24 ppm of the AO-37 antioxidant package, which is the maximum allowable amount. The remainder of the AFPET fuels only contained trace levels of antioxidant, which is typical for jet fuels and most likely acquired from contact with wetted surfaces in the fuel handling system. The antioxidant concentrations in all the test fuels are given in Table 8 as a function of LPR stress duration. As expected, all antioxidant concentrations decreased in proportion to LPR stress.

Table 7. Hydroperoxide concentrations for all fuels before and after LPR stressing.

NRL ID	No.	Fuel Sample	ROOH, meq/kg Hrs LPR stress				
			0	16	24	48	96
10-01	1	HT Jet A#2 + AO (SwRI)	nd*	0.18	0.27	0.18	0.90
10-02	2	HT Jet A #1 (SwRI)	0.02	0.22	0.33	0.75	0.93
--	3	HT Jet A #1 +AO (NRL)	0.03	0.21	0.29	0.55	0.70
10-03	4	HT Jet #2 + JP8 pkg. + AO (SwRI)	0.02	0.09	0.12	1.05	2.11
10-04	5	HT Jet A #1 + JP8 pkg. (SwRI)	0.06	0.75	1.10	1.26	2.57
--	6	HT Jet A #1 + JP8 pkg. + AO (NRL)	0.07	0.67	0.97	1.19	1.47
--	7	HT Jet #2 w/AO + JP8 pkg. (NRL)	0.07	0.44	0.63	1.46	1.46
--	8	HT Jet #1 + JP8 pkg + AO (NRL)	0.04	0.33	0.48	1.03	1.33
10-17	9	Jet A Australian Fuel	0.04	0.18	0.25	0.43	0.86
10-18	10	Jet A (Local Airport)	nd	0.14	0.22	0.35	0.47
--	11	Jet A (Local Airport) + AO	nd	0.07	0.11	0.23	0.43
11-11	12	Jet A (AFPET #29802)	0.01	0.33	0.49	0.73	1.10
11-12	13	Jet A (AFPET #29984)	nd	0.26	0.39	0.54	0.74
11-13	14	Jet A (AFPET #30010)	0.02	0.60	0.89	1.20	2.21
11-14	15	Jet A (AFPET #30035)	nd	0.16	0.23	0.35	1.21
11-15	16	Jet A (AFPET #30041)	nd	0.31	0.47	0.70	0.99
11-16	17	Jet A (AFPET #30042)	0.49	0.98	1.22	1.30	1.45
11-17	18	Jet A (AFPET #30043)	nd	0.59	0.88	1.19	3.41
11-18	19	Jet A (AFPET #30046)	0.08	0.72	1.03	1.51	1.94
11-19	20	Jet A (AFPET #30068)	nd	0.28	0.42	0.64	0.67
11-20	21	Jet A (AFPET #30099)	0.02	0.70	1.05	0.73	0.79
11-21	22	Jet A (AFPET #30100)	0.03	0.54	0.80	1.18	1.68
11-23	23	Jet A (AFPET #30109)	0.04	0.47	0.69	0.96	1.11
11-25	24	Jet A (AFPET #30036)	0.06	0.71	1.04	1.36	1.38
11-26	25	Jet A (AFPET #30017)	0.01	0.21	0.31	0.44	0.57

*nd = not detected, <0.01 meq/kg.

