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FINAL REPORT

RESEARCH AND DEVELOPMENT
IN SUPPORT OF THE
NAVY TECHNOLOGY CENTER
FOR SAFETY AND SURVIVABILITY

GC-IR-OC-1618

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FINAL REPORT

RESEARCH AND DEVELOPMENT IN SUPPORT OF THE NAVY TECHNOLOGY CENTER FOR SAFETY AND SURVIVABILITY

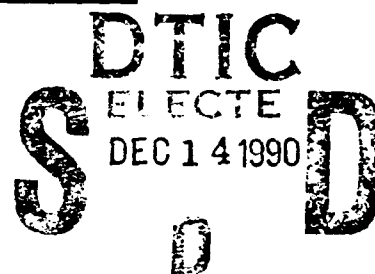
GC-TR-90-1628

Prepared for
Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, D.C. 20375-5000

As Required By
Contract Number
N00014-86-C-2288

Prepared by
GEO-CENTERS, INC.
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October 1990



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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 26 October 1990	3. REPORT TYPE AND DATES COVERED FINAL JULY 1986 - SEPT 1990		
4. TITLE AND SUBTITLE Research and Development in Support of the Navy Technology Center for Safety and Survivability			5. FUNDING NUMBERS N00014-86-C-2288	
6. AUTHOR(S) S. Pande, B. Black, R. Matuszko, S. Darrah, J. Watkins, J. Burnett, L. Isaacson, G. Andrykovitch, M. Tabacco, C. Mitchell, W. Affens, and J. Schreifels				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) GEO-CENTERS, INC. 7 Wells Avenue Newton Centre, MA 02159			8. PERFORMING ORGANIZATION REPORT NUMBER GC-TR-90-1628	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Naval Research Laboratory 4555 Overlook Avenue, S.W. Washington, DC 20375-5000			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) This report summarizes the results obtained for the tasks performed in support of the Navy Technology Center for Safety and Survivability. These tasks address existing Navy problems in the following fuel related areas: thermal stability, long term storage stability, combustion, and fuel handling. Also in areas of Chemical, Biological, and Radiological (CBR) defense technology. Highlights of some of our significant contributions in fuel related problems include the following: 1) development of an optical method for measuring JFTOT heater tube deposits; 2) development of reliable accelerated bench scale test methods for ambient storage stability of middle distillate fuels; 3) development of rigorous and practical criteria for evaluating cetane indices; 4) evaluation of the Shell Premixed Burner; 5) determination of lubricity enhancer additive depletion in jet fuel during fuel handling/transfer and identification of those fuels that did/did not contain naturally occurring lubricity species viz, straight chain alkanolic acids; 6) recommendation that alkalization offers a safer and less costly alternative to biocides; and 7) development of an in-line fiber optic jet fuel contamination monitor. In CBR defense technology, some of our valuable contributions include: characterization of the gases/vapors adsorbed on the collective protective systems filters; and development of a formulation to replace the standard decontaminant currently employed.				
14. SUBJECT TERMS * Jet fuels, diesel fuels, thermal stability, storage stability, cetane index, combustion quality, compositional analysis, fuel handling, collective protection system, and decontamination.			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

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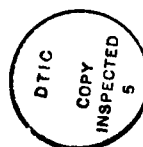
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INTRODUCTION

In this final report, the results obtained by GEO-CENTERS, INC. for the tasks performed in support of Naval Research Laboratory (NRL) Contract Number N00014-86-C-2288 during the period, July 1986 through September 1990 are summarized.

The tasks performed in support of the Navy Technology Center for Safety and Survivability addressed existing Navy problems in the areas listed below:

1. Jet fuel thermal stability
2. Naval Distillate Fuel long term storage stability
3. Jet fuel long term storage stability
4. Fuel combustion: ignition quality and combustion quality
5. Fuel Handling: fuel contamination, fuel lubricity, electrostatic charging, microbial growth, and flash point
6. Chemical, Biological, and Radiological (CBR) defense technology:
 - a. Collective protection
 - b. Decontamination

Results from work performed in the areas listed above have been published either in refereed journals or reported as NRL Memorandum Reports or GEO-CENTERS reports. Additionally, results were presented in various meetings, including the American Chemical Society, the International Conference on Stability and Handling of Liquid Fuels, and the Scientific Conference on Chemical Defense Research. Consequently, in this final report, following a brief background of each problem area investigated, only the salient results and conclusions are reported along with a list of the publications/presentations. Copies of the papers and abstracts of the reports are given for each area in the Appendices.

1.0 JET FUEL THERMAL STABILITY

1.1 Background

New engine designs subject aviation fuels to greater thermal stress thereby increasing their tendency to form gums and precipitates. The formation of insolubles result in decreased efficiency of heat exchangers, seizing of control valves, and injector fouling. The



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problem of thermal instability of fuels is exacerbated by the declining quality of petroleum crudes and the increasing demand for aviation turbine fuel, such as JP-5, by the Navy. The combination of these factors reflect the importance of jet fuel thermal stability to the Navy.

1.2 Results and Conclusions

In support of this ongoing research program at the Naval Research Laboratory, the following areas have been investigated and the results given therein:

1.2.1 The effects of stabilizer additives on the thermal stability of a jet fuel using a modified Jet Fuel Thermal Oxidation Tester (JFTOT) apparatus

The stabilizer additives examined were representative of those commonly used and included a hindered phenol, a phenylenediamine, an aliphatic tertiary amine (FOA-3), the same tertiary amine plus a metal deactivator (FOA-310), and a metal deactivator (MDA): N,N'-disalicylidine-1,2,-diaminopropane. The effects of the additives on the amount of heater tube deposits were based on the quantities of total carbon found on each tube. Total carbon was measured by combustion to carbon dioxide using a Perkin Elmer Model 240 elemental analyzer.

The results of this study, which was conducted at heater tube temperatures of 260, 270, 280, and 310°C indicated, with respect to the neat fuel, that all the additives reduced heater tube deposits at 260°C. As the stress temperature was increased, only the metal deactivator, present either alone or as an additive in FOA-310, continued to reduce the amounts of heater tube deposits. The effectiveness of the other additives decreased with increase in stress temperature.

1.2.2 Development of an optical method for measuring JFTOT heater tube deposits [as stipulated in subtasks (f) and (g) of Task 4 of the Contract]

As revealed in a round-robin effort conducted by the Coordinating Research Council in 1974, the visual method of rating tube deposits (ASTM D3241) is highly subjective. Consequently, development of an optical method, which uses fiber optic probes, computerized data reduction, and graphic display, can be considered a major breakthrough. In a recent evaluation of JFTOT heater tube deposit rating methods, conducted at the Naval Research Laboratory, the GEO-CENTERS tube rating method was found to correlate well with the combustion analytical method. The combustion method of measuring total carbon content, although considered to be most reliable, is a destructive method. In contrast, the GEO-CENTERS method, which is based on interferometry, is non destructive. The optical method can be used as a real time monitor or as a post analysis scanner.



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When in the real time monitor mode, in situ measurements of the thickness of the film formed on the JFTOT metal heater tube can be made. This monitor has been used successfully to measure the rate of deposition. In addition, it shows promise as a method for determining the breakpoint temperature of the fuel. GEO-CENTERS has delivered a real time monitor to the Naval Air Propulsion Center (NAPC) and to the Naval Research Laboratory.

During the conduct of these efforts, GEO-CENTERS, INC. has contributed significantly in the development of a JFTOT heater tube scanner for measuring tube deposits. The scanner utilizes the same optical components of the real time monitor (fiber optic probes, light source, and detector) but different software. This new software, which was also developed by GEO-CENTERS, INC. will operate the analog-digital conversion hardware and acquire the data, as well as analyze the data. This software is currently being used routinely at NRL to determine the thickness of the deposit formed along the JFTOT tube, and hence the volume of deposit.

1.2.3 The Role of Metal Deactivators in Jet Fuels

Metal deactivators (MDA) play a very important role in the inhibition of gum formation on metal surfaces. Although MDA's exact role has not been definitively proven, a mechanism that has been proposed is its role as a surface passivator. Our recent results, however, do not appear to support a surface passivation mechanism. Using three surface sensitive techniques we have found that, under ideal conditions, MDA was present only at very low coverages. Such small amounts are inconsistent with a surface passivation mechanism. Much higher amounts would be evident if metal passivation were the operative mechanism.

1.3 Publications, Reports, and Presentations

Copies of the following publications/presentations and abstracts of the reports are included in **Appendix A1**:

"Fiber Optic JFTOT Monitor Manual," prepared for The Naval Air Propulsion Center, by GEO-CENTERS, INC, November 1986.

S. Darrah, "Development of New Optical Methods for Tube Deposit Rating in JFTOT Procedure," Coordinating Research Council Meeting, Dayton, Ohio, April 23, 1987.

R.E. Morris, R.N. Hazlett, C.L. McIlvaine III, "Comparison of JFTOT Heater Tube Deposit Rating Methods for the Evaluation of Fuel Thermal Stability," NRL Memo Report No. 6147, December 29, 1987.



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R.E. Morris, R.N. Hazlett, and C.L. McIlvaine III, "Effectiveness of Selected Stabilizer Additives in Improving the Thermal Oxidation Stability of Jet Fuel," Preprint Am. Chem. Soc., Div. of Petroleum Chem., 33, (2), 364, 1988.

R.E. Morris, R.N. Hazlett, and C.L. McIlvaine III, "The Effects of Stabilizer Additives on the Thermal Stability of Jet Fuel," *Ind. Eng. Chem. Res.*, August 1988, 27(8), pp. 1524-1528.

