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STORAGE STABILITY OF JET FUEL NOT CONTAINING ANTI-OXIDANT (AO)

**INTERIM REPORT
TFLRF No. 421**

by
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**U.S. Army TARDEC Fuels and Lubricants Research Facility
Southwest Research Institute® (SwRI®)
San Antonio, TX**

for
**U.S. Army TARDEC
Force Projection Technologies
Warren, Michigan**

Contract No. W56HZV-09-C-0100 (WD12)

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Gary B. Bessee, Director
U.S. Army TARDEC Fuels and Lubricants
Research Facility (SwRI[®])

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14. ABSTRACT This program assessed the effectiveness of adding anti-oxidant (AO) to various fuels after the fuels leave the refinery. The project involved storing severely hydro-treated fuels for a period of 12 months to simulate the 36 month storage period for vehicles and equipment aboard pre-positioned ships. One fuel contained AO from the refinery and an additional fuel was procured without AO added at the refinery. Each fuel was divided in half with one half being stored as received at 43°C and the second half treated with the JP-8 additive package and stored at 43°C. The fuel without the AO had AO added upon receipt at TFLRF. A third fuel was added to the matrix that was provided from Australia. This fuel was thought to exhibit poor storage stability characteristics. As with the other fuels, this fuel was divided into two portions with one stored as received and the other additized with the JP-8 additive package and stored at 43°C.					
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EXECUTIVE SUMMARY

Objectives: The objective of this study was to determine the effectiveness of adding Anti-Oxidant (AO) to various fuels after the fuels leave the refinery.

Accomplishments: This study analyzed severely hydrotreated jet fuels (with and without AO added at the refinery) and a fuel from Australia thought to have poor thermal stability. These fuels were stored at 43°C for a period of 36 weeks to simulate 36 months of storage in vehicles/equipment aboard pre-positioned ships. JP-8 samples (with and without AO) from the USAF program were included into the matrix once it was found that the fuel from Australia was not as bad as anticipated.

The Jet A with AO had excellent storage stability. The total acid number for the JP-8 samples increased during the storage tests. These values were below the ASTM D1655 limit but above the MIL-DTL-831331H limits.

A literature review was also performed to assimilate other research that was pertinent to this task. Of the gathered documents, there are two studies that were recently performed. The U.S. Air Force (USAF) and Naval Research Laboratory (NRL) conducted similar research and used some of these fuels in their studies. Their conclusions are similar to what was determined in the study.

Military Impact: This study determined that the current data still supports adding anti-oxidant to Jet A fuel destined for storage, but also demonstrated it could be performed after the fuel has been transported. Additional testing also reinforces the findings in the USAF and NRL reports that demonstrate the addition of the additives required by MIL-DTL-83133 to A-1 is not advisable for stored fuels.

FOREWORD/ACKNOWLEDGMENTS

The U.S. Army TARDEC Fuel and Lubricants Research Facility (TFLRF) located at Southwest Research Institute (SwRI), San Antonio, Texas, performed this work during the period June 2010 through January 2012 under Contract No. W56HZV-09-C-0100. The U.S. Army Tank Automotive RD&E Center, Force Projection Technologies, Warren, Michigan administered the project. Mr. Luis Villahermosa (RDTA-DP/MS110) served as the TARDEC contracting officer's technical representative. Mr. Allen S. Comfort of TARDEC served as project technical monitor.

The authors would like to acknowledge the contribution of the TFLRF technical support staff along with the administrative and report-processing support provided by Dianna Barrera.

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ACRONYMS AND ABBREVIATIONS

°	degree
%	percent
ADDC	Ammonium Diethyldithiocarbamate
ADPA	Alkylated diphenylamine
AO	Anti-Oxidant
BHT	Butylated Hydroxy Phenol
CRC	Coordinating Research Council
DCHPP	Dicyclohexylphenyl-phosphine
DTBP	Ditertiary Butyl Phenol
ETIO	Electron-Transfer-Initiated Oxygenation
FSII	Fuel System Icing Inhibitor
IASH	International Association for Stability Handling

ACRONYMS AND ABBREVIATIONS (Con't)

ICP	Inductively Coupled Plasma
IOA	Isothermal Oxidation Apparatus
JFTOT	Jet Fuel Thermal Oxidation Test
Kg	Kilo-gram
LPR	Low Pressure Reactor
MDA	Metal Deactivator
NAWC	Naval Air Warfare Center
NIPER	National Institute of Petroleum and Energy Research
Nm	Nanometer
NRL	Naval Research Laboratory
PDSC	Pressurized Differential Scanning Calorimetry
RBOT	Rotary Bomb Oxidation Test
SwRI	Southwest Research Institute
TARDEC	Tank Automotive Research Development and Engineering Center
TBMP	2-TERT-BUTYL-4-METHYLPHENOL
TFLRF	U.S. Army TARDEC Fuels and Lubricants Research Facility
USAF	U.S. Air Force
ZDDC	Zinc Dithiophosphate
VTR	Visual Tube Rating

1.0 OBJECTIVE

The objectives of this program were to: 1) perform a literature search to determine previous research performed investigating the effects of anti-oxidants on aviation fuels after the fuel leaves the refinery, and 2) perform storage stability testing to determine the effectiveness of adding anti-oxidants to various fuels after the fuels leave the refinery.

2.0 INTRODUCTION AND BACKGROUND

The USAF performed a storage stability test using severely hydro-treated aviation fuel as part of their JP-8 to Jet A conversion program.¹ These fuels were procured with and without anti-oxidant (AO) being added at the refinery. The USAF mission was to determine if AO would be effective if added upon receipt, instead of at the refinery. In order to optimize the use of the test fuels, the U.S. Army utilized the remaining fuel to determine the effect of storage aboard the U.S. Army pre-positioned fleet for periods up to 36 months.

3.0 LITERATURE SEARCH

A literature search was conducted to determine previous research investigating the effects of AO on aviation fuel after it is transported from the refinery. The literature research encompassed reviews of papers and presentations from various technical societies including the Coordinating Research Council (CRC), International Association for Stability Handling (IASH), SwRI Filtration Conferences, and government agencies. The titles, authors, and other pertinent reference information is provided for each document as well as a brief summary of the paper/presentation.

1. Pande, S.G., Black, B.H., Hardy, D.R., *“Development of a Test Method for the Determination of the Hydroperoxide Potential and Anti-Oxidant Effectiveness in Jet Fuels During Long Term Storage”*, Coordinating Research Council, Atlanta, GA, 1998.

The objective of this research was to develop an accelerated test method to predict within 24–48 hours the peroxidation potential of aviation turbine fuels for an ambient storage period of at least six months and the effectiveness of anti-oxidants when added to fuels that are stored for long periods. The test method developed determined that 100°C at 50psia air overpressure for 24 hours would realistically predict storage stability at ambient conditions for approximately 9 months. Anti-oxidants developed for gum control in gasoline and their effectiveness for peroxide control in aviation turbine fuels had never been documented. The overall effectiveness to control hydroperoxide formation was evaluated by implementing the stress test in a Low Pressure Reactor (LPR). The results confirmed previous findings regarding the effect of anti-oxidant structure on its efficacy. Electron releasing groups in the ortho and para positions markedly increase anti-oxidant activity. Alpha branched ortho alkyl groups considerably increase anti-oxidant activity whereas such group substitutions in the para position decrease it. For petroleum, the combination of two ortho tertiary alkyl groups are not as effective as one methyl and one tertiary butyl.

2. Sharma, B.K., Perez, J.M., Erhan, S.V., “*Soybean Oil-Based Lubricants: A Search for Synergistic Anti-oxidants*”, American Chemical Society, 2007.