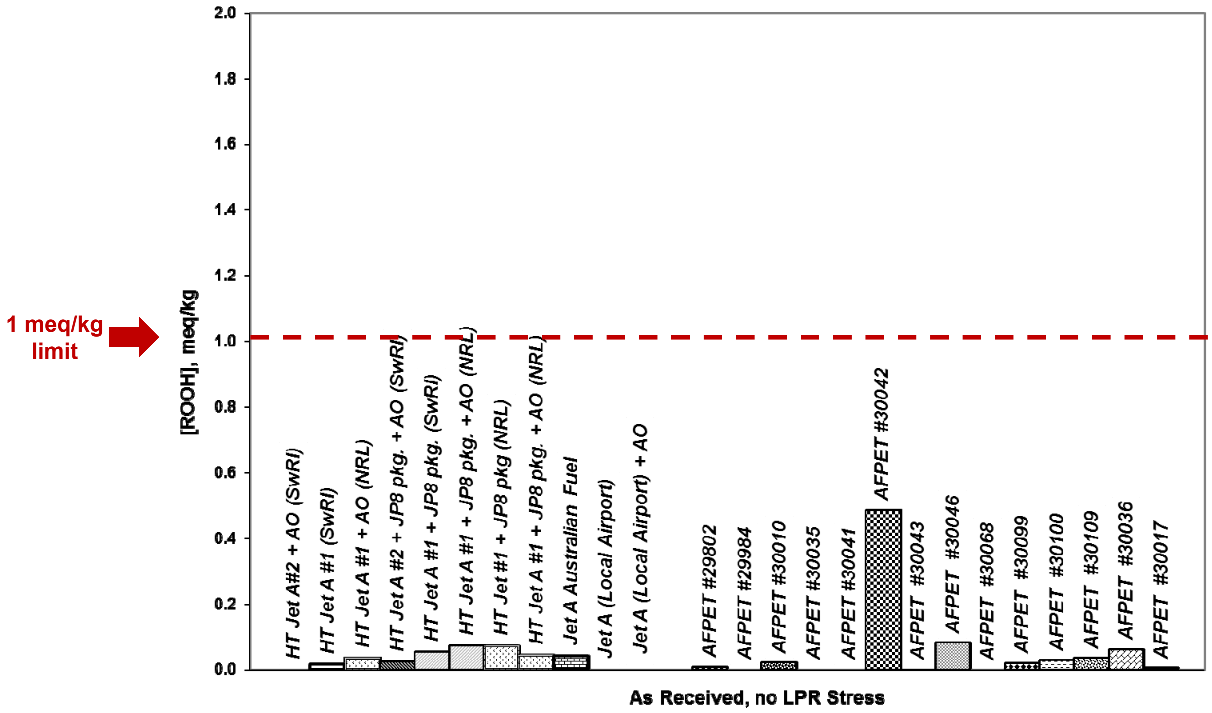

Figure 17. Initial hydroperoxide concentrations measured prior to LPR stressing.

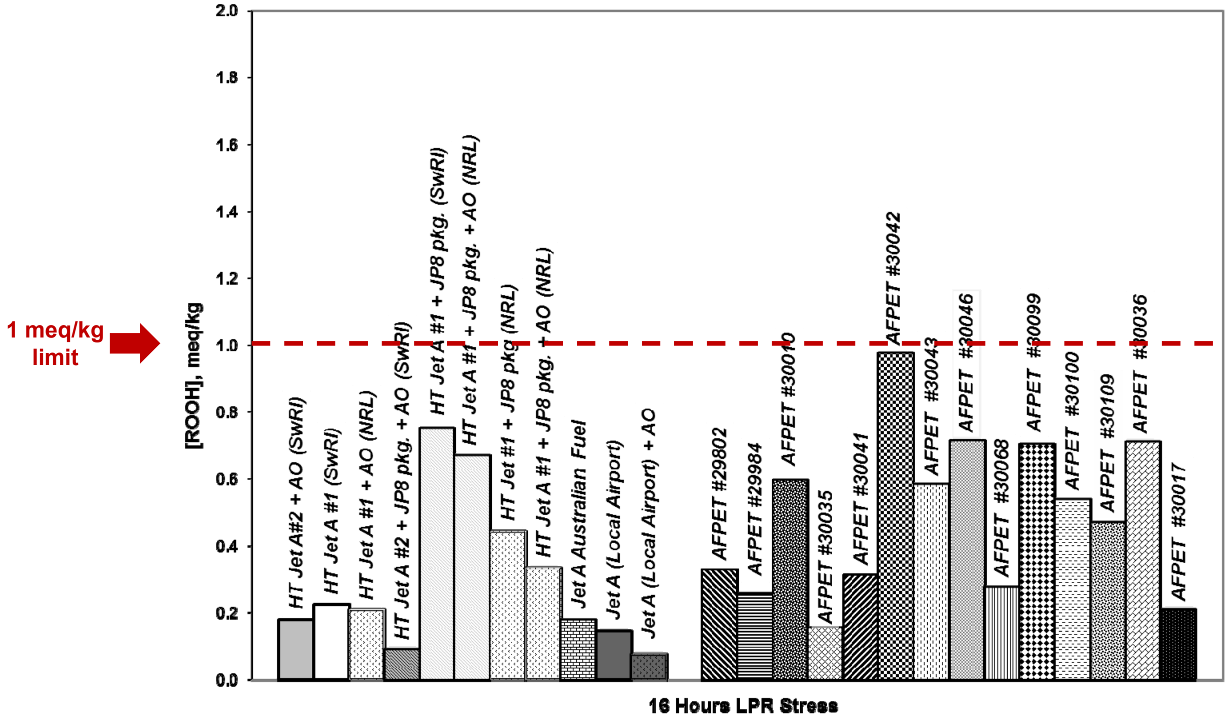

Figure 18. Calculated hydroperoxide concentrations after 16 hours LPR stress.