R.E. Morris, R.N. Hazlett, C.L. McIlvaine III, "Comparison of JFTOT Heater Tube Deposit Rating Methods for the Evaluation of Fuel Thermal Stability," Conference Proceedings, 3rd International Conference on Stability and Handling of Liquid Fuels, London, Vol. 1, pp. 226-239, September, 1988.

R.E. Morris, R.N. Hazlett, and C.L. McIlvaine III, "Influences Exerted by Selected Stabilizer Additives on the Thermal Stability of Jet Fuel," Conference Proceedings, 3rd International Conference on Stability and Handling of Liquid Fuels, London, Vol. 1, pp. 260-267, September, 1988.

J.A. Schreifels, R.E. Morris, N.H. Turner and R.L. Mowery, "The Interaction of a Metal Deactivator with Metal Surfaces," Preprints, Am. Chem. Soc., Div. Fuel Chem., 35, (2), pp. 555-562, 1990.

J.A. Schreifels, R.E. Morris, N.H. Turner and R.L. Mowery, "The Interaction of a Metal Deactivator with Metal Surfaces," ACS National Meeting, Boston, MA, April 22-27, 1990.

J.A. Schreifels, R.E. Morris, N.H. Turner and R.L. Mowery, "The Interaction of a Metal Deactivator with Metal Surfaces," Annual meeting of the Coordinating Research Council, Arlington, VA, April 24-26, 1990.

2.0 NAVAL DISTILLATE FUEL LONG TERM STORAGE STABILITY

2.1 Background

Naval Distillate (MIL-F-16884H), the primary mobility fuel used in U.S. Navy ships and boats is frequently stored for several years in strategic reserves. Consequently, its deterioration in long term storage is of great concern. Insoluble sediment and gum, which are formed during deterioration, plug fuel system filter separators and engine nozzles thereby hindering efficient engine operation. In extreme cases, engine shut down has resulted from this problem.



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2.2 Results and Conclusions

The two subtasks specified in Task 1 of the Contract were successfully completed and the results are presented below:

2.2.1 Development of a Reliable Accelerated Bench Scale Test for Ambient Storage Stability

The results of previous and ongoing storage stability research in support of the Navy's programs, confirmed the inadequacy of the storage stability specification test, ASTM D2274, which is an accelerated stress test conducted at 95°C for 16 hours. For example, it is not a good predictor of storage stability for freshly refined middle-distillate fuels that contain catalytically cracked stocks, e.g. light cycle oil (LCO). Also, the stress time of 16 hours appears to be too short for many fuels.

GEO-CENTERS, INC. has contributed significantly to the development of the Low Pressure Reactor (LPR) method which is expected to replace ASTM D2274. Advantages of this new method over previous methods are its greatly reduced test times and its excellent precision for replicate samples. Other major advantages include its excellent correlations with lower temperature bottle tests, its good discrimination of stability between fuels and, most importantly, its ability to accurately predict insolubles formation of various fuels during ambient storage. In addition, the new LPR method appears to adequately predict the stability of fuels containing LCO, as well as to accurately evaluate the stability additives for use in mid-distillate diesel fuels.

2.2.2 Recommendations for a New Navy Quality Product List (QPL) for Antioxidant Additives and Additive Packages Storage Stability Additives for Naval Distillate Fuels

Based on the results of the additive qualification program conducted for improving the long term storage stability of Naval Distillate Fuels for a period of three years at ambient temperature, two single component additives can be recommended for decreasing the formation of total insolubles (filterable and adherent gum). These additives include a tertiary amine containing 100% active ingredient, and a proprietary amine containing 80% active ingredient. These two additives have been found to be effective in decreasing the amount of total insolubles of unstable fuels both in bottle tests at 43°C for 18 weeks and 65°C for 8 weeks and in the new LPR test method mentioned in section 2.2.1.

2.3 Publications, Reports, and Presentations

Copies of the following publications/presentations and abstracts of the reports are included in **Appendix A2**:



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D.R. Hardy, E.J. Beal, R.N. Hazlett, and J.C. Burnett, "Evaluation of Commercial Stability Additives for Naval Distillate Use," Conference Proceedings, 3rd International Conference on Stability and Handling of Liquid Fuels, London, Vol. 2, pp. 399-411, September, 1988.

E.J. Beal, D.R. Hardy, R.N. Hazlett, and J.C. Burnett, "Stability Measurements of Military and Commercial Marine Fuels from a Worldwide Survey," Conference Proceedings, 3rd International Conference on Stability and Handling of Liquid Fuels, London, Vol.2, pp. 465-471, September 1988.

D.R. Hardy, E.J. Beal, R.N. Hazlett, and J.C. Burnett, "Assessing Distillate Fuel Storage Stability by Oxygen Overpressure," Conference Proceedings, 3rd International Conference on Stability and Handling of Liquid Fuels, London, Vol. 2, pp. 647-658, September, 1988.

E.J. Beal, G.W. Mushrush, J.V. Cooney, and J.M. Watkins, "Chemical Factors Affecting Insolubles Formation in Shale Derived Diesel fuel," *Fuel Science and Technology Int'l*, 7(1), 15-31, 1989.

D.R. Hardy, R.N. Hazlett, E.J. Beal, and J.C. Burnett, "Assessing Distillate Fuel Storage Stability by Oxygen Overpressure," *Energy and Fuels*, 3 (1), 1989, pp. 20-24.

E.J. Beal, D.R. Hardy, and J.C. Burnett, "Assessing Distillate Fuel Storage Stability by Oxygen Overpressure at Higher Temperatures," Preprints American Chemical Society, Div. of Petr. Chemistry, Vol. 34, No. 3, pp. 654-657, August, 1989.

2.4 Patents

D.R. Hardy, E.J. Beal, and J.C. Burnett, "Method for Assessing Distillate Fuel Storage Stability by Oxygen Overpressure," Navy Case No. 70634, May 1989.

3.0 LONG TERM STORAGE STABILITY OF JP-5 JET FUEL

3.1 Background

The declining quality of petroleum feedstocks in recent years has necessitated the use of more severe refinery processes to produce jet fuel of higher thermal stability and cleanliness. However, such processing severity removes certain chemical species that inhibit the formation of hydroperoxides in jet fuel. Because hydroperoxides and related species are deleterious (e.g. they attack elastomers) maintenance costs are increased. In addition, down-time of aircraft can ensue, thereby leading to a decreased state of readiness.



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The storage stability of a jet fuel is measured by its tendency to form hydroperoxides. The currently accepted accelerated test method, developed in the third Coordinating Research Council Round Robin for Accelerated Peroxide Formation in Jet Fuel, has serious drawbacks. These include the test duration, which is 4 weeks, and its limitation as a Go/No Go (pass/fail) test. Because of this limitation, this method can neither rank fuels relative to each other nor differentiate the relative effectiveness of the various antioxidant additives.

The goals of this ongoing research are to develop a rapid and reliable test to rank fuels by their tendency to form peroxides during storage and to screen various antioxidant additives.

3.2 Results and Conclusions

3.2.1 Development of Reliable Accelerated Test for Determining Chemical Changes in Various Oxidation Regimes

Recent results indicate that accelerated storage stability tests of JP-5 jet fuels conducted in vented bottles at 100°C appear promising as an improved and reliable method for evaluating the long term storage stability of jet fuels. Furthermore, it is felt that peroxidation of a JP-5 fuel sample stressed at 100°C can be related to ambient storage conditions. This project is ongoing and future results will be reported in accordance with contractual requirements.

3.2.2 Development of a Method for Determining the Effectiveness of Anti-oxidants in Jet Fuels

Current methods for determining peroxide inhibition by phenolic antioxidants involve preparing the fuel sample with the maximum allowable concentration of an antioxidant (24 mg/L) and subjecting it to accelerated storage conditions, typically at 100°C and 100 psig oxygen. Aliquots of the fuel sample are removed at intervals of two to four hours and analyzed for peroxide concentration. The effectiveness of a particular additive is based on the time it takes to reach the breakpoint of the induction period compared to the neat fuel.

A different approach to measuring additive effectiveness was taken. Since MIL-T-5624M specifies that peroxide levels in JP-5 fuel shall not exceed 8 ppm, and the breakpoint, i.e., the point at which the rate of peroxidation dramatically increases, generally occurs at peroxide levels significantly higher than 8 ppm, it was felt that breakpoint is not an acceptable criterion for testing additive effectiveness.

GEO-CENTERS developed a method that rapidly differentiates the relative effectiveness of various antioxidants. Because the method is based on a concentration/serial dilution technique, the experimental problems associated with either breakpoint or



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induction period rate are of no concern. Furthermore, this method, which is less labor intensive and significantly faster, measures the effect of the additives at all concentrations in less than 48 hours. The details of this method were recently presented at the American Chemical Society (August 1990) and published in the corresponding Preprints.

3.2.3 Mechanistic Studies on the Effect of Sulfur Dopants on Hydroperoxide Formation in Jet and Model Fuels

Hydroperoxides in jet fuels attack elastomers in aircraft fuel systems resulting in leaks or inoperability of fuel controls. Examination of fuels refined by different processes has indicated that significantly higher peroxide concentrations exist in fuels which have been severely hydrotreated.