Focus of this report was the enhanced ability of additive combinations to resist oxidative deterioration at elevated temperatures to extend the applicability of vegetable oil-based lubricants, the effectiveness of three different classes of anti-oxidants using Rotary Bomb Oxidation Test (RBOT) and Pressurized Differential Scanning Calorimetry (PDSC), and the synergistic effects of suitable combinations of anti-oxidants with anti-wear additives. PDSC was used as it inhibits the volatilization loss of lubricants and saturates the liquid phase with oxygen, which results in an acceleration of oxidation as well as a sharpening of the lubricant exotherm. PDSC is ran using either an isothermal mode to measure oxidation induction time or a programmed temperature mode to measure the onset temperature of lubricant oxidation.

Anti-oxidant, Zinc Dithiophosphate (ZDDC) functions as both a radical scavenger and hydroperoxide decomposer that reduces the hydroperoxides formed during the oxidation process to nonradical products like alcohols while being oxidized and thus preventing chain propagation.

Data showed ZDDC and Butylated Hydroxy Phenol (BHT) had identical responses to Pressurized Differential Scanning Calorimetry (PDSC) testing but differed by Rotary Bomb Oxidation Test (RBOT). ZDDC has a metal-deactivating functionality that inhibits catalyzed reactions by chelation, thus showing an anti-oxidant effect.

The current accepted theory of the role of anti-oxidants as radical scavengers or hydroperoxide decomposers explained as oxidation: initiation, propagation, branching, chain inhibition and peroxide decomposition. Anti-oxidants like ZDDC acting as a peroxide decomposer and metal deactivator inhibits the chain initiation step of oxidation, thus preventing the formation of free radicals and hydroperoxides. Anti-oxidants like BHT and Alkylated Diphenylamine (ADPA) act as radical scavengers and inhibit the propagation step.

Scant literature data is available to explain the synergism of anti-oxidant ZDDC and antiwear additive Ammonium Diethyldithiocarbamate (ADDC). The presence of sulfur in metal dithiocarbamates has been attributed to the formation of various sulfur oxyacids during hydroperoxide decomposition. These acids participate in the anti-oxidant mechanism by an acid-catalyzed ionic decomposition of the hydroperoxides. The dithiocarbamates and their oxidation products prevent the formation of lubricant radicals and hydroperoxides and increase the anti-oxidant efficacy of mixtures of metal dithiocarbamates synergistically. The high anti-oxidant efficiency of ZDDC may have been regenerated using the dithiocarbamate ligands of ADDC. During peroxide radical scavenging, ZDDC may form dithiocarbamate radicals and antimony of ADDC may form a stable chemical bond with the N or S atoms of these radicals by the coordination effect and prevent the molecule from chemical decomposition due to steric effects. This coordinated intermediate radical will be much less sensitive against oxidation and more stable than the original radical. The strongest synergistic response was due to the ability of dithiocarbamates to function as hydroperoxide decomposers/metal deactivators/radical scavengers and an additional radical scavenging effect by the amino group of the anti-oxidant.

3. Turbine and Diesel Fuels Panel of the Fuel Storage Stability Group, "*Jet Fuel Storage Stability*", Coordinating Research Council, Atlanta, GA, 1957.

This report covered a study of the effect of several storage environments on the stability of jet fuels. No correlation was found between peroxide number and insoluble residue formed in storage. There was some indication that the phenylene diamine-type additive was more effective in controlling soluble gum while the alkyl phenol-type was more effective in controlling insoluble residue. Eleven of the fuels in desert storage showed a high final gum content; a delay period was followed by a rather rapid increase in gum content that appeared to be approximately a linear function in time. Fuels that were exposed to the air had appreciably higher soluble gum content than those which were not deliberately exposed, but not applicable to insoluble residue. Drums that formed large amounts of soluble gum (>10 mg/dl) also had the greatest oxygen depletion. Fuels made up of 100% straight run distillate, were all relatively low in soluble gum.

Filterability appears to be more closely related to hydrocarbon type than to insoluble or soluble residue levels. Straight-run fuels had poor filterability characteristics with low insoluble residue levels. Many of the blended fuels contained cracked components and were high in soluble and insoluble residue but had good filterability characteristics. Effects of anti-oxidants on filterability appear to be random. No direct relationship exists between peroxide number and filterability characteristics. Fuels undergoing the least change in filtration properties during storage were blends containing cracked components.

4. Beaver, B.D., Gao, L., Fedak, M.G., Coleman, M.M., Sobkowiak, M., *"JP-900 From Coal Liquids? The Use of Dicyclohexylphenyl-phosphine to Enhance the Oxidative and Thermal Stability of a Model Coal Liquid"*, IASH 2000 International Conference, 2000.

An inverse relationship between the temperature at which a fuel absorbs oxygen and the amount of deposit formation during the oxidative degradation of various jet fuels exists. Fuels that tend to absorb the dissolved oxygen at lower temperatures (such as highly hydrotreated fuels) tend to produce smaller amounts of oxidative deposits. Henegan and Zabarnick proposed that this inverse behavior is consistent with a peroxy-radical chain mechanism for fuel degradation with free radicals derived from indigenous anti-oxidants being direct precursors. If correct, then the thermal oxidative stability would result from the direct reaction of an oxygen scavenger with molecular oxygen before the fuel is degraded.

This report discussed developing oxygen scavengers for JP-900. Electron-Transfer-Initiated Oxygenation (ETIO) should be amenable to oxygen scavenging functions. ETIO is an oxygenation reaction in which the rate limiting step involves an electron transfer from the substrate to molecular oxygen or an activated form of oxygen. ETIO mechanism does not involve a peroxy-radical or a free radical intermediate, ETIO should not be affected by the presence of classical hydrogen donor antioxidants such as BHT. Experiments with Dicyclohexylphenyl-Phosphine (DCHPP) and dodecane as the model coal derived jet fuel showed that rapidly deoxygenating the model fuel systems by DCHPP provides oxidative and pyrolytic stability.

5. Zabarnick, S., West, Z., Kuprowicz, N., Balster, L., Ervin, J., Minus, D., Striebich, R., *“Measurement of Key Species and Development of a Chemical Kinetic Model Toward the Prediction of Jet Fuel Thermal Stability”*, IASH 2005 International Conference, 2005.

Complementary experimental and computational techniques were developed to enable the prediction of jet fuel oxidation and deposition. Data was obtained using a near-isothermal thermal stability flow rig at 185°C for seven fuels with measurement of oxygen consumption, hydroperoxide production and surface deposition.

Many factors are involved in the production and destruction of hydroperoxides in fuel. Metals catalyze oxidation and thus increase the oxidation rate and hydroperoxide production rate. Reactive sulfur species remove hydroperoxides and thus lower the hydroperoxide level and increase the removal rate. Phenols react with peroxy radicals and thus slow the oxidation rate and slow the rate of production of hydroperoxides. Oxidation rates of fuel samples and the amount of deposition produced was measured using the following species class. Fuel polars, and phenol in particular. Sulfides and disulfides react with fuel hydroperoxides to produce non-radical products. Nitrogen compounds such as amines, indoles, carbozels, etc. The importance to thermal oxidation and deposition is poorly understood. Dissolved metals increase the deposition rate by a catalytic pathway and also may provide catalysis of other reactions. Proportional relationships between the measured species class concentrations and model inputs were obtained except for the metals.

6. Gernigon, S., Sicard, M., Ser, F., Bozon-Verduraz, F., “*Hydrocarbon Liquid Fuels Thermal Stability, Anti-oxidant Influence and Behavior*”, IASH 2009 International Conference, 2009.