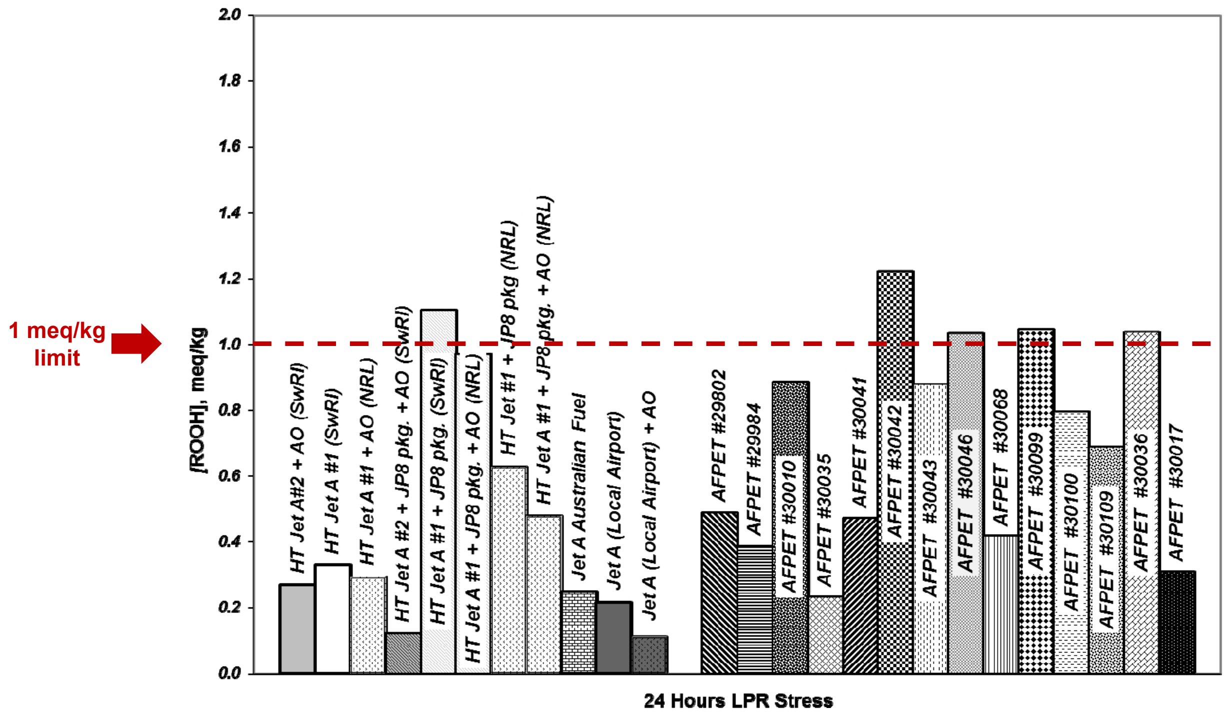

Figure 19. Hydroperoxide concentrations measured after 24 hours of LPR stress.

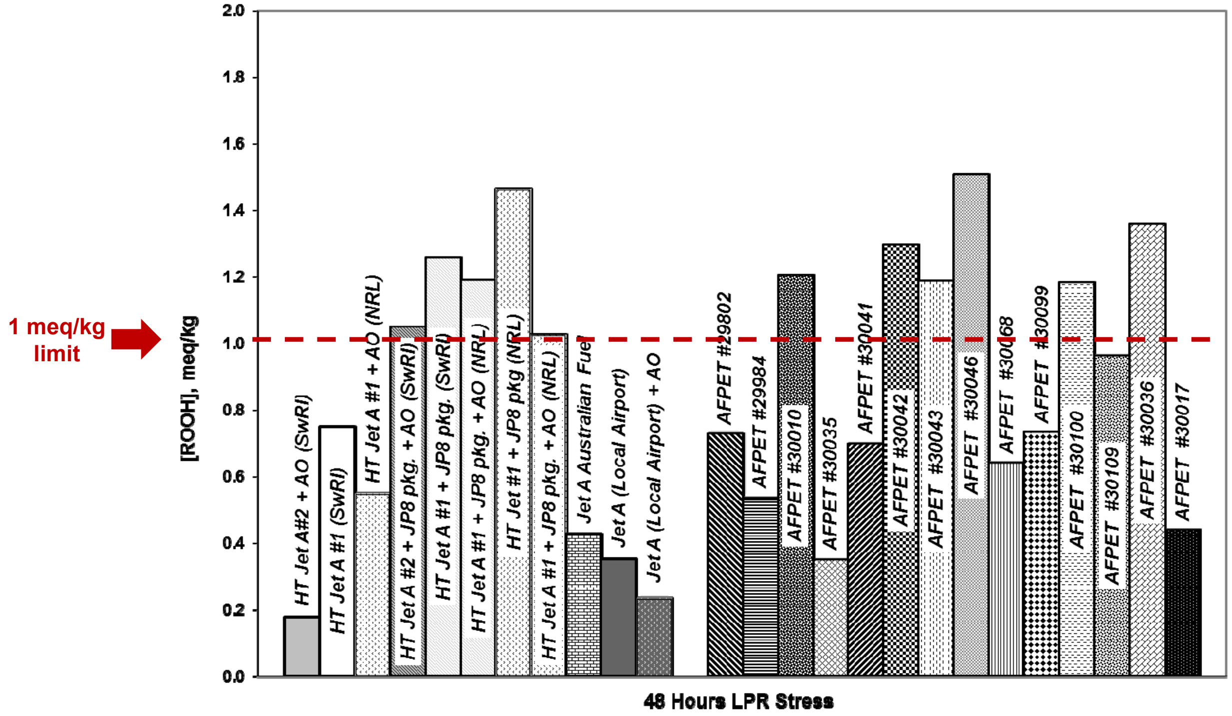

Figure 20. Hydroperoxide concentrations measured after 48 hours of LPR stress.