It is believed that hydrogenation is responsible for removing natural inhibitors of peroxide formation. Such inhibitors include sulfur compounds. In testing this thesis, GEO-CENTERS has examined the effect of various sulfur compounds on the peroxidation of jet fuels in model dopant studies conducted under 65°C accelerated storage conditions. Sulfur compounds which have been found to be effective in reducing/controlling hydroperoxide formation include thiophenol, n-nonyl thiol, and, to a lesser degree, n-butyl sulfoxide. Those which appear to promote peroxidation include n-butyl sulfone, n-butyl thiophene, and benzothiophene. It is interesting to note that the thiols, which appear to be effective as inhibitors of peroxidation oxidize readily, whereas sulfones which are promoters of peroxidation are stable at temperatures well above 120°C.

GEO-CENTERS has also contributed in the characterization of the slate of products formed in the liquid phase oxidation of various sulfur compounds in de-aerated benzene and in a model fuel (tetradecane).

3.3 Publications, Reports, and Presentations

Copies of the following publications/presentations and abstracts of the reports are included in **Appendix A3**:

G.W. Mushrush, R.N. Hazlett, D.R. Hardy, and J.M. Watkins, Jr., "Liquid Phase Oxidation of Sulfur Compounds," Conference Proceedings from The 2nd International Conference on Long Term Storage Stabilities of Liquid Fuels, San Antonio, Texas, October 1986, Vol 2, pp. 512-525.

G.W. Mushrush, R.N. Hazlett, D.R. Hardy, and J.M. Watkins, Jr., "Liquid Phase Oxidation of Hexyl Sulfide and Dodecanethiol by tert-Butyl Hydroperoxide in Benzene and Tetradecane," *Ind. Eng. Chem. Res.*, 26, (4), pp. 662-667, 1987.



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J.M. Hall and R.N. Hazlett, "Results of the Third CRC Cooperative Test Program on Hydroperoxide Potential of Jet Fuels" NRL Memo Report No. 5985, May 21, 1987.

J.M. Watkins, Jr., G.W. Mushrush, and R.N. Hazlett, "Reactions Involving Hydroperoxide Formations in Jet Fuels," Preprints Am. Chem. Soc., Div. Fuel Chem. 1987, 32 (1), pp. 513-521.

G.W. Mushrush, J.M. Watkins, Jr., R.N. Hazlett, D.R. Hardy, and H.G. Eaton, "Liquid Phase Oxidation of Thiophenol and Olefins by Oxygen and t-Butyl Hydroperoxide," Preprints Am. Chem. Soc., Div. Fuel Chem. 1987, 32 (1), pp. 522-529.

G.W. Mushrush, J.M. Watkins, Jr., R.N. Hazlett, D.R. Hardy, and H.G. Eaton, "Liquid Phase Oxidation of Thiophenol and Indene by t-Butyl Hydroperoxide and Oxygen," *Fuel Science and Technology Int'l.*, 6(2), 165-183, 1988.

G.W. Mushrush, J.M. Watkins, Jr., E.J. Beal, R.E. Morris, and C.L. McIlvaine, "Organo-Sulfur Compounds and Distillate Fuel Stability," Confab 88, August 1988.

G.W. Mushrush, R.N. Hazlett, D.R. Hardy, and J.M. Watkins, Jr., "Hydroperoxide Formations and Reactivity in Jet Fuels," Conference Proceedings, 3rd International Conference on Stability and Handling of Liquid Fuels, London, Vol. 1, pp. 294-306, September, 1988.

J.M. Watkins, Jr., G.W. Mushrush, R.N. Hazlett, and D.R. Hardy, "Hydroperoxide Formations and Reactivity in Jet Fuels," Conference Proceedings, 3rd International Conference on Stability and Handling of Liquid Fuels, London, Vol. 1, pp. 307-320, September, 1988.

J.M. Watkins, Jr., G.W. Mushrush, R.N. Hazlett, and E.J. Beal, "Hydroperoxide Formation and Reactivity in Jet Fuels," *Energy and Fuels*, 3, (2), pp. 231-236, 1989.

G.W. Mushrush, E.J. Beal, J.M. Watkins, Jr., R.E. Morris, and D.R. Hardy, "Interactive Chemical Effects and Instability of Shale Derived Middle Distillate Fuels," in Proceedings of Twenty-Second Oil Shale Symposium, Dr. James H. Gary, Ed., Colorado School of Mines, Golden, CO, July 1989.

G.W. Mushrush, J.M. Watkins, Jr., E.J. Beal, R.E. Morris, and D.R. Hardy, "Hydroperoxide Formation and Decomposition Pathways and Their Relationship to Jet Fuel Instability," Confab 89 (National Fossil Fuel Conference), July 31-August 4, 1989, Laramie, WY.



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G.W. Mushrush, J.M. Watkins, Jr., E.J. Beal, R.E. Morris, J.V. Cooney, and R.N. Hazlett, "Characterization of Polar Extracts from Two Petroleum-Derived Fuels," *Fuel Science and Technology International*, 7, (7), 931-949, 1989.

G.W. Mushrush, J.M. Watkins, Jr., R.N. Hazlett, B.H. Black, and D.R. Hardy; "Liquid Phase Cooxidation of Thiophenol and Styrene by Oxygen and t-Butyl Hydroperoxide," *Fuel Science and Technology International*, 8(7), 753-767, 1990.

B.H. Black, D.R. Hardy, R.E. Morris, and G.W. Mushrush; "Liquid Phase Oxidation Studies: Chemical Ionization of Alkyl Ketones in an Ion Trap Mass Spectrometer," *Fuel Science and Technology International*, 8 (9), 935-945, 1990.

B.H. Black, S.M. Rosenberg, E.J. Beal, R.N. Hazlett, and D.R. Hardy; "Peroxide Formation in Jet Fuel by Oxygen Overpressure," Technical Presentation to the Naval Air Propulsion Center, West Trenton, NJ, October, 1989.

B.H. Black, D.R. Hardy, and E.J. Beal; "Accelerated Peroxide Formation in Jet Fuel," Technical Presentation, Naval Air Propulsion Center, West Trenton, NJ, March, 1990.

B.H. Black, D.R. Hardy, and E.J. Beal; "Accelerated Peroxide Formation in Jet Fuel," Technical Presentation to the Hydroperoxide Potential Panel of the Coordinating Research Council, Arlington, VA, April, 1990.

B.H. Black, D.R. Hardy, and E.J. Beal; "Accelerated Peroxide Formation in Jet Fuel by Conventional and Oxygen Overpressure Methods," Preprints Am. Chem. Soc., Div. Fuel Chem., 35, (4), pp. 1277-1284, August, 1990.

4.0 FUEL COMBUSTION: IGNITION QUALITY AND COMBUSTION QUALITY

4.1 IGNITION QUALITY OF DIESEL FUELS

4.1.1 Background

An accurate and reliable method of measuring the ignition quality of diesel fuels, i.e., cetane number, is important since diesel fuel is the primary mobility fuel used in the U.S. Navy's ships, and boats as well as in the nation's trucks, buses, etc. For convenience purposes, most refineries do not use the engine test method for determining cetane number. Instead, they rely on the calculated cetane index. This is a predictive equation of cetane number and is based on distillation temperature and density. Continuing revisions of the calculated cetane index, which include ASTM D976-66, D976-80, and the current ASTM D4737-87, is indicative of fuel compositional changes. Consequently, there is need for a



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cetane index based on fuel composition rather than on its physical properties. In addition, there is need for a practical method for evaluating the predictabilities of the various published cetane indices. The current method, which is based on regression analysis, does not address the tendency of the cetane index to over/underpredict.

4.1.2 Results and Conclusions

4.1.2.1 Development of a Trial Index Based on Compositional Analysis

A trial index was formulated based on percent straight chain and branched chain saturates, and percent monocyclic and dicyclic aromatics. These components were determined by a combination of HPLC and proton NMR analyses. For the 53 worldwide survey II fuels examined and from which the regression equation was formulated, the trial index appear to be a promising predictor of ignition quality. These results are encouraging. Consequently, in the establishment of a definitive cetane index based on fuel composition, the fuel set should contain a larger number of fuels, and their composition should be more diverse. Furthermore, the predictabilities of this cetane index should be tested on fuel sets that were not employed in deriving the regression equation from which it was formulated.

4.1.2.2 A Practical Evaluation of Published Cetane Indices

Simple, but rigorous and practical criteria were adopted in evaluating six published cetane indices. The fuel set examined comprised 63 worldwide survey II fuels with cetane numbers generally ranging from 45 to 57. Furthermore, the fuel set included only those fuels that met the application range specified by ASTM D4737-87. The evaluation was based on % predictability, over-predictability, and under-predictability as defined by the criteria for predictability. The results indicate that the most recent calculated cetane index, ASTM D4737-87 exhibited a tendency to overpredict and did not appear to be an improvement over ASTM D976-80. A modified calculated carbon aromaticity index (CCAI), which is based simply on density and viscosity, appears promising as a predictor of cetane number. Since such an equation would be particularly useful in cases of emergency re-fueling onboard ship, the regression equation, used as the modified CCAI, should be reformulated based on a larger fuel set with fuels of more diverse composition.

4.2 COMBUSTION QUALITY OF JET FUELS

4.2.1 Background

The combustion behavior of Navy fuels impacts both economically and strategically on the fleet. For example, the production of soot on the combustion of poor quality fuels increases the combustor liner temperature. As a result, the life of the combustor liner is



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decreased thereby increasing the cost of replacement. Also, soot production creates signature concerns in cases of military defense.

The methods currently available for predicting the combustion performance of aviation fuels such as JP-5, which is used by the Navy, have been found to be inadequate. GEO-CENTERS, INC. participated in an ongoing study at the Naval Research Laboratory, to address the Navy's needs for adequate test methods that will be better predictors of fuel combustion performance than the current Smoke Point test method, ASTM D1322. Ongoing research in this area includes the evaluation of bench scale test methods such as the recently developed Shell Premixed Burner versus the standard Smoke Point as predictors of combustion performance and the compositional analysis of aviation fuels with respect to correlation with combustor performance.