Grinstead and Zabarnick showed that an inverse relationship between thermal stability and oxidative stability exists. The more fuel oxidizes rapidly the less likely it is to form deposits. Walter J. Balster and Lori M. Blaster studied the behavior of a metal deactivator, an anti-oxidant (BHT) and a dispersant (8Q405) and found additive pairs inhibit autoxidation more effectively than an individual additive, and the combination of all three show the best slowing of autoxidation. This paper evaluated three anti-oxidants on hydrocarbon oxidation; BHT, 2,4-DTBP, and 2-Tert-Butyl-4-Methylphenol (TBMP). 2,4-Ditertiary Butyl Phenol (DTBP) and TBMP were selected due to similar chemical structure to BHT. The three anti-oxidants were more effective for alkanes than for cyclic compounds with BHT being the most effective. The degradation products for all hydrocarbons tested were identified as alcohols and ketones.

7. Grinstead, B., Zabarnick, S., “*Studies of Jet Fuel Thermal Stability, Oxidation, and Additives Using an Isothermal Oxidation Apparatus Equipped with an Oxygen Sensor*”, University of Dayton Research Institute, Dayton, OH, 1998.

An Isothermal Oxidation Apparatus (IOA) with an oxygen sensor was used to provide real time data for the oxidation of jet fuels blended with additives in addition to deposition data at the end of the run. Oxidation behavior as studied with a fast oxidizing JP-5 that produces no deposits under operating conditions. BHT (a hindered phenol), AO-24 (a phenylenediamine), hexyl sulfide (a peroxide decomposer) and MDA (metal deactivator) – N.N-disalicylidene -1.2-propane diamine were blended into the fuel. AO-24 and BHT showed progressively longer delays in oxidation with increasing anti-oxidant concentration. Hexyl sulfide had no effect on the induction period but did change the final oxidation rate by improving oxygen consumption by 70%. The hexyl sulfide decomposes the hydroperoxides by a nonradical pathway. MDA had little effect on the oxidation, just a slight delay in onset of oxidation was observed. Deposition was evaluated with a commercial Jet A that oxidizes slowly and produces a moderate amount of deposit under current conditions. The amount of deposits and oxygen consumed are less when

BHT and MDA are present, but the amount of solids produced per mole of oxygen consumed is about the same as the unadditized fuel. This indicates that MDA and BHT are slowing the oxidation rate, which directly results in less deposition. When MDA is present the amount of oxygen consumed decreases. The amount of oxygen consumed with SPEC AID 8Q405 is slightly greater than the neat fuel but deposition is greatly decreased. This is expected with a dispersant type additive. SPEC AID 8Q462 is the best combination because the oxygen consumption and deposition are both minimized. This is currently being used in the field as an additive for JP-8+100.

8. Hydroperoxide Potential of Jet Fuels Panel, "*Determination of the Hydroperoxide Potential of Jet Fuels*", Coordinating Research Council, Atlanta, GA, 1988.

Instances of rubber attack by peroxides were found by the British in the Far East in 1962. It was determined that hydrogen treating had removed natural antioxidants, leading to the formation of peroxides during fuel storage. In Spring 1976, the U.S. Navy found cracking of rubber fuel control diaphragms when engines were operated on certain Japanese JP-5 fuels. MIL-T-5624K was amended to require the addition of oxidation inhibitors to all JP-5 and JP-4 fuels containing hydrotreated blending stocks. The additive inclusion prevented further problems but a shortage of inhibitor in 1974 and later created the need for a procedure that would identify peroxide-forming problem fuels. CRC was requested to develop a technique to determine the hydroperoxide-forming tendencies of jet fuels. Heating the fuel at 65°C for four weeks and measuring the peroxide number was determined to be the technique for a Go/No Go test, under the criterion of a peroxide number of 1.0 meq/kg, equivalent to 8.0 mg/kg in ASTM D3703. This readily distinguished between stable and unstable fuels and was useful for screening jet fuels for their long-time oxidation stability. This is not a precise quantitative tool due to the variability in results between eight laboratories.

9. Waynick, A., "*The Development and Use of Metal Deactivators in the Petroleum Industry: A Review*", Southwest Research Institute, San Antonio, TX, 2001.

Anti-oxidants were used in gasoline to control gum formation, but gave reduced performance when copper was present. Metal deactivators were used in gasoline in 1939 and have been used in other fuels, such as jet fuel, without further modification. Use of the metal deactivator MDA in jet fuels has become controversial as it can improve Jet Fuel Thermal Oxidation Test (JFTOT) results even when deleterious metals are not present. Many researchers have indicated that mechanisms other than chelation also exist, such as surface passivation and bulk phase reactivity. Despite numerous efforts these continue to be less than adequately defined.

At the trace levels often found in copper containing fuels, 50 µg/kg and above, hydrocarbon peroxidation is greatly accelerated. Other trace metals can cause similar effects but the size of the effect is strongly dependent on the metal. Dissolved transition metals are thought to initiate hydrocarbon peroxidation by catalyzing the formation of free radicals or by catalyzing the decomposition of hydroperoxides. Copper, cobalt, and manganese act as both an oxidizing agent and reducing agent allowing a non-stoichiometric catalytic process to occur where a very small concentration of metal can decompose large amounts of hydroperoxides. Copper is considered the most catalytically active metal found in fuels. The chelate effect is that the greater the number of donor sites in a metal deactivator the better the deactivation of the metal in fuel. Surface effects relates to the fuels propensity to form deposits on the hot surfaces. Bulk phase reactivity refers to any chemical activity of MDA (metal deactivator) other than chelation that changes the fuel thermal stability and occurs in solution where reaction with metal surfaces does not occur.

10. Nixon, A.C., "*Autoxidation and Anti-Oxidants of Petroleum*", Lundberg, W.O.; Wiley, New York, 1962, Chapter 17.

The vast petroleum industry is based upon the premise that most of its products will be combined with oxygen for the production of energy in the form of heat or power; either intermittently as in gasoline and diesel engines, or continuously as in jet engines, industrial energy sources, and domestic heating units. In all of these uses oxygen is often more an enemy than a friend, and much effort on the part of the petroleum chemist has been expended in trying to circumvent its attack. Section VI provides the following topics of discussion for jet fuels:

- History
- Specifications
- Composition
- Anti-oxidation
- Effect of composition on storage stability
- Effect of treatment
- Effect of metal and contaminant
- Effect of additives
- Effect of instability on filterability
- Thermal stability

11. Henry, C.P., “*Additives for Middle Distillates and Kerosene Fuels*,” Proceedings of 2nd International Conference on Long Term Storage Stability of Liquid Fuels, Stavinoha, L.L., Southwest Research Institute, San Antonio, TX 1986.

The benefits achievable from stabilizer additives and the effects of the other additives on stability properties are discussed. Anti-oxidants, metal deactivators, and dispersants are used to improve the stability of middle distillate fuels; the range of benefits obtained and factors that affect performance are discussed. Different anti-oxidants are used in jet fuels to prevent formation of peroxides. Metal deactivators are used in all fuel types to prevent oxidation catalysis by dissolved metal salts. The effects of the other additives including corrosion inhibitors, electrical conductivity additives, and cetane improvers were considered.

12. Stavinoha, L.L. and Westbrook, S.R., “*Accelerated Stability Test Techniques for Middle Distillate Fuels*,” ASTM Special Technical Publication, Distillate Fuel Stability Cleanliness, 1981, pages 3-21.

Improved test techniques are needed for evaluating the inherent stability of middle distillate fuels both in surveillance and in procurement activities. A project was initiated to define and evaluate the contributing conditions leading to the formation of deleterious products in accelerated aging

tests of middle distillate fuels and to relate these results to an experimental definition of more repeatable/reliable middle distillate fuel stability test technique(s).