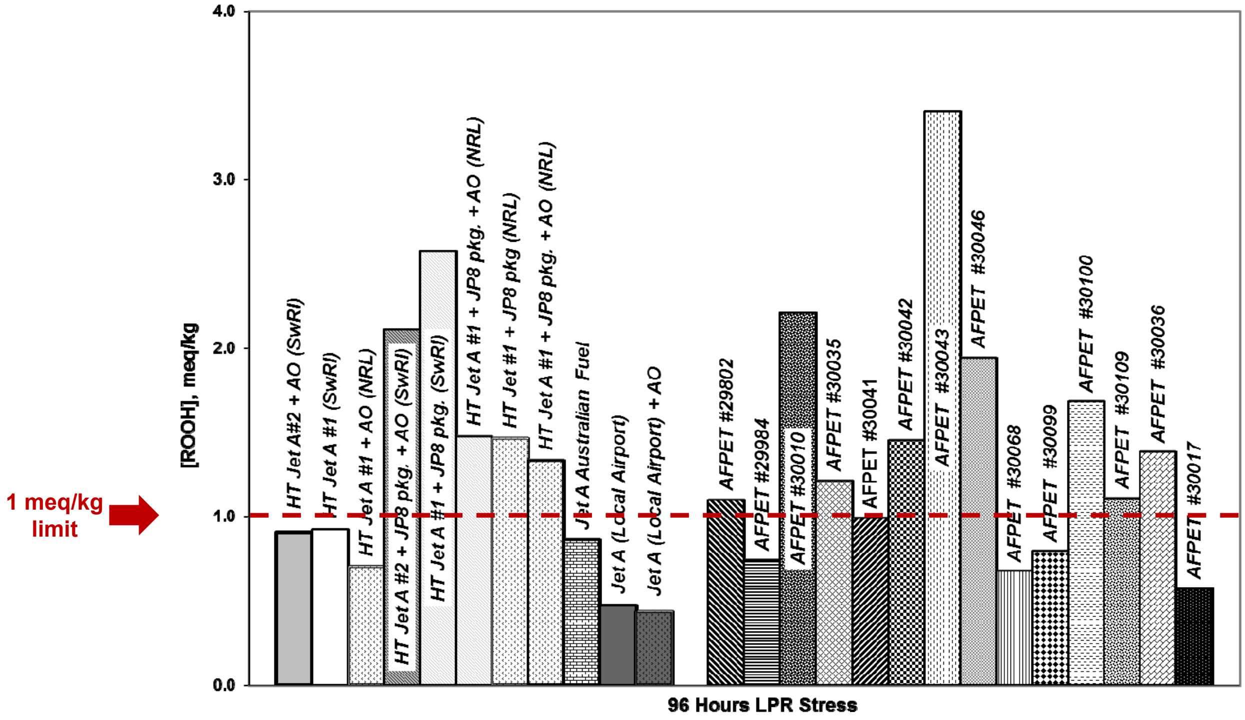

Figure 21. Hydroperoxide concentrations measured after 96 hours of LPR stress.

Table 8. Antioxidant concentrations in all fuel samples, determined by GC-MS-SIM, as 2,4,6-TTBP.

NRL ID	No.	Fuel Sample	AO (TTBP), ppm Hrs LPR stress			
			0	**24**	**48**	**96**
10-01	1	HT Jet A#2 (SwRI)	5.77	4.72	5.54	4.67
10-02	2	HT Jet A #1 (SwRI)	0.69	0.63	0.60	0.53
--	3	HT Jet A #1 +AO (NRL)	5.82	5.13	4.88	4.24
10-03	4	HT Jet #2 + JP8 pkg. (SwRI)	3.19	1.39	0.62	0.14
10-04	5	HT Jet A #1 + JP8 pkg. (SwRI)	0.68	0.30	0.26	0.13
--	6	HT Jet A #1 + JP8 pkg. + AO (NRL)	5.59	2.52	1.52	1.04
--	7	HT Jet #2 w/AO + JP8 pkg. (NRL)	0.36	0.30	0.14	0.20
--	8	HT Jet #1 + JP8 pkg + AO (NRL)	5.59	5.44	4.60	4.49
10-17	9	Jet A Australian Fuel	3.99	3.57	2.69	2.11
10-18	10	Jet A (Local Airport)	0.37	0.36	0.34	0.34
--	11	Jet A (Local Airport) + AO	5.05	4.92	4.75	4.56
11-11	12	Jet A (AFPET #29802)	1.96	1.82	1.71	1.64
11-12	13	Jet A (AFPET #29984)	*nd	nd	nd	nd
11-13	14	Jet A (AFPET #30010)	nd	nd	nd	nd
11-14	15	Jet A (AFPET #30035)	3.25	3.03	2.80	2.16
11-15	16	Jet A (AFPET #30041)	0.57	0.54	0.53	0.50
11-16	17	Jet A (AFPET #30042)	nd	nd	nd	nd
11-17	18	Jet A (AFPET #30043)	nd	nd	nd	nd
11-18	19	Jet A (AFPET #30046)	0.32	0.30	0.28	0.27
11-19	20	Jet A (AFPET #30068)	nd	nd	nd	nd
11-20	21	Jet A (AFPET #30099)	nd	nd	nd	nd
11-21	22	Jet A (AFPET #30100)	nd	nd	nd	nd
11-23	23	Jet A (AFPET #30109)	1.08	1.00	0.96	0.91
11-25	24	Jet A (AFPET #30036)	nd	nd	nd	nd
11-26	25	Jet A (AFPET #30017)	0.49	0.46	0.48	0.44