4.2.2 Results and Conclusions

4.2.2.1 Evaluation of the Shell Premixed Burner

On behalf of the Naval Research Laboratory, GEO-CENTERS, INC. participated in Shell's Proof of Concept Exercise to evaluate their Burner. The results of our evaluation indicated that the concepts on which the Shell Burner is based are both sound and rigorous. However, there appears to be need for an improved detection system. The use of an eye response detector (Centronic OSD 50-E) in conjunction with an 11K resistor, which was recommended by GEO-CENTERS is being adopted by Shell.

More important, however, are the results obtained from a comparative evaluation of the Shell Premixed Burner and the Smoke Point method based on (a) combustor data and (b) model fuel components and mixtures thereof.

(a) Based on Combustor Data - The Premixed Burner Number (PMBN), the index used by Shell as a predictor of combustion performance, exhibited poor differentiation with combustor performance for three of the nine fuels examined. This problem is significant since the combustion quality of these three fuels can be considered as being marginal, and it is precisely such fuels that an improved test method should adequately differentiate. In addition to these problems, R^2 values derived from linear regression analysis for a limited fuel set suggest no significant advantage over the Smoke Point method. Finally, based on the limited fuel set examined, neither method appears to be an adequate predictor of combustor performance.

(b) Based on Model Fuel Components/Mixtures - The compounds examined were typical of those found in aviation fuels and included dodecane and decalin (representative of the straight chain and cyclic saturates, respectively), as well as



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tertiary butylbenzene and 1-methyl naphthalene (representative of monocyclic and dicyclic aromatics, respectively). This comparative study is particularly important since PMBN measurements for known components/model mixtures have not been reported. For qualitative and quantitative differences in the compound classes examined, the differentiation in PMBNs was generally less than that of Smoke Point. Nonetheless, consistent with the literature on the sooting tendency of the various types of saturates, both Smoke Point and PMBNs indicated a greater sooting tendency of the cyclic saturate, decalin, vs the straight chain saturate, dodecane (see also Compositional Analysis, section 4.2.2.2).

In conclusion, based on the fuels and model mixtures examined, the Shell Premixed Burner Number does not appear to be a better predictor of combustor performance than Smoke Point. Also, further improvement of the Shell Premixed burner would be necessary if this method were to replace Smoke Point.

4.2.2.2 Fuel Compositional Analysis

The sooting tendency of fuels has classically been ascribed to its aromatic content. Nevertheless, the %-aromatics has not been found to be a reliable predictor of combustion performance. Since saturates comprise the bulk percentage (70-80%) of present day aviation fuels, in addition to examining the sooting tendency of the monocyclic and dicyclic aromatics, the sooting tendency of the various types of alkanes, specifically, the branched and the cyclics, was also examined.

HPLC is a well known and accurate method for determining the %- total saturates, monocyclic and dicyclic aromatics. However, there is need for a reliable method of determining the different types of saturates. The use of Gas Chromatography/Mass Spectrometry, in conjunction with the algorithms as specified in ASTM D2789 and ASTM D2425 did not appear promising. Techniques which appeared promising include the urea extraction method for separating the linear from the branched and cyclic alkanes and a recently published method¹ based on refractive index and density for determining the molar fractions of paraffins and naphthenics. The results of the urea extraction method are included in this report.

¹Nwadinigwe and Okoroji, *FUEL*, 1990, 69, 340-343.



Urea extraction of five NAPC fuels, for which Smoke Point and combustor data are available², was performed. Based on the yields obtained in conjunction with GC qualitative analysis, the urea extraction method for separating linear alkanes appeared to be both qualitative and quantitative. This was further verified using a model fuel mixture.

4.2.2.2.1 Correlation of Selected Combustor Data with Fuel Compositional Data

On examination of the combustor data, which were available for three Navy aircraft combustors (TF30, T56, and T53) at various operating conditions, it is readily apparent that the sooting tendency of fuels is dependent on both the type of combustor and its operating conditions. Based on Smoke Number data for the T56 combustor, the sooting tendency of the fuels examined appear to correlate better with compositional data based on the %-dicyclic aromatics, monocyclic aromatics, and branched/cyclic saturates than with Smoke Point data or %- total aromatics. Although only five fuels were examined, the diversity in their compound class composition enabled meaningful comparisons to be made.

Furthermore, the results indicate that, although from a qualitative viewpoint branched/cyclic saturates soot less than the aromatics, from a quantitative aspect, because branched/cyclic saturates are present in larger amounts, their contribution to sooting is important and must be considered. The significance of these results is that the sooting tendency of the branched/cyclic saturates is based on combustor performance. In view of these promising results, this investigation on the feasibility of fuel compositional analysis being an improved predictor of combustor performance should continue. For example, the compositional analysis of the Shell fuels for which combustor data are available should be performed.

4.3 Publications, Reports, and Presentations

Copies of the following publications/presentations and abstracts of the reports are included in **Appendix A4**:

S.G. Pande, "Literature Review of Cetane Number and its Correlations," GEO-CENTERS, INC., GC-TR-86-1628, May 1987.

S.G. Pande, "Evaluation of Cetane Indices For Marine Fuels," GEO-CENTERS, INC., GC-TR-1628-1, November 1987.

²Gill and Olson, "Fuel Effects on Soot formation in Turbojet Engines," AeroChem Report TP-451, May 1985.



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S.G. Pande and D.R. Hardy "Cetane Number Predictions of a Trial Index Based on Compositional Analysis," *Energy and Fuels*, 3, (3) pp. 308-312, 1989.

S.G. Pande and D.R. Hardy "A Rigorous and Practical Evaluation of Published Cetane Indices," Preprints Am. Chem Soc., Div. Pet. Chem., 34 (3) pp. 659-662, 1989.

S.G. Pande and D.R. Hardy "A Practical Evaluation of Published Cetane Indices," *FUEL*, 69, pp. 437-442, 1990.

5.0 FUEL HANDLING

5.1 Jet Fuel Lubricity [as stipulated in subtasks (a) and (b) of Task 2 of the contract]

5.1.1 Background

The declining quality of petroleum feedstocks in recent years has necessitated the use of severe refinery processes in order to produce jet fuels of higher thermal stability and cleanliness. However, such processes, which include hydrotreatment, hydrocracking, and clay-filtration, remove boundary lubricating species that impart a jet fuel's inherent lubricity. As a result, jet fuel lubricity has decreased.

Adequate lubricity is necessary to operate and maintain aircraft fuel systems, for as lubricity decreases, failures of fuel-lubricated components increase. Historically, carboxylic acid types of corrosion inhibitors were found to increase jet fuel lubricity. Such additives, which are now called lubricity enhancer additives, are highly effective boundary lubricant additives. They are based on a dimer of linoleic acid and are mandatory in all U.S. Navy jet fuels.

5.1.2 Results and Conclusions

GEO-CENTERS, INC., refined a previously developed method to measure lubricity enhancer additive concentration in jet fuel. This method has been applied to the following:

- **The determination of additive depletion during fuel handling and transfer.** Numerical adsorption constants have also been developed for predicting potential additive loss during fuel handling operations.
- **The quantification of naturally occurring lubricity imparting species.** The results of these analyses indicate a relation between the concentration of base extractable species and jet fuel lubricity as measured by the Ball-on-Cylinder Lubricity Evaluator



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(BOCLE). In general, lubricity of the fuel increased as its concentration of base extractable material increased.

Whereas base extractable species have been characterized as including alkyl phenols and straight chain alkanolic acids, it is likely that the latter compounds contribute to fuel lubricity. This supposition is consistent with the fact that such species are known to enhance boundary lubrication and that most lubricity enhancer additives are based on mixtures of alkanolic acids.

Finally, this analytical technique has successfully been employed to identify those fuels that did not contain the alkanolic acid type of lubricity enhancer additive, as well those that contained insufficient quantities. With respect to naturally occurring base extractable materials, the technique consistently showed a concentration/lubricity correlation. The fuels examined comprised a variety of JP-5 jet fuels from different sources. These included fuels used in a Coordinating Research Council, round robin during development of the BOCLE, JP-5 jet fuels obtained from storage depots during worldwide fuel survey #2, JP-4 fuel samples from Wright-Patterson Air Force Base, and, most recently, the JP-5 jet fuel diagnostics program.

5.1.3 Publications, Reports, and Presentations

Copies of the following publications/presentations and abstracts of the reports are included in **Appendix A5.1**:

B.H. Black, D.R. Hardy, and M.A. Wechter; "Determination of Corrosion Inhibitor/Lubricity Additives in Middle Distillate Jet Fuels by Size Exclusion Chromatography," 11th International Symposium on Column Liquid Chromatography, Amsterdam, The Netherlands, July, 1987.

B.H. Black, D.R. Hardy, and M.A. Wechter; "Analysis of Corrosion Inhibitor Depletion in Fuel Handling and Storage Systems" 194th National Meeting of the American Chemical Society, New Orleans, LA, September, 1987.

B.H. Black, M.A. Wechter, and D.R. Hardy; "Determination of Corrosion Inhibitor/Lubricity Enhancer Additives in Jet Fuels by Size Exclusion Chromatography," *J. Chromatogr.* 437, pp. 203-210, 1988.

B.H. Black, D.R. Hardy, and M.A. Wechter; "Lubricity Properties of Jet Fuel as a Function of Composition," 9th Rocky Mountain Regional Meeting of the American Chemical Society, Las Vegas, NV, March, 1988.