A literature search was conducted to provide a list of stability test techniques and their interpretations which could be used in a correlative middle distillate fuel stability test program. For this program, seven accelerated stability tests were chosen and evaluated using a set of six test fuels. The test techniques were selected to represent a wide variety of test conditions, including temperature, aging time, and oxygen availability. These six test fuels were purposely chosen to represent a wider range of stabilities than would necessarily be commonly available for procurement. The fuel properties generally measured included both adherent and suspended particulates, steam jet gum, color, and light absorbance at 540nm. Accelerated stability test results were then related to test results obtained at a storage temperature of 43.3°C, which has generally been regarded as showing good correlation with long-term ambient storage.

13. Garner, M.Q. and White E.W., *“Accelerated Stability Test Techniques for Middle Distillate Fuels,”* ASTM Special Technical Publication, Distillate Fuel Stability Cleanliness, 1981.

Three-year outdoor bottle and column storage tests described in ASTM STP 531 have been completed on four Navy distillate fuels. The total insolubles were linear functions of the time in storage in both the bottle tests and in the accelerated 43.3°C beaker tests. About the same amount of new total insolubles formed in one week of beaker storage as formed in one month of bottle storage at an effective temperature of 19°C. The stability ranking of the four fuels was essentially the same regardless of which test was used and regardless of whether total insolubles or the rate at which additional insolubles were formed was used as the basis of the ranking. The geographic location for outdoor bottle tests was an important factor and was probably related to the average annual temperature at the location.

14. *“Development of a Test Method for the Determination of the Hydroperoxide Potential and Anti-oxidant Effectiveness in Jet Fuels During Long Term Storage,”* Report AFRL-PR-WP-TR-1999-2119, September 1999, Coordinating Research Council, Atlanta, GA.

A reliable test method is needed for predicting the long term storage stabilities of military aviation turbine fuel reserves as well as for evaluating the effectiveness of anti-oxidants approved for these fuels. This report addresses this need. It describes a reliable and practical accelerated test method for predicting the peroxidation potential of aviation turbine fuels that are stored for long term periods. A test methodology is also proposed for evaluating anti-oxidants for future qualification in the military specification, MIL-T-5624. This paper is based on the collective results of extensive rigorous studies performed by the four participating laboratories: Southwest Research Institute (SwRI), San Antonio, TX; Naval Research Laboratory (NRL), Washington, D.C.; Naval Air Warfare Center (NAWC), Trenton, NJ; and the National Institute of Petroleum and Energy Research (NIPER), Bartlesville, OK.

15. Hardy, D.R. and Black, B.H., "*Navy Aircraft Mobility Fuels R&D Program: Status of NRL Contributions for Second, Third, and Fourth Quarter, FY92*", Ser. 6180/644.2, October 1992, Naval Research Laboratory, Washington, D.C.

The Navy Aircraft Mobility Fuels Program Book, June 1989 provides the task assignments to NRL in seven elements for FY92. Status and significant progress summaries are provided in this report for the referenced work elements as provided below:

- Fuel Deposition Mechanism Studies
 - Effects of Copper
 - The effects of copper on the gravimetric JFTOT device
- Fuel Peroxidation Mechanism Studies
- Effect of Fuel Composition/Properties on Combustion
- Perform Analytical/Hardware Tests on As Received Fuel Samples

16. Morris, R.E., Hughes, J.A., and Colbert, J.E., *Energy & Fuels*, "*The Impact of Copper on the Liquid-Phase Oxidation of Jet Fuel for Advanced Aircraft*", 2004, 18, pages 490-496.

The fuel systems in advanced aircraft will subject the fuel to more severe thermal stress and increased recirculation than in current designs. This work was undertaken as part of a study to

determine the impact of copper contamination on the suitability of current JP-5 fuels in such advanced aircraft systems. Three issues were addressed in this study: 1) the impact of temperature and dissolved copper concentration on oxidation, 2) the catalytic activity of copper entrained in fuel sediment, and 3) the validity of the use of copper dop-ants to simulate exposure to copper-containing alloy surfaces. Examinations of liquid-phase oxidation by analyses of oxygen consumption and hydroperoxide formation rates were used to characterize the impact of copper to accelerate fuel oxidation in a flow system as a function of both temperature and copper concentration. From these measurements, the oxidation regime was represented graphically in a plot that expresses the impact of temperature and copper concentration on liquid-phase oxidation for that particular fuel. It was also found that if the time that the fuel was exposed to copper was relatively short, i.e., days or weeks, as opposed to months or years, it made no appreciable difference whether copper was introduced from exposure to copper-containing surfaces or from addition of a chemical compound. A stirred glass reactor was employed to measure the catalytic activity of copper entrained in fuel sediments on fuel oxidation. It was found that the catalytic activity of copper-containing sediments was negligible at up to 150°C.

17. Cuellar, Jr., J.P. and Russell, J.A., "*Additive Depletion and Thermal Stability Degradation of JP-5 Fuel Shipboard Samples*", Interim Report BFLRF No. 195, Southwest Research Institute, San Antonio, TX Contract No. DAAK70-85-C-007, June 1985.

Fleet samples of JP-5 fuel from U.S. Navy aircraft carriers and attendant refueling ships were acquired for analysis for the critical additives of Fuel System Icing Inhibitor (FSII) and corrosion inhibitor/lubricity improver. Trace metal content by Inductively Coupled Plasma spectroscopy (ICP) was also determined in order to evaluate the relationship between metals and fuel thermal stability. FSII depletion in the carrier fuel distribution system was appreciable, but only two samples out of 87 (carrier and refueler) analyzed contained less than the current Navy minimum of 0.05 volume percent at the aircraft refueling nozzle. Corrosion inhibitor loss on board the carrier was negligible. Eleven of the 81 samples examined were below the JP-5 specification minimum for corrosion inhibitor content. However, none of those eleven indicated unsatisfactory lubricity properties. Thermal stability was measured per ASTM D3241 (JFTOT), using MIL-T-5624L pass/fail criteria. All samples tested having copper concentrations in excess of

50 ppb failed the ΔP criteria; there were occasional failures in the 25-50 ppb range. The other three trace metals examined (Ni, Fe, and Zn) were rarely present at measurable levels (>10 ppb) and did not appear to contribute to thermal stability degradation.

18. Heneghan, Shawn O. and Harrison, William E., “*Anti-Oxidants in Jet Fuels: A New Look*”, Preprints of the American Chemical Society, Division on Petroleum Chemistry, 1992, 37 (2), pages 404-411.

Conventional wisdom holds that fuels which are more easily oxidized will exhibit less thermal stability. That is fuel stability as measured by deposits on metal surfaces and oxidation are strongly and positively correlated. This notion is based on the observation that the deposition of solid material, the consumption of oxygen and the production of peroxides are seemingly all related. Recent experiments have begun to question this understanding. For example, a single tube heat exchanger has shown inverse relation between the temperature required to force oxygen consumption and the amount of deposits produced in three fuels. Hardy has shown a similar relation for 13 fuels under storage conditions. A new look at the chemistry of anti-oxidants can help to explain those observations of inverse relation of oxidizability and thermal stability of jet fuels.

19. Hazlett, Robert N. and Hall, James M., “*Chemical Aspects of Jet Fuel Thermal Oxidation Stability*”, Preprints of International Conference on Fouling Heat Transfer Equipment, 1981, pages 501-510.

Jet fuels, under thermal stress in aircraft fuel systems, form solid material on heat exchanger surfaces and in combustion nozzles and controls. The reactions are triggered by the trace oxygen which dissolves in fuel by exposure to air. The total amount of insoluble solid formed may amount to only a few ppm based on the total fuel flow.

Studies with n-dodecane, a representative hydrocarbon in jet fuel, demonstrate the importance of hydroperoxides in thermal oxidation stability. Solid formation seems to be associated with temperature regimes characterized by free radical reactions.

Studies with fuels show that the deposits contain large amounts of oxygen, sulfur, and nitrogen. The concentration of oxygen may exceed 30 percent and sulfur and nitrogen exceed 10 percent each. Enhancement of sulfur in the deposit compared to the fuel sometimes reaches a value of 100 and enhancement values as high as 10,000 have been observed for nitrogen.