*nd = not detected, <0.01 ppm.

5.0 SUMMARY

5.1 Long-Term Storage Stability

- The AO-37 antioxidant additive package was shown to be effective in suppressing autoxidation in a reactive ultralow sulfur diesel fuel, during low-pressure reactor (LPR) accelerated storage stability testing performed in accordance with ASTM D5304.
- Based on the D5304 behavior of the hydrotreated Jet A provided by SwRI, and a typical Jet A obtained at a local airport, none of the fuels produced unacceptable levels of insolubles in LPR testing considered equivalent to storage of up to 2 years.
- Addition of 24 mg/L AO-37 antioxidant to the HT Jet A did not significantly reduce hydroperoxidation in D5304 testing.
- Analysis during 12 month bulk storage by SwRI indicates the HT Jet A fuel was stable during extended ambient storage with hydroperoxide (ROOH) levels remaining below 1 meq/kg (8 ppm active oxygen), regardless of whether or not AO was present.
- Analysis of 14 U.S. AFPET into plane Jet A fuels indicated that all of these fuels were stable in storage for 2 years according to ASTM D5304 accelerated storage testing.
- The long-term storage stabilities of the HT Jet A fuels provided by SwRI with and without an approved antioxidant, were similar to that observed with the 14 AFPET Jet A fuels.

5.2 Fuel Characterization

- An AO-free Jet A was used to prepare the AO-free JP-8 fuel and that a different Jet A with AO from a different refinery was used to prepare the JP-8 + AO fuel at SwRI. It was therefore not possible to compare the impact of AO on either of these fuels as received since we were not provided with the same fuel with and without AO.
- Testing verified that the JP-8 fuels contained fuel system icing inhibitor, and Jet A fuels did not.
- Even the “AO-free” fuels contained traces of 2,4,6-tri-t-butylphenol, one of the components of AO-37 (~ 0.7 ppm vs ~ 4.0 ppm @ 24 ppm AO-37).

- Subsequent experiments were carried out with AO-free Jet A, adding AO-37 at NRL and/or the JP-8 additive package.

- The AFPET Jet A fuels were tested for hydroperoxides and antioxidants under the same test regimen that the original test fuels were measured. Three of the AFPET fuels contained measureable concentrations of antioxidant, with one fuel containing the maximum allowable concentration.

5.3 General Observations

- All test fuels produced very few insolubles after up to 96 hours D5304 stress; all within the limits of the 16 hour test for certification of 2 years ambient storage for diesel fuel.

- During D5304 stress, the antioxidant concentrations decreased and hydroperoxides increased concurrently for all samples tested.

- Testing conducted with the SwRI AO-free HT Jet A fuels and the AO-free JP-8, produced from the Jet A, indicate measureable differences in hydroperoxidation and antioxidant depletion rates, suggesting differences in reactivity, possibly due to one or more of the JP-8 additives.

- Presence of the "JP-8 additives" (SDA, DCI-4A, DiEGME) did not affect short-term (16 hrs) stability in D5304, but *did* decrease stability for longer stress durations.

- Addition of a phenolic antioxidant or antioxidant package to a fuel that has undergone autoxidation, will not reduce existent hydroperoxides but will suppress further autoxidation until the antioxidant is consumed.

- A phenolic antioxidant added to a fuel contaminated with dissolved copper will be rapidly consumed and will only provide a temporary benefit in suppressing autoxidation.

6.0 CONCLUSIONS

Laboratory testing performed on a total of 25 fuels, including two hydrotreated Jet A fuels, a Jet A fuel from a local airport, and 14 AFPET Jet A samples, indicate that these fuels could be stored for at least two years with no significant accumulation of hydroperoxides or insolubles. There were no obvious benefits for storage stability observed from the addition of antioxidants to these stable fuels. However, while the addition of phenolic antioxidants will not reduce hydroperoxides that have already accumulated in a fuel, an antioxidant will serve to suppress further autoxidation, until it has been consumed.