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B.H. Black, D.R. Hardy, and M.A. Wechter; "The Relation Between Fuel Composition and Ball-on-Cylinder Lubricity Evaluator (BOCLE) Measurements," Technical Presentation and Program Review, Naval Air Propulsion Center, West Trenton, NJ, April, 1988.

B.H. Black, D.R. Hardy, and M.A. Wechter; "Lubricity Properties of Jet Fuel as a Function of Composition," Technical Presentation to the Lubricity Panel of the Coordinating Research Council, Arlington, VA, April, 1988.

B.H. Black, D.R. Hardy, and M.A. Wechter; "The Lubricity Properties of Jet Fuel: An Update on Recent Work," Technical Presentation to the Lubricity Panel of the Coordinating Research Council, Arlington, VA, April, 1989.

M.A. Wechter, B.H. Black, and D.R. Hardy; "Determination of Mandatory Additive Levels in U.S. Navy JP-5," Final Report, NRL Contract Report Number N00014-86-M-0247, Naval Research Laboratory, Washington, DC, 8 November 1988.

B.H. Black, D.R. Hardy, and M.A. Wechter; "Determination and Use of Isothermal Adsorption Constants of Jet Fuel Lubricity Enhancer Additives," *Ind. Eng. Chem. Res.*, 28, 2, pp. 618-622, 1989.

B.H. Black and D.R. Hardy; "The Lubricity Properties of Jet Fuel as a Function of Composition: Part 1- Method Development," Preprints of the Division of Fuel Chemistry, American Chemical Society, 34, 2, pp. 573-580, 1989.

B.H. Black and D.R. Hardy; "The Lubricity Properties of Jet Fuel as a Function of Composition: Part 2- Application of the Analysis Method," Preprints of the Division of Fuel Chemistry, American Chemical Society, 34, 2, pp. 581-588, 1989.

B.H. Black, D.R. Hardy, and M.A. Wechter; "The Lubricity Properties of Jet Fuel as Measured by the Ball-on-Cylinder Lubricity Evaluator," Preprints of the Division of Fuel Chemistry, American Chemical Society, 35, 2, pp. 547-554, 1990.

5.2 Electrostatic Charging

5.2.1 Background

Whenever a hydrocarbon liquid, such as a jet fuel, flows with respect to another surface, through a fuel transfer line for instance, an electrostatic charge is generated in the liquid. The presence of ionic impurities in jet fuels at concentrations as low as a few parts per million or parts per billion are believed to be responsible for the generation of the electrostatic charge.



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One of the key measurements in the study of the electrostatic properties of jet aircraft fuels is the measurement of charging tendency. Attempts have been made by the Coordinating Research Council (CRC) to establish correlations between unexplained ignitions of fuel fires and the charging tendencies of the fuels that were involved. There are no specification requirements for the charging tendency of any of the jet fuels. Also, MIL-T-5624M does not specify the conductivity requirement of JP-5, nor does it specify the use of static dissipator additives.

5.2.2 Results and Conclusions

A study was conducted by GEO-CENTERS, INC. to determine whether laboratory filter papers might be suitable as reference filters for the determination of the charging tendencies of jet fuels as measured in the EXXON Mini-Static Tester. The results indicated that the filters examined did not generate enough charge to afford repeatable and reliable measurements. Preliminary results also indicated some correlation between the polarity of the generated charges and the nature of the filter paper surfaces.

Repeatability of the results has been complicated by variations due possibly to relative humidity and temperature changes in the laboratory or changes in fuel composition. In order to ensure accurate flow rate data, which is required to calculate the charging tendency from the streaming current, a method was devised to make this measurement.

5.2.3 Publications, Reports and Presentations

A copy of the following abstract is given in Appendix A5.2:

W.A. Affens, "Reference Filters for Electrostatic Charging Tendency Measurement of Fuels" GEO-CENTERS, INC. Report No. GC-TR-87-1628, September 1987.

5.3 Microbial Growth

5.3.1 Background

Most of the problems originating with microbial deteriorogens of fuels stored on naval ships or in land-based tanks have arisen from fungi or sulfate-reducing bacteria. Fungi contribute to particulate matter and sludge, and sulfate reducers produce fuel soluble sulfides and sulfur. Both groups of micro-organisms contribute to corrosion. Although the effects of microbial fuel contamination can be satisfactorily controlled by minimizing the



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presence of water and maintaining the purification equipment, other measures may occasionally be needed.

5.3.2 Results and Conclusions

In support of the Naval Research Laboratory ongoing programs, GEO-CENTERS, INC. successfully investigated the use of biocides for controlling both fungi and sulfate-reducing bacteria contamination in fuels. The results are as follows:

5.3.2.1 For controlling fungus, *Amorphotheca* (*Cladosporium*) *resinae*

Three fuel-soluble commercial biocides have been identified. These include the following: (a) a mixture of dioxaborinanes [2,2'-methyl-trimethylene-dioxy-bis-(4-methyl-1,3,2-dioxaborinane) and 2,2'-oxy-bis-(4,4,6-trimethyl-1,3,2-dioxyborinane)]; (b) a mixture of isothiazolones (5-chloro-2-methyl-isothiazolin-3-one and 2-methyl-4-thiazolin-3-one); and (c) a tertiary butylamine pyridinethione.

5.3.2.2 For controlling the growth of a pure culture of sulfate-reducing bacteria and a mixed culture containing sulfate-reducers in fuel/water test tube systems

Of the previous three biocides evaluated, the mixture of isothiazolones was found to be effective at the lowest concentration.

5.3.2.3 A safer and less costly alternative to biocides

The disadvantages of using biocides are their cost and the potential hazards to personnel and to the environment. The results of a recent study indicate a less objectionable alternative, viz, the alkalization of the aqueous phase in contact with the fuel. In buffered water/fuel systems, at pH 8.5 and above, fungal growth of *A. resinae* was inhibited. A higher pH (9.1) was required to inhibit a common yeast co-contaminant, *Candida sp.* At similar pH of 9.0, the growth of both pure and mixed cultures of sulfate-reducing bacteria was also inhibited. These promising results indicate that major microbial contaminants of fuels could be controlled in the water bottoms of fuel storage tanks by simply maintaining a high pH.

5.3.3 Publications, Reports, and Presentations

Copies of the following publications/presentations and abstracts of the reports are included in Appendix A5.3:

G. Andrykovitch and R.A. Neihof, "Fuel soluble biocides for control of fungal contaminants in hydrocarbon fuels," In Proceedings of Second International Conference on Long Term Storage Stabilities of Liquid Fuels, October 1986, pp 352-362.



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G. Andrykovitch and R.A. Neihof "Fuel-soluble Biocides for Control of Cladosporium Resinae in Hydrocarbon Fuels," *J. Industrial Microbiol.* 1987, 2, 35-40.

G. Andrykovitch and R.A. Neihof, "Alkalization to Control Microbial Contamination of Naval Fuels" Presented at the Annual Meeting of the Society of Industrial Microbiology; SIM News:37:P15, 1987.

G. Andrykovitch and R.A. Neihof, "Control of Sulfate-reducing Bacteria in Hydrocarbon Fuel Tanks," *Biodeterioration Research*, 2 61-66, 1989.

5.4 Fuel contamination Monitor (as stipulated in Task 3 of the Contract)

5.4.1 Background

The U.S. Navy has need for an accurate and reliable in-line continuous aviation fuel monitor. Without such a monitor, reduced engine lifetime and performance can result from the burning of contaminated fuels. The major contaminants in aviation fuels are free water and solid particulates such as rust, dirt, organic matter, and other debris. Both these contaminants can be present in varying concentration and (droplet) size.

5.4.2 Results and Conclusions

GEO-CENTERS, INC. developed an in-line fiber optic jet fuel contamination monitor with real time response and improved accuracy compared to current methods for free water. The design specifications are given below:

Detectable contaminant concentration: Min: < 2 ppm; Max: > 100 ppm
Detectable contaminant size: Min: ~ 1 μ ; Max: ~ 30 μ
Response Time: 0.5 seconds
Nominal flow rate range: 0-100 GPM
Pipe Size: 2 inches SCH80
Mounting Interface: 150 lbs ASA B 16.5 standard flanges
Overall Length: 9.5 inches

The monitor determines the concentration of contaminants using the light scattering technique (both narrow and large angle). It employs fiber optic conduits in conjunction with solid state laser sources and detectors. Data acquisition and analysis are performed by a microprocessor.

The fuel contamination monitor has been tested in the GEO-CENTERS handling system, as well as at the Naval Air Propulsion Center (NAPC), and at the Naval Sea



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Systems Engineering Station Separator Test Facility. The results of these tests show that the monitor performs equally well in flow systems simulating shipboard conditions as in the static laboratory tests. Furthermore, measurements of contaminant concentrations were reliable for both water droplets and particulates. A fuel contamination monitor was delivered to NAPC for long term testing under this contract.

5.5 Flash Point

5.5.1 Background

In view of the dangerous nature of their missions and cargo of munitions, naval vessels must take extraordinary measures to prevent fires. Uncontrolled fires in the presence of large quantities of munitions and missile propellants can lead to catastrophe.

Flash point is one of the methods of gauging the relative fire hazard of shipboard fuels. The flash point of JP-5 jet fuel is controlled by Military Specification, MIL-T-5624M. This specification limits the minimum temperature for flash point, as measured by ASTM D93, to 60°C (140°F). The flash point of JP-5 is influenced by the presence of volatile low molecular weight hydrocarbons. As the concentration of these compounds increases, the flash point decreases. In general, JP-5 fuel does not undergo chemical changes in which the flash point spontaneously decreases. Certain fuel handling procedures, however, can, and do, lead to a decrease in flash point temperature.