20. Rabaev, Moshe, Shapira, Daniela, and Ben-Asher, Josefa, "*The Effects of Long-Term Storage on Jet Fuel in Aircrafts*", Preprints of the 9th International Conference on Stability, Handling and Use of Liquid Fuels, 2005, pages 200-213.

Although long-term storage of jet fuel in large storage tanks and depots has been extensively studied, little work has been conducted on jet fuel stored in smaller containers. Because the surface area to volume ratio for fuels in small tanks is much larger than the ratio for large tanks, it was assumed that fuel aging and deterioration would be accelerated when stored in smaller tanks.

In this study, Jet A-1 grade fuel was stored in small, 30 liter, onboard aircraft fuel tanks. The fuel's physical and chemical properties were monitored for 24 months. Most of the fuel's characteristics showed no significant changes over the course of the study. Rises in both initial boiling point and flash point were noted, as well as some fluctuation in total acidity and water separation.

The only significant change in fuel properties found during the study was a drop in JFTOT thermal stability, which, for most of the systems monitored, went off specification after a short 6 month period. In an attempt to identify the causes of this drop, further tests were conducted on the samples monitored in the program, as well as other samples taken from similar aircraft systems. No correlation could be found between off-specification JFTOT results and other parameters tested, such as trace metal concentration, sediment, water content, and microbial growth. Although the cause for the off-specification JFTOT could not be determined, the assumption was that it was caused by degradation processes in the fuel. Furthermore, it was found that for the aircraft fuel system being studied, poor fuel thermal stability has little impact on engine performance.

The test program showed that for the particular fuel system being studied, no significant changes in the jet fuel's properties and composition were noted over a 2 year period. The higher surface area to volume ratio of the fuel tanks studied did not have an adverse effect on the fuels physical and chemical composition.

21. Roan, Melissa A., and Boehman, Andre L., "*Thermal Stability as a Function of Fuel Composition*", Petroleum Chemistry Division Preprints, 2002, 47(3), pages 174-177.

The presence of hydroaromatics and cycloalkanes has been shown to increase the thermal stability of jet fuels. Six fuels which had high concentrations of either hydroaromatics or cycloalkanes, were stressed in a flow reactor. Although all of the fuels examined demonstrated marked improvement in thermal stability when compared to JP-8, the fuels rich in cycloalkanes proved to be more stable than those containing large concentrations of hydroaromatics. This is especially true at the lower temperatures characteristic of the autoxidative regime of jet fuel degradation.

22. Bessee, Gary B. and Wilson, George R. III, "*USAF Plan for Converting from JP-8 to Jet A*", SwRI Interim Report 08.15254, U.S. Army TARDEC Fuels and Lubricants Research Facility (SwRI), Southwest Research Institute, Contract Number SP060005D55020012, January 2012.¹

The objective of this program was to obtain and/or generate data to answer a variety of technical and logistical questions concerning the conversion from JP-8 to Jet A and support the current field demonstrations, as required. Multiple tasks were performed to investigate various potential problem areas. These included the requirement for static dissipater additive, a filtration study, an evaluation of Aquarius as an alternative water management option, an evaluation of the need/feasibility to inject anti-oxidant upon base receipt of the fuel, and an additive cocktail blending study to reduce the logistics of additive addition.

If the conversion from JP-8 to Jet A was authorized, the aviation fuel may or may not have anti-oxidant added at the refinery. Therefore, one task was to determine what issues the lack of

anti-oxidant might cause. The acid number, Jet Fuel Thermal Oxidation Test (JFTOT), gum content, and peroxide number were determined for the various fuels.

Selected samples were also provided to the Naval Research Laboratory (NRL) for thermal stability testing using the Navy's low pressure reactor (LPR) test method. Based upon the data generated in this report and support data generated by NRL, Jet A shows no issues with long-term storage stability up to 24 months. The USAF also obtained 16 into-plane Jet A samples to ensure that the findings from the limited set of fuel samples were generally applicable to the fuels from in the field. The data generated by both SwRI and NRL from the into-plane Jet A samples agrees with the data generated from the selected four fuels used for this study. Material compatibility testing was performed using buna-n, Viton, and fluorosilicon elastomers soaked in the four fuel types. There were no apparent material compatibility issues between the material and the fuel with or without anti-oxidant.

23. Morris, Robert E., Hughes, Janet M., Begue Nathan J., and Myers, Kristina M., *“Assessment of the Effectiveness of Antioxidant Additions to Jet A Fuel Downstream at Point of Use”*, 12th International Conference on Stability, Handling and Use of Liquid Fuels, Sarasota, FL, October 16-20, 2011.²

The question of whether Jet A can be used as a drop-in replacement for JP-8 in military tactical platforms was investigated. Since commercial Jet A does not contain any anti-oxidants, the focus of this work was to determine if Jet A fuel stability could be mediated appropriately by adding an approved anti-oxidant (AO) to purchased product downstream in the supply chain.

In order to make an educated decision regarding the substitution of Jet A for JP-8, two issues had to be resolved. The first was to understand the extent to which anti-oxidant-free hydrotreated Jet A fuels tend to undergo autoxidation degradation in the supply chain. The second issue was to determine the relative effectiveness of adding approved anti-oxidants to a reactive jet fuel at the refinery versus adding the anti-oxidant after the fuel has undergone autoxidative degradation in the supply chain or during extended storage.

Twenty-two Jet A samples, some with and some without anti-oxidant, were stressed in a low pressure reactor (LPR) at 90°C and 100 psig O₂ for 24, 48, and 96 hours. Autoxidation during this stress was monitored by measuring hydroperoxide concentrations and anti-oxidant consumption. It was found that all Jet A fuels tested in the LPR under these conditions were stable for up to 16 hours stress time, which is generally considered to predict roughly two years of ambient storage. However, a review of the origins of this correlation in the literature, in addition to our findings obtained under different LPR test conditions, have placed into question the applicability of such accelerated stress testing to predict storage stability of reactive fuels. There was also evidence that addition of the JP-8 additive package (corrosion inhibitor, fuel system icing inhibitor, static dissipater) served to increase the extent of autoxidation of these fuels in the LPR.

4.0 STORAGE STABILITY TESTING

The USAF performed storage and thermal stability testing of severely hydro-treated aviation fuel as part of the JP-8 to Jet A conversion program. The U.S. Army used the fuel from the .USAF study as part of their storage and thermal stability. Whereas the USAF stored the fuel under ambient conditions, the U.S. Army stored the fuel samples at 43°C. The objective of the storage test was to store and analyze these fuels for a period of 36 weeks to simulate 36 months of storage in vehicles/equipment aboard pre-positioned ships. It was not possible to receive small quantities of Jet A with and without anti-oxidant from the same refinery, but TFLRF was able to get the two fuels from the same oil company (ConocoPhillips).

The four test fuels initially used for this study were:

1. A severely hydro-treated Jet A delivered without anti-oxidant, tested as received
2. A severely hydro-treated Jet A delivered with anti-oxidant, tested as received
3. Jet A1 from Australia (It was not known if it contained anti-oxidant or not)
4. Jet A1 from Australia – anti-oxidant added upon receipt to TFLRF

The fuel from Australia was thought to have poor thermal stability and no history or certificate of analysis was available for this fuel.

At fifteen weeks, the fuels from Australia had not shown the expected poor thermal stability as suggested from the field. These samples remained in storage, but the sampling time was extended to every six weeks. The two Jet A samples from the USAF study that had the military additive package added to the fuel was included in this matrix for the remainder of the study. Although referred to as JP-8 for this report, these fuels do not necessarily meet the freeze point requirement for JP-8.