Therefore, if these 25 fuels are representative of all fuels encountered in the field, and given the relatively short turnover times reported by DLA-E, then the results obtained in this study indicate that it would be acceptable to add antioxidants downstream of the refinery to adequately mediate storage stability. However, it is also recommended that periodic monitoring of hydroperoxidation be undertaken during storage of additive-free Jet A fuels.

7.0 RECOMMENDATIONS FOR FURTHER STUDY

The Applicability of the LPR Method. Anecdotal evidence from storage stability of hydrotreated diesel fuels, such as ultra-low sulfur diesel (ULSD), in accordance with ASTM D5304 has indicated that these reactive fuels can develop much greater levels of hydroperoxides than during ambient storage. This suggests that in some reactive fuels, accelerated testing by oxygen or air overpressure at elevated temperatures, may force certain chemical processes forward that would not occur under ambient conditions. If this is the case, then this could constitute a situation where the LPR will provide false failures. It is recommended that the LPR procedure be re-evaluated with reactive hydrotreated diesel and jet fuels to assess the applicability and linearity of this technique as a tool for predicting storage stability during ambient storage. Concurrent experiments by LPR, ASTM D4625 (43°C for 16 weeks in vented borosilicate bottles), and actual ambient storage should be conducted to resolve this.

Impact of Storage on Thermal Stability. While it has been established that stability of Jet A fuels for up to a year ambient storage will generally not be an issue, there remains the question regarding the impact of autoxidation during storage on thermal stability of these fuels. Several studies have shown a relationship between storage and thermal stability. One such observation was that it is expected that the least thermally stable fuel would also tend to exhibit an inability to consume oxygen or form hydroperoxides at low temperatures.[21] Other work indicates conflicting results; that is, that some jet fuels that were aged at ambient conditions for extended periods of time exhibited both improved thermal stability for some fuels and poorer thermal stability for others.[22] In another more recent study[23], the authors concluded that over a two year period of storage, a stable Jet A-1 grade fuel did not change its physical and chemical properties, with the notable exception of JFTOT thermal stability. One report suggests that both storage and thermal stability of jet fuels depends on the fuel composition; where HT fuels may be thermally stable and not storage stable; or saturated fuels can be storage stable but not thermally stable.[24] With this information, it would suggest that before a final decision is made regarding the use of Jet A as a replacement for all CONUS JP-8 and JP-5 fuels, it is recommended that the issue of thermal stability be addressed, particularly in light of the apparent deleterious effects on stability observed from addition of the JP-8 additive package.

8.0 ACKNOWLEDGEMENTS

This work was supported by the Defense Logistics Agency Energy (DLA-E), with Philip Chang as the DLA-E point of contact.

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APPENDIX A: NRL GC-MS Method to Monitor Phenolic Antioxidant Concentrations in Jet Fuels.

Objective: To investigate the feasibility of determining the concentration of AO-37 in neat fuels without liquid-liquid extraction or sample concentration.

Reference: Shin *et al.* "Determination of Phenolic Antioxidants in Spilled Aviation Fuels by Gas Chromatography-Mass Spectrometry" *Chromatographia*, **2003**, 58, p 495-499.

Method Summary. A method was developed to detect and quantify four of the antioxidant compounds specified in MIL-DTL-83133G by GC-MS. The four compounds are the three major components of AO-37, specifically 2-tert-butylphenol (TBP), 2,6-di-tert-butylphenol (DTBP) and 2,4,6-tri-tert-butylphenol (TTBP), and 2,6-di-tert-butyl-4-methylphenol (TDBMP). The method employed dodecane as a fuel simulant and has detection limits of less than 40 ng/mL for all four analtyes.

GC-MS Method. Samples were analyzed using an Agilent 7890A GC, 5975C MS with a 7693 autosampler. One microliter of sample was injected using a 100:1 split ratio with an injector temperature of 260 ˚C. The initial oven temperature was 170 ˚C which was held for 5 minutes, then ramped at 10 ˚C min^{-1} to 230 ˚C. A 3 min post time at 300 ˚C was used to bake off residual material from the column. The column was an Agilent DB-1MS, 60 m x 250 µm x 0.25 µm using helium as the carrier gas with a flow rate of 1.2 mL min^{-1}. The MS was run in SIM mode with the target ions listed in Table A-1. Target analytes TBP (Aldrich, 99%), DTBP (Aldrich, 99%), DTBMP (Fischer Scientific, HPLC grade) and TTBMP (Aldrich, 98%) and fuel simulant dodecane (Sigma Aldrich, 99+%) were used as received.

Table A-1. Retention times and target ions for target compounds.

Compound	Acronym	RT (min)	Target Ions, m/z*
2-tert-butylphenol	TBP	5.97	135P, 107, 150
2,6-di-tert-butylphenol	DTBP	8.08	191P, 163, 206
2,6-di-tert-butyl-4-methylphenol	DTBMP	8.94	205P, 177, 220
2,4,6-tri-tert-butylphenol	TTBP	10.17	247P, 248, 262

*"P" indicates the primary ion.