If a Navy aircraft, for example, were fueled during a stopover at an Air Force Base with JP-4, a fuel for which the flash point temperature is so low that it is neither measured nor specified, subsequent off-loading of this fuel after landing aboard ship into a JP-5 storage tank will significantly lower the flash point of the fuel stored in the tank. This can lead to a potentially hazardous situation on board a U.S. Naval Vessel. At present, in many cases, this hazardous situation is avoided by off-loading the aircraft's fuel into the ocean.

5.5.2 Results and Conclusions

5.5.2.1 Effect of Ullage on Flash Point Using the Pensky-Martens Test Method

For the Navy, GEO-CENTERS participated in a continuing study of the effect of ullage on lower flammability temperature. A series of lower flammability temperature tests, using the Pensky-Martens closed cup flash point testing apparatus, were conducted for various ullage volumes. The fuels examined were JP-5, JP-5 mixed with 5% JP-4, decane and undecane. These tests showed that as ullage volumes decrease, the lower flammability temperature decreases, and as the ullage approaches zero, the temperature at which the fuel vapors ignite can be as much as 7 to 10 °F below the flash point, significantly increasing the flammability hazard.



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The effect of equilibrium conditions on the lower flammability temperatures was also examined using a modified Pensky-Martens flash point apparatus. The Pensky-Martens flash point apparatus cup was immersed in a constant temperature bath (ethylene glycol/water) such that the liquid level outside the cup was equal to the level of fuel in the cup. The fuels examined were JP5, JP5 adulterated with 5% JP4, and decane at 42.5% and 20% ullage. At 42.5% ullage, the temperature at which the vapors in the ullage space would flash was determined at equilibration times of 5, 10 and 15 minutes. At 20% ullage, the flash temperatures were determined at 5, 10, 15 and 20 minutes. The results (see Table 1) indicate that for the various equilibration times, the flash temperatures of the two ullage volumes differed only slightly. This is probably due primarily to the formation of condensation under the lid of the apparatus and possibly loss of light ends (vapor) due to leakage around lid/cup seal.

Table 1: EQUILIBRATION TIME vs LOWER FLAMMABILITY TEMPERATURE
(Pensky-Martens)

Sample	Equilibration Time (min)	Lower Flammability Temp °F	
		42.5% Ullage	20% Ullage
JP-5	5	141	143
	10	140	143
	15	140	140
	20	ND	142
JP-5/5% JP-4	5	93	92
	10	92	93
	15	92	94
	20	ND	95
Decane	5	124	125
	10	124	123
	15	126	123



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5.5.2.2 Effect of Ullage on Flash Point Using the Setaflash Test Method

A similar experiment was performed using the Setaflash apparatus. The results (see Table 2) indicate that the small differences in flash temperatures are similar to those obtained with the Pensky-Martens apparatus; however, unlike the results obtained with the modified Pensky-Martens, as the ullage decreased, the flash temperatures tend to increase. This effect is believed to be due to the formation of condensation under the lid of the cup and possible leakage of vapor past the shutter on the cup lid. To get more meaningful results from these experiments, a method of heating the lids of the Pensky-Martens and Setaflash apparatus must be devised to eliminate the condensation that forms on the underside during long equilibration times.

Table 2: EQUILIBRATION TIME vs LOWER FLAMMABILITY TEMPERATURE (Setaflash)

Sample	Equilibration Time (min)	Lower Flammability Temp °F		
		90% Ullage	60% Ullage	40% Ullage
JP-5	1	144	148	ND
	2	143	146	151
	4	144	147	151
	8	ND	147	151
	12	ND	ND	151
JP-5/5% JP-4	1	97	100	ND
	2	97	98	102
	4	98	98	102
	8	ND	99	103
	12	ND	ND	103
Decane	1	122	125	ND
	2	123	125	131
	4	122	126	131
	8	ND	126	130
	12	ND	ND	130



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6.0 CHEMICAL, BIOLOGICAL, AND RADIOLOGICAL, (CBR) DEFENSE TECHNOLOGY (as stipulated in Task 5 of the Contract)

6.0.1 Background

The use of chemical and biological warfare (CBW) agents in military combat operations threatens the lives of the crew and the accomplishment of the mission. Thus, a vital need exists for adequate collective protection systems to remove chemical warfare vapors and for effective decontamination of personnel, equipment, and affected areas.

6.1 Collective Protection

6.1.1 Background

The Collective Protection System (CPS) on U.S. Navy vessels currently employs single-pass adsorptive carbon filters to remove chemical warfare vapors from ventilation air. Single-pass adsorptive filters suffer from their transient nature since, as they get used, they lose their ability to filter and thus must be replaced. Because filter elements are expensive, and failure of an individual element is disastrous, an accurate measure of residual filter capacity becomes increasingly important.

Predictive methods using mathematical computer models of the system can be quite good at determining filter change out times. However, variability in the manufacture of these filters (e.g. differences in adsorbency from lot to lot, differences in packing, channeling, and/or leaking filters) can compromise the accuracy of the computer predictions. For this reason, a monitor which gives real-time information on the residual capacity of a given filter element is an important component in any single pass filtration system.

6.1.2 Results and Conclusions

6.1.2.1 Filter Life Monitor

Metal oxide semiconductor (MOS) sensors were evaluated for initial use as the reference sensor in a filter life monitor system. A modification was made to the stock sensor which stabilized the output and thus enabled it to perform within a concentration range well below that of previously published specifications. Methyl salicylate, a chemical agent simulant, was the first challenge vapor calibrated with the modified MOS sensor. Various challenge profiles have been run with methyl salicylate on ASC whetlerite. The



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results indicate that an imbedded sensor probe can effectively predict a concentration change in the effluent of the carbon bed.

6.1.2.2 External Shipboard Characterization of Gases/Vapors

GEO-CENTERS has been involved in an extensive NRL program to sample, and in some cases quantify, shipboard atmospheric environments. Weathered carbon samples taken from the Collective Protection System (CPS) filters used on-board selected Navy ships were sent to NRL when their filter elements were replaced. In addition, long-term sampling units, using the same Navy impregnated carbon employed in the CPS systems, were placed on a number of Navy ships.

Upon removing the samples from the ships, the activated carbon was partitioned into sections perpendicular to the flow of air through the filter. The CPS filters were segmented into three sections representing the inlet, center, and outlet portions of the bed. Filter tubes from the long-term samplers were broken into four 3/4-inch sections with the excess carbon lumped together into a remainder sample.

From this segmentation, the carbon bed was found to be a dynamic system. Lightly adsorbed components adsorb onto the carbon but are later displaced by more strongly adsorbed compounds. This adsorption and displacement produces a chromatograph effect where the more strongly adsorbed (higher boiling) compounds are found on sections near the inlet of the bed. Such compounds include C12-C17 aliphatic hydrocarbons and C4 substituted benzenes. The less strongly adsorbed (or lower boiling) compounds are found on sections near the outlet of the bed. Such compounds include C9-C11 aliphatic hydrocarbons, C1-3 substituted benzenes, and selected halogenated hydrocarbons.

6.2 Decontamination

6.2.1 Background

GEO-CENTERS has been involved in a Navy program to develop a new decontamination solution to replace the standard calcium hypochlorite ($\text{Ca}[\text{OCl}]_2$) solution. Hypochlorite is recognized as the single best detoxifier of the full spectrum of chemical and biological agents; however, hypochlorite suffers from unacceptable levels of corrosivity. In addition, using $\text{Ca}[\text{OCl}]_2$ as the oxidant source creates additional problems such as low solubility in water, low rate of dissolution in water, and bulk storage problems (i.e., fire hazard).



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6.2.2 Results and Conclusions

6.2.2.1 Formulation Development

A final formulation was developed and recommended to the Navy to replace the standard decontaminant presently in use. The formulation uses a surfactant for wetting, a buffer for pH control, and sodium dichloroisocyanurate as the oxidizer. It was found that, in the laboratory, the new formulation addresses the problems found with the $\text{Ca}[\text{OCl}]_2$ based decontaminant, while providing the same oxidative strength.

6.3 Publications, Reports, and Presentations

Copies of the following publications/presentations and abstracts of the reports are included in **Appendix A6**:

L. Isaacson and R.E. Pellenbarg, "Shipboard Atmospheric Monitoring for Collective Protection Applications," Presented at the 1986 CRDEC Conference on Chemical Defense, Aberdeen Proving Ground, MD, November, 1986.

R. Matuszko and R. Little, "A System for Evaluating Sorbent Lifetimes", NRL Memorandum Report No. 6052, Naval Research Laboratory, Washington DC, September, 1987.

R. Matuszko, S. Smidt, J. Shirley, and R. Little, "Component Compatibility and Effectiveness of Decontamination Formulations", Presented at the 1987 CRDEC Conference on Chemical Defense, Aberdeen Proving Ground, MD, November, 1987.

R. Matuszko, R. Lamontagne, and L. Isaacson, "Characterization of Weathered Air Purification Carbons", Presented at the American Chemical Society's 22nd Middle Atlantic Regional Meeting, Millersville, PA, May, 1988.

R. Matuszko, R. Lamontagne, and L. Isaacson, "Multi-Component Adsorption on Activated Carbons", Presented at the American Institute of Chemical Engineers' Summer National Meeting, Denver, CO, August, 1988.