Samples were analyzed every three weeks using the four tests shown below.

1. ASTM D3242 – Total Acid Number
2. ASTM D3703 – Peroxide Number
3. ASTM D3241 – Jet Fuel Thermal Oxidation Test (JFTOT) at 260°C
4. ASTM D3241 – JFTOT Breakpoint

The fuels had good thermal oxidative stability to start. The specification requirement, essentially, that the fuel have a minimum breakpoint of 260°C. The CRC World Fuel Survey showed the median breakpoint to be 285°C and the data for all of the fuels during the first 21 weeks of storage hovered around that value. At week 24, the JFTOT breakpoint for the Jet A with AO maxed out (>320°C). This is unusual but not unheard of and previous instances of this had a key characteristic – the failing temperature (breakpoint +5°C) is characterized by an Abnormal deposit, usually of the light blue translucent variety.

The data for the tests was reduced and it indicated that the failing tests that defined the Week 0 through Week 21 breakpoints were indeed Abnormal ratings. The heater tubes were inspected and confirmed the ratings. As suspected, the failing Abnormal ratings were of the light, translucent blue variety. The deposits at higher temperatures, in Weeks 24–36, were visible but not Abnormal.

TFLRF ran representative heater tubes from Week 21 and Week 24 on the ellipsometer. The ellipsometer is a valuable research tool for evaluating heater tube deposits. In its most basic format the ellipsometer can give comparison data to the visual rating, Table 1.

Table 1. Ellipsometer Comparison Data to the Visual Rating

Time, weeks	Fuel Description	Temperature, °C	Visual Tube Rating, VTR	Ellipsometer Tube Rating, ETR
Week 21	Jet A with AO	295	2	13
Week 21	Jet A with AO	300	2A	50
Week 24	Jet A with AO	305	2	21
Week 24	Jet A with AO	310	2	16
Nominal	Jet A	285	3	85

Table 1 provides representative analyses from the testing. The Week 21 data shows the tube results that define the breakpoint. The Week 24 data are two higher temperatures, passing tests. Below are nominal values for normal testing. The median breakpoint is 285°C, most fuels fail on normal deposition and the limit is a Visual Tube Rating (VTR) Color Code of three and the latter corresponds to an ellipsometer depth of approximately 85nm.

As indicated above, the ‘failing’ Abnormal deposit is well below the typical deposition for failures from normal deposits. Another way to look at this is to inspect the deposition maps for these tubes.