An example chromatogram is shown in Figure A-1. The TBP elutes with the solvent tail of the dodecane fuel simulant, but is not interfered with by any of the impurities within the dodecane. The remaining three analytes are cleanly resolved. Four criteria were used to define a hit. First, the candidate peak must have a retention time within +/- 0.20 minutes of the average retention time observed in the standards. Second, the target ions must co-maximize within +/- 2 scans. Third, at least one secondary ion must be present with a signal-to-noise ratio (SNR) greater than 3. Lastly, at least one of the ion ratios of the primary to secondary ions must be within 20% relative to the calibration standards.

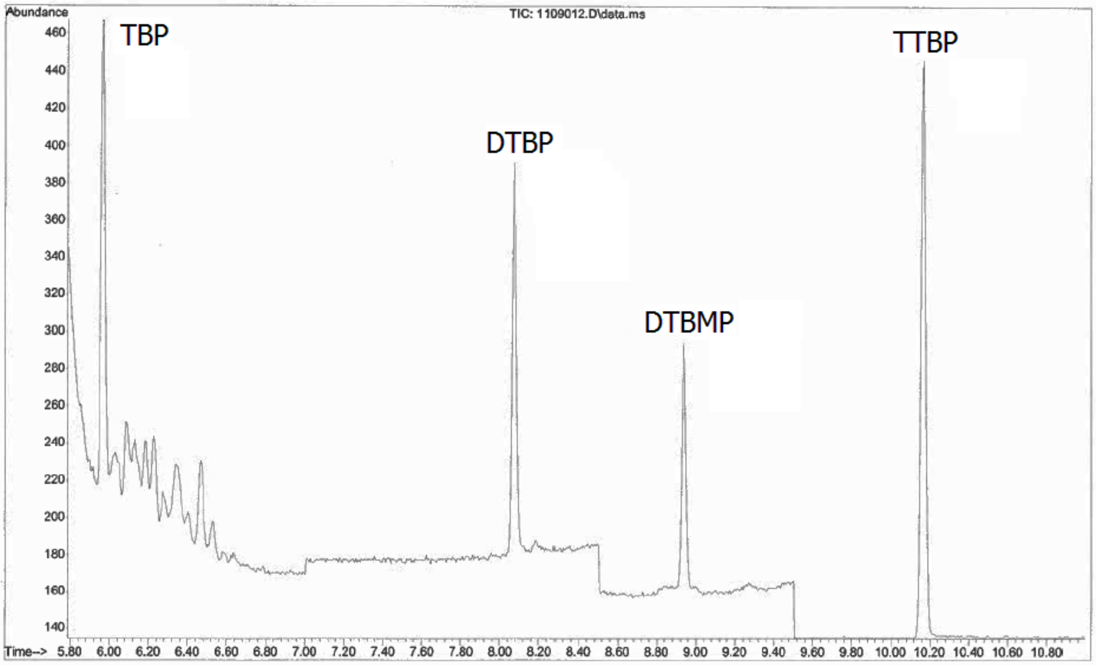

Figure A-1. Example total ion chromatogram for a 0.40 μg/mL standard of the AO blend. Discontinuous breaks in the baseline mark the changes between different sets of SIM ions.

Method detection limits (MDL) and method quantitation limits (MQL) were determined by preparing seven spiked samples. The samples were prepared at a nominal concentration of 40 ng/mL and all analytes were detected with a SNR between 3 and 7 for the largest secondary ion. Method detection limits (MDL) and method quantitation limits (MQL) were determined at the 90% and 95% confidence limits and are reported in Table A-2. These detection limits could be lowered if the hit criteria were changed to only require a signal-to-noise ratio SNR > 3 for the TIC as the secondary ions for multiply substituted phenol analytes are generally less than a third of the intensity of the primary ions. However this would significantly reduce the quality of the identification in a more complex matrix, such as a fuel.

The detection limits reported in Table A-2 could likely be reduced by an additional two orders of magnitude by modifying the method to use a splitless injection. If this method is to be applicable to the entire expected concentration range, up to 24 ug/mL as specified by MIL-DTL-83133G, a calibration curve covering three orders of magnitude in concentration will be required.

Maintaining linearity over such a wide concentration range is challenging on a GC-MS, and would likely require two separate calibration curves; one for concentrations greater than 1 µg/mL and one for concentrations less than 1 µg/mL. Alternatively, previous work not reported here has shown, a quadratic calibration curve could be generated that can cover the entire expected concentration range with an R^2 value greater than 0.999 and a mean relative prediction error of less than 15%.

Table A-2. Summary of MDL and MQL for 90% and 95% confidence intervals.