R. Taylor, S. Smidt, J. Shirley, R. Matuszko, and R. Little, "Decontamination/Contamination Avoidance Solutions and Materials", NRL Memorandum Report No. 6282, Naval Research Laboratory, Washington, DC, August, 1988.

R. Lamontagne, L. Isaacson, and R. Matuszko, "Characterization of Contaminated Air Purification Carbons", Presented at the 1988 CRDEC Conference on Chemical Defense, Aberdeen Proving Ground, MD, November, 1988, proceeding published 1989, p. 285.



GEO-CENTERS, INC.

R. Matuszko, R. Lamontagne, and L. Isaacson, "Dynamic Adsorption Behavior of Collective Protection Air Filtration Carbons versus a Binary Vapor Challenge", Presented at the 1988 CRDEC Conference on Chemical Defense, Aberdeen Proving Ground, MD, November, 1988, proceeding published 1989, p. 293.

R. Matuszko, D. Friday, R. Lamontagne, and L. Isaacson, "Single and Binary Adsorption of Low Volatility Organics on BPL Carbon", Presented at the American Institute of Chemical Engineers' 1989 Annual Meeting, San Francisco, CA, November, 1989.

R. Lamontagne, R. Colton, H. Hoff, J. Rossin, R. Matuszko, and L. Isaacson, "Characterization of Weathered Carbon Displaying Agglomeration Tendencies", Presented at the 1989 CRDEC Conference on Chemical Defense, Aberdeen Proving Ground, MD, November, 1989, to be published in proceedings.

R. Matuszko, D. Friday, R. Lamontagne, and L. Isaacson, "Single and Binary Adsorption of n-Nonane and Xylene on BPL Carbon", Presented at the 1989 CRDEC Conference on Chemical Defense, Aberdeen Proving Ground, MD, November, 1989, to be published in proceedings.

L. Isaacson, R. Lamontagne, E. Riley, and J. Rossin, "Environmental Weathering of a Radial Flow Carbon Filter," Presented at the 1989 CRDEC Conference on Chemical Defense, Aberdeen Proving Ground, MD, November, 1989, proceedings to be published in 1990.



GEO-CENTERS, INC.

FIBER OPTIC JFTOT MONITOR

MANUAL

PREPARED FOR

THE NAVAL AIR PROPULSION CENTER
UNDER CONTRACT NUMBER
N00014-86-C-2288

PREPARED BY

GEO-CENTERS, INC.
SEVEN WELLS AVENUE
NEWTON CENTRE, MASSACHUSETTS 02159

NOVEMBER, 1986



GEO-CENTERS, INC.

INTRODUCTION

The GEO-CENTERS, INC. fiber optic JFTOT monitor is a micro-processor controlled instrument which yields reliable real-time measurements of deposit accumulation rates at multiple temperatures simultaneously. This monitor is used on a standard JFTOT apparatus with the only modification being replacement of the standard heater tube holder by one on which fiber optic probes are mounted. The ends of the probes are flush with the interior surface of the heater tube holder and, therefore, are non-intrusive to the fuel flow. Also, the use of optical fibers allows the location of the electro-optic components at a remote location eliminating the danger of electrical hazards in the vicinity of the fuel. The use of optical fibers also leads to sufficient spatial resolution to provide data on film formation within a narrow temperature range. Data acquisition and analysis by a microprocessor leads to convenience of operation and real-time monitoring.

The optical diagnostic technique employed is based on principles of interferometry. When light is reflected from a medium of refractive index greater than that in which it is traveling it undergoes a phase change. For the case of thin films deposited on heater tubes, the refractive index of the film is greater than the refractive index of air, and the refractive index of the metal is greater yet. Thus, light reflected from both the front and back surfaces of the film undergoes a phase change. If the film is vanishingly thin, the light undergoes a phase change at both surfaces and because of the short distance traveled in the film, the two wave trains are almost in phase and interfere constructively, resulting in a maximum intensity in the reflected light. As the film becomes thicker, the phases of the two emerging wave



trains become more mismatched. When the thickness of the film is such that the light travels one half wavelength through it, then the two waves emerge in opposite phase and the waves destructively interfere giving a minimum in the intensity of the reflected light. On further build-up of the film, the waves come back into phase until a thickness where the light travels a whole wavelength through the film resulting in constructive interference and another maximum in the reflected light intensity. As the film thickness increases, the reflected light intensity will cycle between maxima and minima as the thickness is such that the light travels an integral number of wavelengths or an integral number plus a half wavelength, respectively.

The thickness of the film can then be determined from the wavelength of the light and the number of cycles observed. The thickness must also be corrected for the refractive index of the film and the angle at which the light passes through the film. the thickness of the film, d , is then given by

$$d = \frac{m \lambda}{2n \cos \theta}$$

where m is the number of cycles observed, λ is the wavelength of the light, n is the refractive index of the film, and θ is the angle from the normal at which the light passes through the film. In the fiber optic monitor, the wavelength of the light is 0.88 microns, $\cos \theta$ is 1.0 and n is 1.6. Therefore, a complete cycle is observed for every 0.28 microns of film formed.



OPERATION

The JFTOT equipped with fiber optic monitor is operated in the same manner as a standard JFTOT apparatus. The only difference in the two assemblies is the replacement of the standard heater tube holder with a heater tube holder containing fiber optic probes. The preparation of the JFTOT apparatus proceeds according to the standard ASTM D3241 procedure through steps 6.6.6. Note that the heater tube must be inserted into the holder BEFORE the fiber optic probes are connected to the holder. The fiber optic probes are fragile and should be handled with extreme care.

After completing step 6.6.6, perform the following steps.

a. Clean the ends of the fiber optic probes by gently wiping them with a cotton swab saturated with hexane.

b. Attach the ends of the fiberoptic cables which contain all seven fibers to the heater tube holder by screwing the connectors onto the mounts on the holder. The connectors should be made finger tight and then given 1/8 additional turn.

c. Attach the bifurcated ends of the cables to the electronic unit. The branch containing a single fiber is connected to the source output and the branch containing six fibers is connected to the corresponding detector input. The cable which is connected to position 28 on the heater tube holder (closest to the fuel inlet) should be connected to source and detector #1 on the electronics unit and so on up the heater tube holder.



Continue with the standard JFTOT procedure from steps 6.6.7 Through steps 7.2.9.

The Start-Up is according to the following procedure:

a. Turn on the computer and insert the operating system floppy disk which is labelled "MS/DOS" into the top disk drive (Drive A).

b. The computer now boots and when it finishes the prompt "A>" appears.

If a new floppy disk is to be used for data storage it must now be formatted. These disks must be double sided and double density. Formatting is achieved by placing a disk in the lower disk drive and typing "FORMAT B:" then press "RETURN" key. A used disk may be formatted, but any information already on the disk will be erased. A single disk may be used for several runs, but it must contain no other information when used the first time. After formatting, the disk may be left in Drive B.

c. Remove the operating system disk from Drive A and insert the Acquisition program disk into Drive A.

d. If a Data Storage disk is not already in Drive B, one should now be inserted.

e. Type "ACQ" and press the "RETURN" key.

f. Turn on the power to the electronics unit.



The computer provides prompts which the operator follows to complete the start-up procedure. The first set of prompts ask for relevant information which identifies the run. The operator types the replies at the keyboard.

After the run time is entered, the computer checks the available space on the floppy disk. If it is insufficient, the operator must replace the disk by a new formatted one. After replacing the disk press "RETURN". The computer will then return to the prompts which ask for the run information. These must be re-entered before the run proceeds.

The computer then checks the signal level being received from the probes and prompts the operator to switch on the electronics if no signal is detected. An option is provided for the operator to eliminate data collection from any probe(s). If a probe fails the self-test this option allows the operator to continue the run without that probe or the operator may stop and correct the problem before proceeding.

Prompts are given to:

- a. Pressurize the system
- b. Switch on the pump
- c. Check fuel flow (according to step 7.3.6)
- d. Turn on heater element

The operator sets the timer on the JFTOT to zero and checks the maximum temperature reading.

Three minutes after turning on heater element, press RETURN key on keyboard. This brings the axes for the data plot to the screen and the computer then begins plotting data. The operator

should check that the voltage of each channel as displayed on the screen agrees with the voltage for that channel on the meter on the electronics unit. Each channel on the electronics unit is accessed by turning the channel selector switch.

The monitor plots the inverse of the reflected light intensity normalized to the initial value as a function of time. When the run time is entered into the computer, the length of the time axis is adjusted so that the plot for the full run fills the screen. The data from each probe is automatically stored on the disk and simultaneously plotted on the screen with a different color for each probe. The traces are offset so that the data from the probe at station 28 is lowest on the screen and data from station 48 is highest with the intervening traces corresponding to the order of the probes on the heater tube. The voltage and temperature displays are arranged so that station 28 is represented on the left and succeeding values represent increasingly higher positions on the tube to station 48 which is represented on the far right.

The run may be terminated at any time by pressing the "ESC" key.

Shutdown Procedure

When the run time has elapsed, the computer will "beep" and data acquisition will terminate. The computer provides the operator with prompts. Among the prompts is one which instructs the operator to turn off the sources in order to take a zero reading. The switch for the sources is located on the back of the electronics unit. When the switch is turned off, the computer instantly does the zero reading. The operator continues by pressing the



RETURN key. After following the prompts, the operator exits the computer program by pressing "ESC."

NOTE: THE DATA STORAGE DISK MUST NOT BE REMOVED FROM THE DISK DRIVE BEFORE EXITING THE PROGRAM OR THE DATA WILL NOT BE STORED.

After following these prompts, the operator follows the standard JFTOT shutdown and disassembly steps 7.4.1 through 8.5.