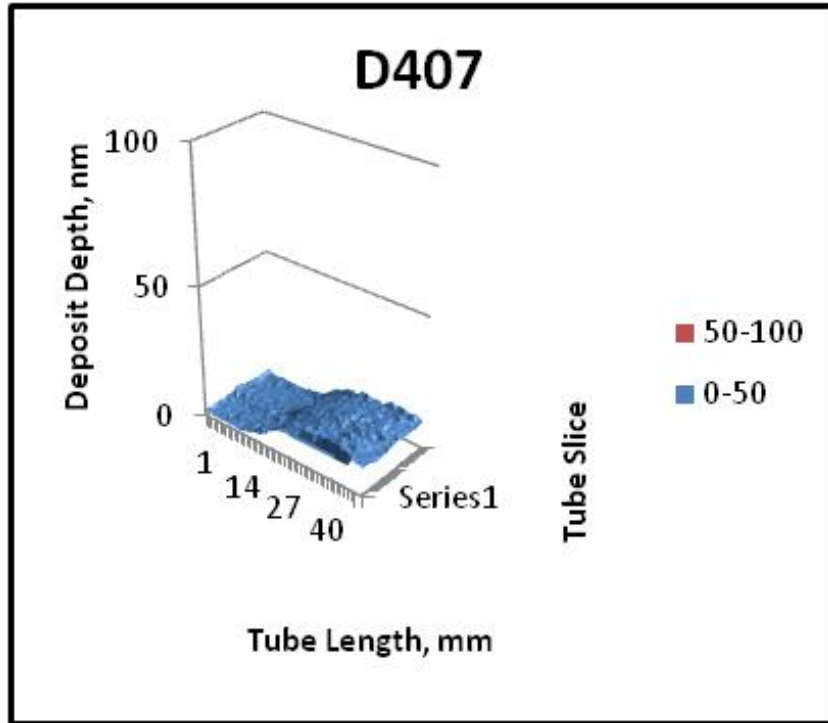


Figure 1. Deposition Map for Jet A with AO at 295°C

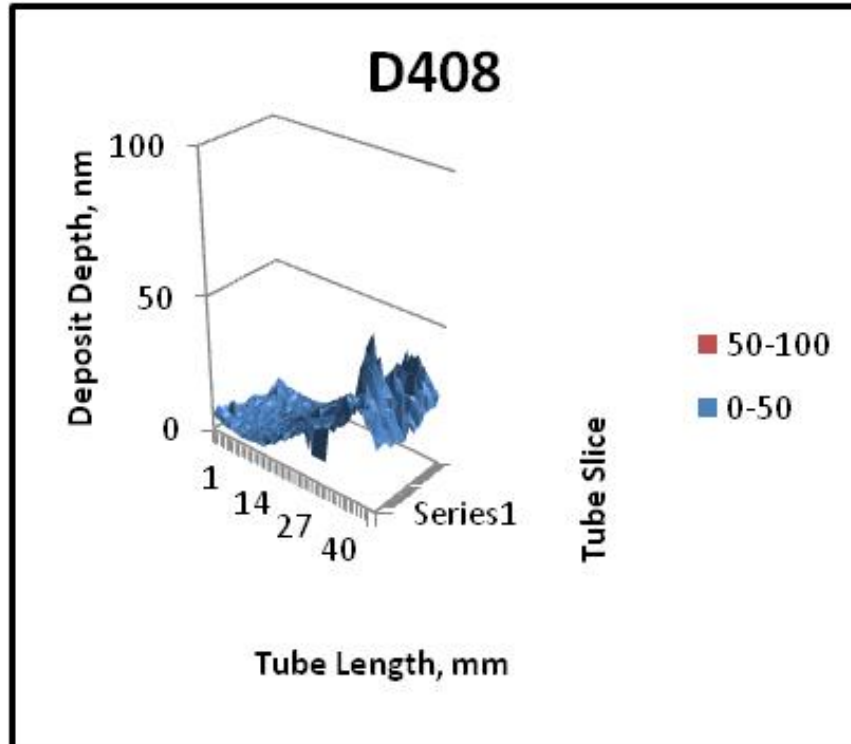


Figure 2. Deposition Map for Jet A with AO at 300°C

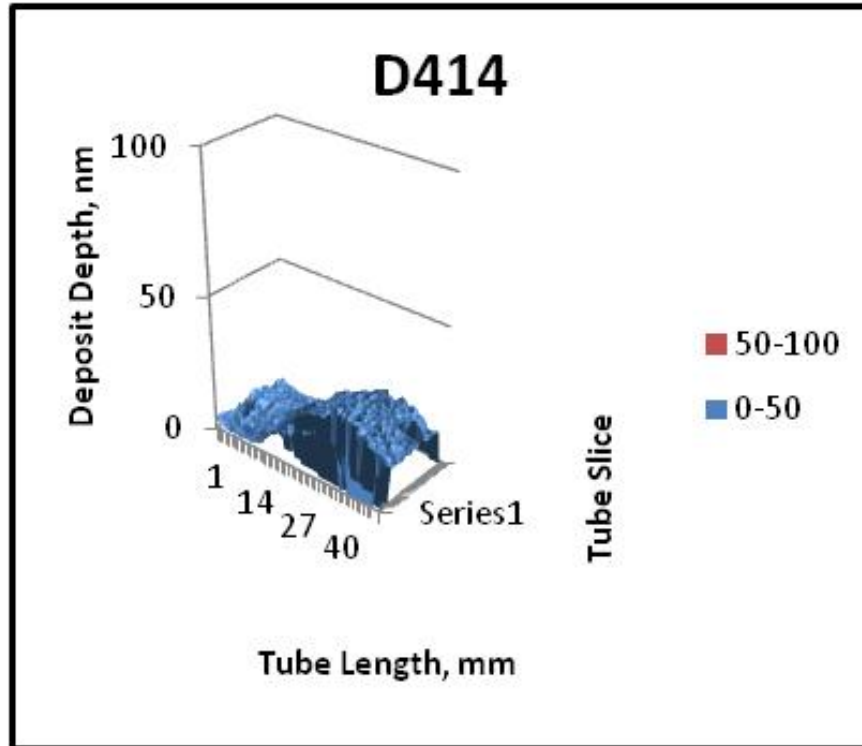


Figure 3. Deposition Map for Jet A with AO at 305°C

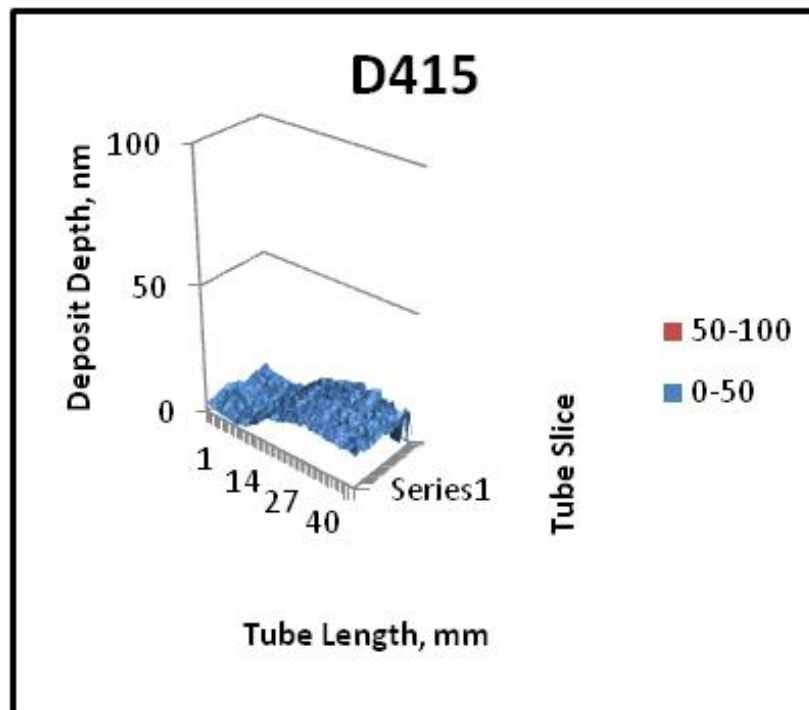


Figure 4. Deposition Map for Jet A with AO at 310°C

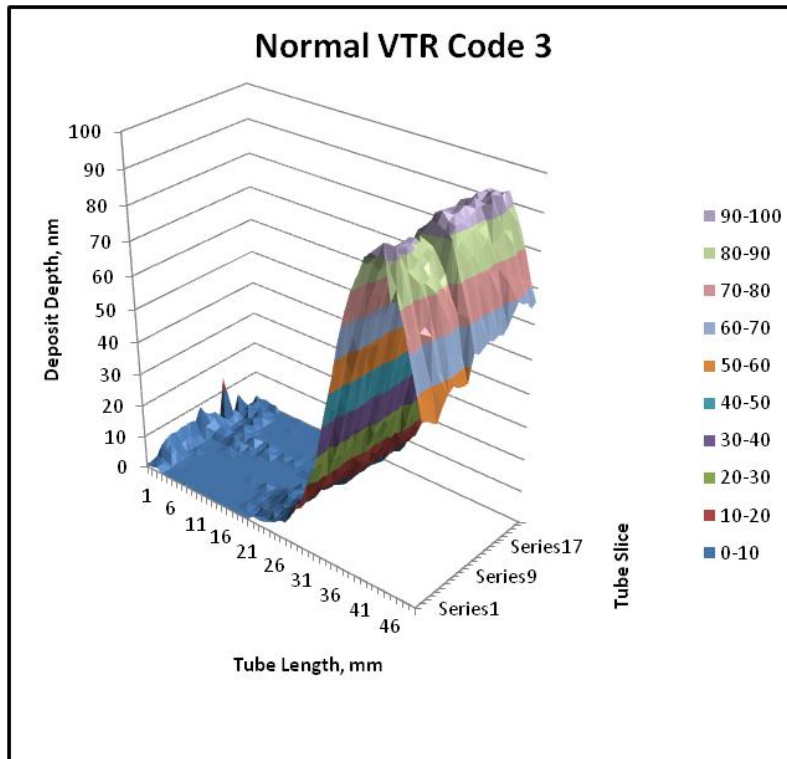


Figure 5. Deposition Map for Normal Visual Tube Rating Code 3

Figures 1–5 show how incidental the deposit levels are for the Jet A with AO tubes compared to a representative failing deposit. Looking at the deposit maps, one might even speculate that whatever caused the Abnormal in test D408 was a separate effect over a base level deposit of the basic fuel.

All of the breakpoint samples for Jet A with AO were in individual one gallon epoxy lined cans. However, all of those cans were filled from a single drum of filtered fuel and they were all, except for Week 0, stored in the same 43°C walk in oven. The Abnormal deposits are there and then they are not. This is unusual but not unheard of.

While this effect is startling, the change from a good fuel to an exceptionally good fuel is not an operational issue. More important is the less dramatic but steady trending of the fuel supplied without AO from good to marginal. This is not particularly important for commercial use of Jet A as it is not stored for long periods but it definitely reinforces the earlier SwRI

recommendation to the USAF¹ to introduce AO into fuel destined for long term storage (within 24 weeks).

Another key point to consider is the additional information that shows the other JP-8 additives have a negative impact on thermal oxidative stability with time. In the USAF report on this issue, this observation was stronger in the fuel delivered without AO than for the fuel with AO. In this report the aged fuels show an essentially equivalent decline into marginal performance characteristics.

5.0 ACID NUMBER AND PEROXIDE NUMBER RESULTS

The acid number and peroxide number data is shown for the entire storage period in Figures 6-7 respectively. As in the previous USAF¹ and NRL² reports the acid number and peroxide number do not show any definitive trend in relation to long term storage. None of the samples exceed the specification limit for acidity of Jet A (D1655), 0.10 mg KOH/g, or the informal peroxide limit for turbine fuel, 8 mg/Kg. The only interesting effect was caused by adding JP-8 additives, without AO, to the aged Jet A with AO. This fuel, which was delivered with JP-8 passing acid numbers, had an order of magnitude increase in acid number. Contrary to the field information, the fuel samples obtained from Australia produced comparable data to the Jet A fuel with AO.

The peroxide data shows fluctuations in the results which is common but the values did not approach the limits per ASTM D3703 of 8 mg/Kg, Figure 7.