	MDL (ng/mL)		**MQL (ng/mL)**	
Analyte	**90%**	**95%**	**90%**	**95%**
TBP	33.7	36.3	113	121
DTBP	37.1	39.3	124	131
DTBMP	29.2	29.9	97.4	100
TTBP	31.4	32.8	105	109

The antioxidant additive package used in the test fuels, AO-37, was analyzed. The results of the analysis are shown in Figure A-2 and summarized in Table A-3. Seven substituted phenols were identified, of which three accounted for nearly 97.5 % of the total integrated area (excluding the peak attributed to column bleed). The largest component is 2,6-di-tertbutylphenol (2,6-DTBP) which accounts for 76.42 % of the total integrated area with smaller peaks for 2,4,6-tri-tertbutylphenol (2,4,6-TTBP, 17.34 %) and 2-tertbutylphenol (2-TBP, 3.66 %). The lesser components detected were 4-tertbutylphenol (4-TBP), 2,4-di-tertbutylphenol (2,4-DTBP), 2,5-di-tertbutylphenol (2,5-DTBP) and 2,4-di-tertbutyl-4-sec-butylphenol (2,4-DTB-4-SBP). While area% is not exactly equivalent to mass%, in this instance, due to the similar chemical nature of the analytes of interest, it is a reasonable approximation. Additionally the specification sheet received with the AO-37 sample (originally procured from Innospec) specifies a 2,6-DTBP concentration >75 mass% and a 2,4,6-TTBP concentration of >15 mass%. Both concentrations are consistent with the GC-MS data.

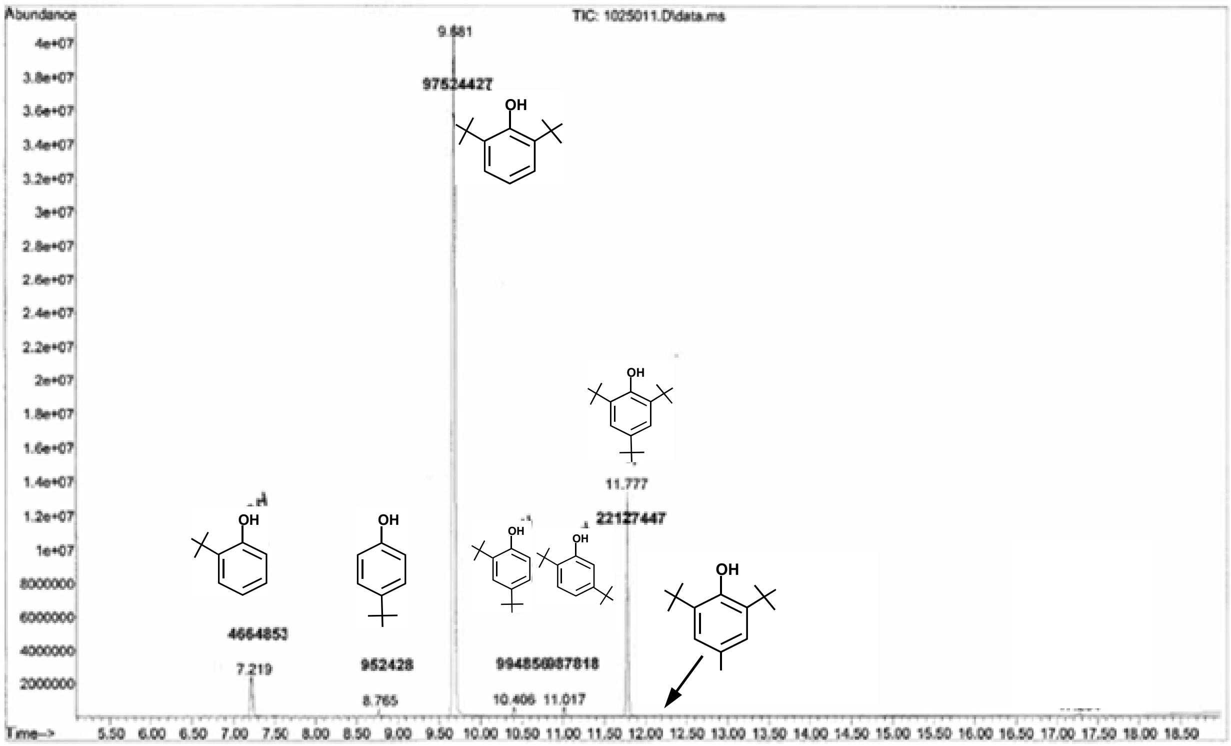

Figure A-2. Components found in AO-37 antioxidant package by GC-MS analysis utilizing a 24 mg/L spike.

Table A-3. Components found in AO-37 antioxidant package.

Compound	Abbreviation	Expected* (mg/L)
2,6-di-t-butylphenol	2,6-DTBP	18.00
2,4,6-tri-t-butylphenol	2,4,6-TTBP	4.20
2-t-butylphenol	2-TBP	0.88
2,4-di-t-butylphenol	2,4-DTBP	0.19
2.5-di-t-butylphenol	2,5-DTBP	0.18
4-t-butylphenol	4-TBP	0.18
2,6-di-t-butyl-4-methylphenol	2,6-DTB-4-MP	0.07

*based on a 24 mg/L spike.