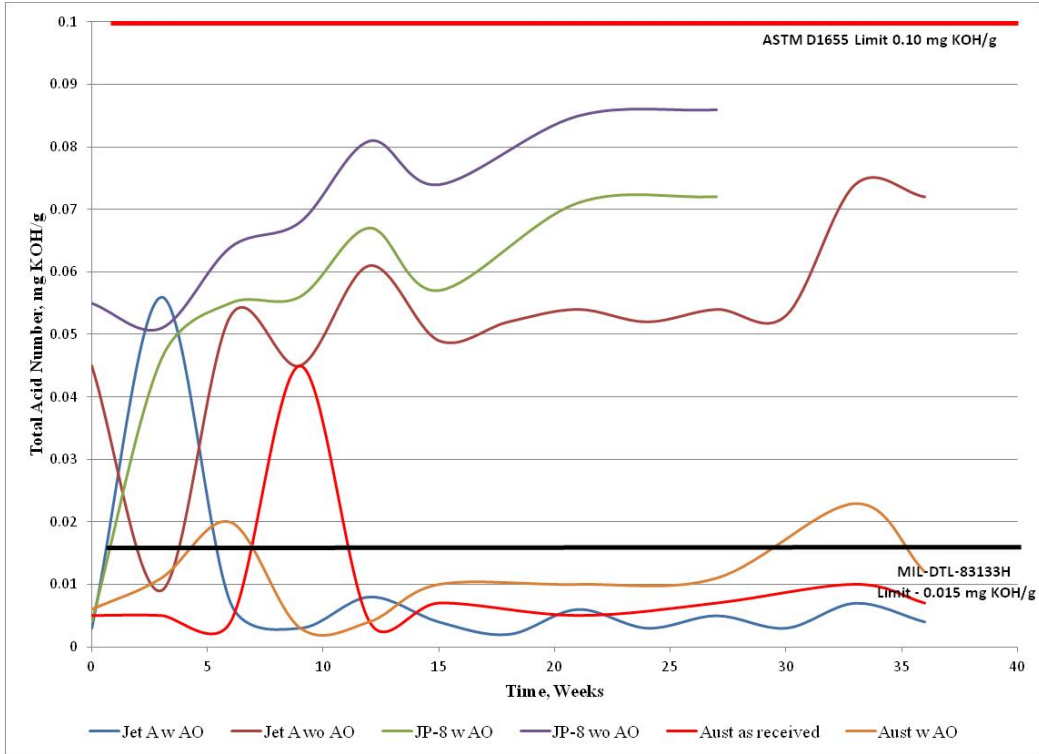


Figure 6. ASTM D3242 – Total Acid Number for Aged Fuel Samples

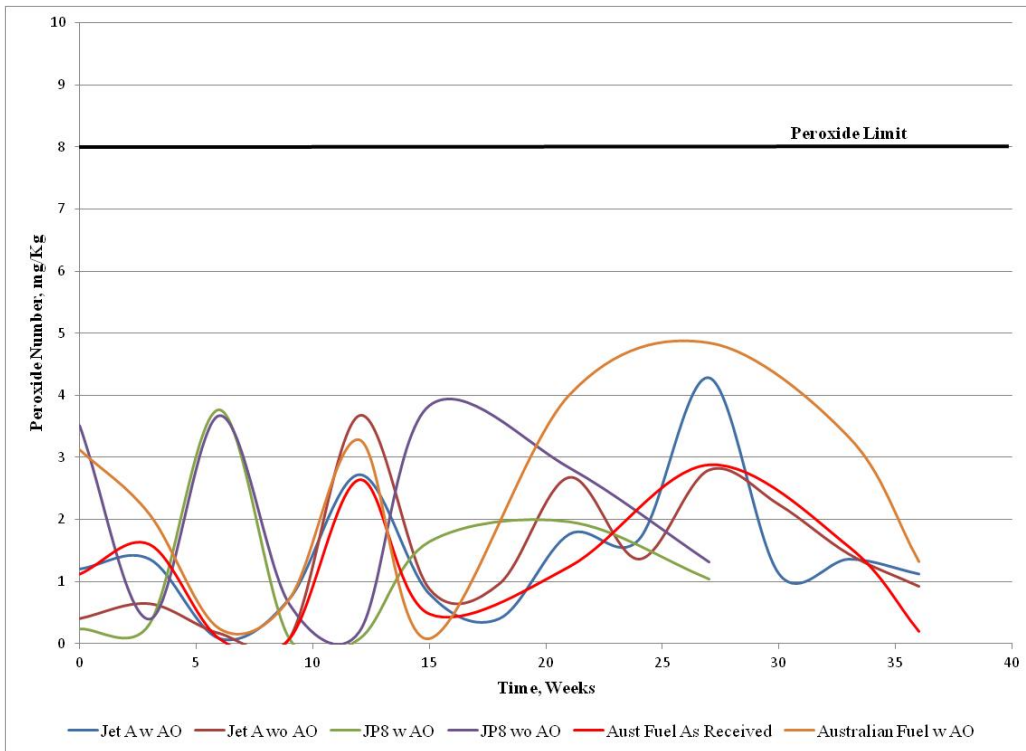


Figure 7. ASTM D3703 – Peroxide Number for Aged Fuel Samples

The current data still supports adding AO to Jet A fuel destined for storage. This additional testing also reinforces the findings in the USAF and NRL reports that adding the other JP-8 additives in storage is not advisable.

6.0 CONCLUSION

A literature search was conducted to determine previous research investigating the effects of anti-oxidants on aviation fuel after it is transported from the refinery. The literature research encompassed reviews of papers and presentations from various technical societies including CRC, IASH, SwRI Filtration Conferences, and government agencies. Emphasis for this report includes research conducted by the USAF¹ and NRL² that supports the conclusions of this research.

Two severely hydro-treated Jet A was procured for thermal and storage stability analysis. One sample contained anti-oxidant while the second Jet A sample did not. Military fuel are required to contain anti-oxidant, whereas commercial Jet A does not require anti-oxidant to be added to the fuel. A fuel from Australia was included in the test matrix as it was thought to have poor storage stability properties. The fuel was tested under two test conditions – as received and with anti-oxidant added.

Based upon the initial results, the data revealed the fuel from Australia was stable. Therefore, JP-8 fuel, with and without anti-oxidant, was added to the test matrix until the conclusion of the storage test.

The test fuels were stored at 43°C for 36 weeks to simulate storage at ambient temperature for 36 months³. A summary of the results for each fuel type is provided.

1. Australian Jet A1, as received and with AO: both fuel were remarkably stable with no significant change in any of the properties.

2. A hydro-treated Jet A delivered without AO, tested as received and with the JP-8 additives (without AO): As shown in the USAF¹ and NRL² research, the overall fuel thermal oxidative stability quality declined with time, worse with JP-8 additives. Anti-Oxidant itself has no direct impact on thermal oxidative stability but it can prevent the formation of chemicals that do.
3. A hydro-treated Jet A delivered with AO, tested as received and with JP-8 additives (no additional AO): This testing fell into two categories, predictable and not. As might be expected the addition of the JP-8 performance additives was not kind to the fuel. The unpredictable point was the sudden, dramatic increase breakpoint just past midway in the storage testing.

The current data still supports adding anti-oxidant to Jet A fuel destined for storage. As part of the USAF and NRL conclusions, it was determined Jet A could conservatively be stored without problems for 24 months. However, this research demonstrates Jet A with AO can be stored without issues for 36 months. There is some indication from other studies, that the standard CI/LI material might be the source of long term storage issues for JP-8 additives but proving that would take additional effort. This additional testing also reinforces the findings in the USAF and NRL reports that adding the military additives in storage is not advisable.

7.0 REFERENCES

1. *“USAF Plan for Converting from JP-8 to Jet A,”* Bessee, Gary B. and Wilson, George, R. III, U.S. Army TARDEC Fuels and Lubricants Research Facility (SwRI), San Antonio, TX, Contract No. SP060005D55020012, SwRI Project No. 08.15254, January 2012.
2. *“Assessment of the Effectiveness of Antioxidant Additions to Jet A Fuel Downstream at a Point of Use,”* Morris, Robert E., Hughes, Janet M., Begue, Nathan J., and Myers, Kristina M., 12th International Conference on Stability, Handling and Use of Liquid Fuels, Sarasota, FL, 16-20 October 2011.

3. **“Appendix X1. Correlation of 43°C Stability Test Results with Actual Field Storage”**, ASTM D4625, ASTM International, 2009