Following step 8.5, remove the fiber optic probes from the heater tube holder. NOTE: The fiber optic probes must be removed BEFORE the heater tube is removed from the holder.

Continue with the remainder of the standard disassembly procedure beginning with step 8.6.

To make a back-up copy of any disk including the operating system, acquisition program or data storage disks, place that disk in Drive A and place an empty, formatted disk in Drive B and type "Copy A:*. * B:". "



DATA ANALYSIS

The data analysis software supplied with the fiber optic JFTOT monitor calculates the thickness of the film formed at each probe position at any time during the run. It also provides options for plotting or printing the raw data or for plotting or printing the thickness as a function of time or position at a given time. The film thickness can only be calculated for data in which at least one half cycle of oscillation has been observed. The thickness calculation is based on an average rate of accumulation.

Procedure

1. Switch on the analysis computer and printer.
2. After the prompt "C>" appears, type "CD JFTOT" to enter the appropriate directory.
3. Insert the floppy disk with data from the JFTOT acquisition computer.
4. Copy the JFTOT data from the floppy disk to the hard disk by typing "COPY A:*" where * represents the Run Number. Press RETURN key.
5. The archive file may be copied from the floppy disk to the hard disk by typing "COPY A:ARCHIVE.LIB C:FL*.LIB" where * is the floppy disk number. Each floppy disk must be given a



different number. The archive file contains the information entered into the JFTOT acquisition computer at the beginning of each JFTOT run.

6. Type "ANL".

The main menu now appears on the screen. Any of these options may be chosen by pressing the appropriate function key on the left side of the keyboard. To exit the program at any time press <ESC>.

Main Menu

F1 - Read in file for functions F2 - F5.

This function reads the raw data for a given run which has already been copied from the floppy disk to the hard disk. It must be performed before functions F2 - F5 can be performed on that data.

F2 - Plot attenuation vs. time.

The raw data is plotted on the screen. The plot on the screen has the same appearance as the screen on the acquisition system at the end of the JFTOT run.

F3 - Calculate thickness for functions F4 - F5.

The operator has the option of eliminating any probe(s) from this calculation. Data in which irregularities occurred during the run should be eliminated. If a probe is eliminated, it will not be available for functions F4 or F5.



F4 - Plot thickness vs. time for 8 probes from 1 file.

The screen displays in color a plot of thickness vs. time for all probes used in F3. The temperature at the position of the probe is indicated on the right side of the screen at the end of the trace corresponding to that probe.

F5 - Plot thickness vs. tube position at one time interval.

The operator chooses the time interval and the screen shows a plot of thickness vs. position for each probe used in F3.

F6 - Calculate thickness vs. time for selected probes from up to 4 runs.

The operator chooses a maximum of four probes which can be from any run stored on the hard disk. The raw data for these probes is read and the thickness calculation is performed.

F7 - Plot thickness vs. time for selected probes from up to 4 files.

The plot of thickness vs. time for these probes is displayed in color on the monitor.

F8 - Print menu

Selection of this option brings the print menu to the screen.

Print menu

F1 - Read in file for functions F2 - F7.

If function F1 of the main menu has already been performed, then this need not be repeated.

F2 - Print plot of attenuation vs. time.

This function prints a hard copy of the plot generated in the JFTOT acquisition system. It has headers which give the relevant information for the run. The plot is displayed on the monitor in black and white while the printing is occurring.

F3 - Calculate thickness for functions F4 - F7.

If function F3 of the main menu has been performed, this function need not be repeated.

F4 - Print plot of thickness vs. time (8 probes - 1 file).

A plot is printed for the probes chosen in the previous F3. The plot has a header with the run information and it is displayed in black and white on the monitor during printing.

F5 - Print plot of thickness vs. tube position.

A plot is printed for thickness vs. tube position at a time selected by the operator. This plot also has a header with run information and the monitor shows a black and white display.



F6 - Print table of thickness vs. time.

This function prints a list of thickness at ten minute intervals for one probe selected by the operator. It has a header with run information.

F7 - Print table of probe number vs. thickness.

A list of the thickness observed by each probe at a time selected by the operator is printed with header containing run information.

F8 - Print table of inflection points vs. time.

This function provides a table of the times at which maxima or minima were observed in the data for all probes selected in F3.

F9 - Calculate thickness vs. time for probes from up to 4 files.

The operator chooses a maximum of four probes from any runs. The raw data for these probes is read and the thickness calculation is performed.

F10 - Print a plot of thickness vs. time for probes from up to 4 files.

The plot of thickness vs. time for the four probes selected in F8 is printed and simultaneously displayed in black and white on the monitor. The run number and probe number are printed on the right side of the screen next to the corresponding trace.

Pressing <ESC> exits the print menu and returns to the main menu.

**DEVELOPMENT OF NEW OPTICAL METHODS FOR
TUBE DEPOSIT RATING IN JFTOT PROCEDURE**

**SPONSORED BY:
NRL CONTRACT # N00014-86-C-2288
IN CONJUNCTION WITH
NAVAL AIR PROPULSION CENTER**

**PRESENTED BY:
SHIRLEY D. DARRAH
GEO-CENTERS, INC.**

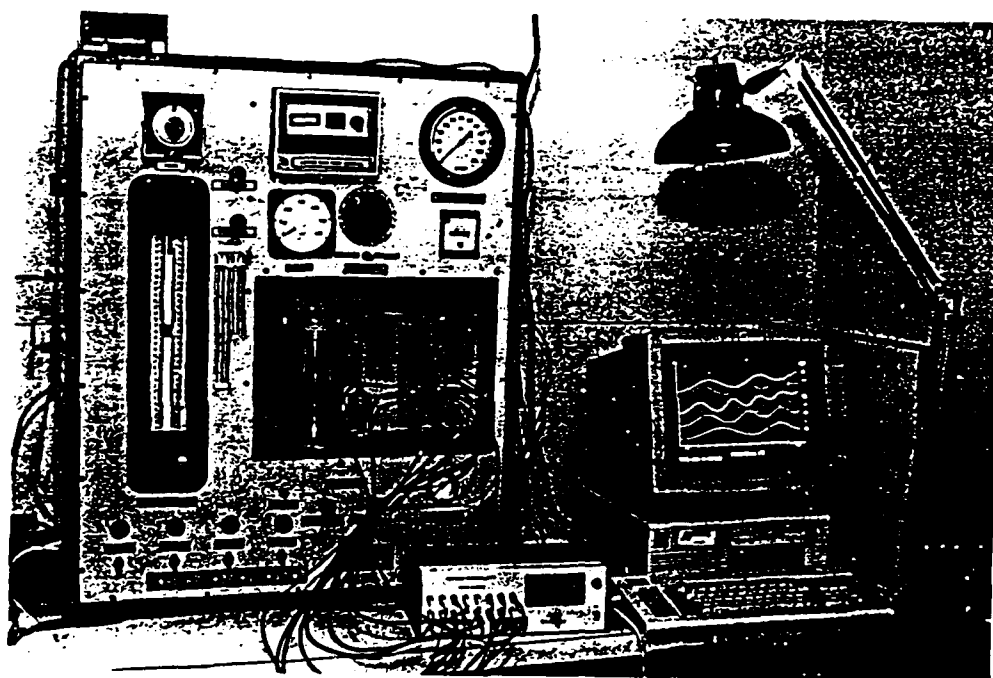
1628-004-MM100619-IL

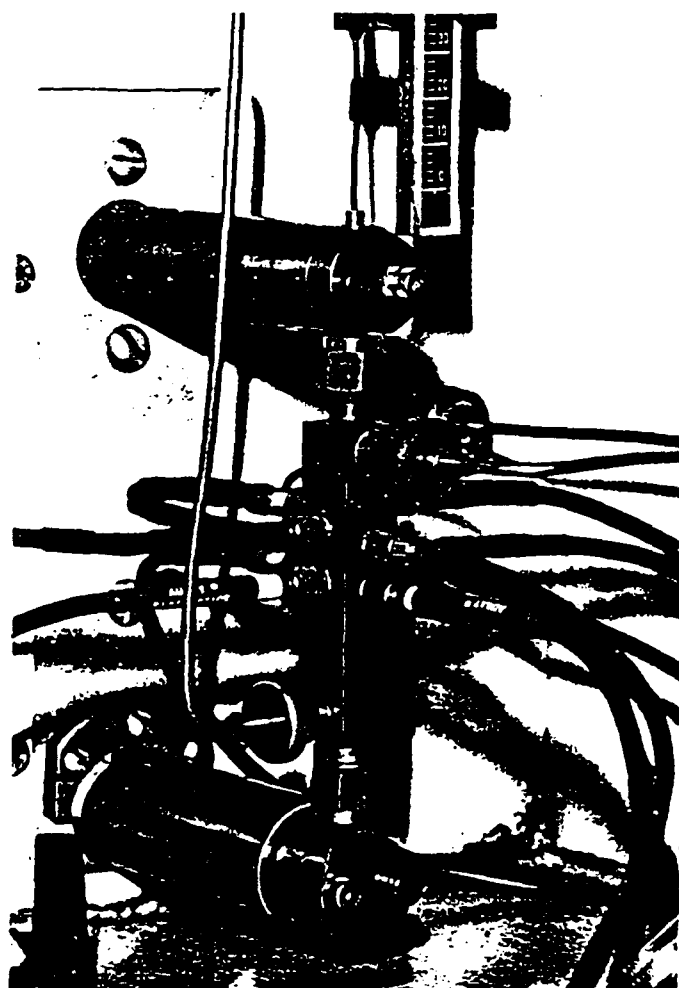


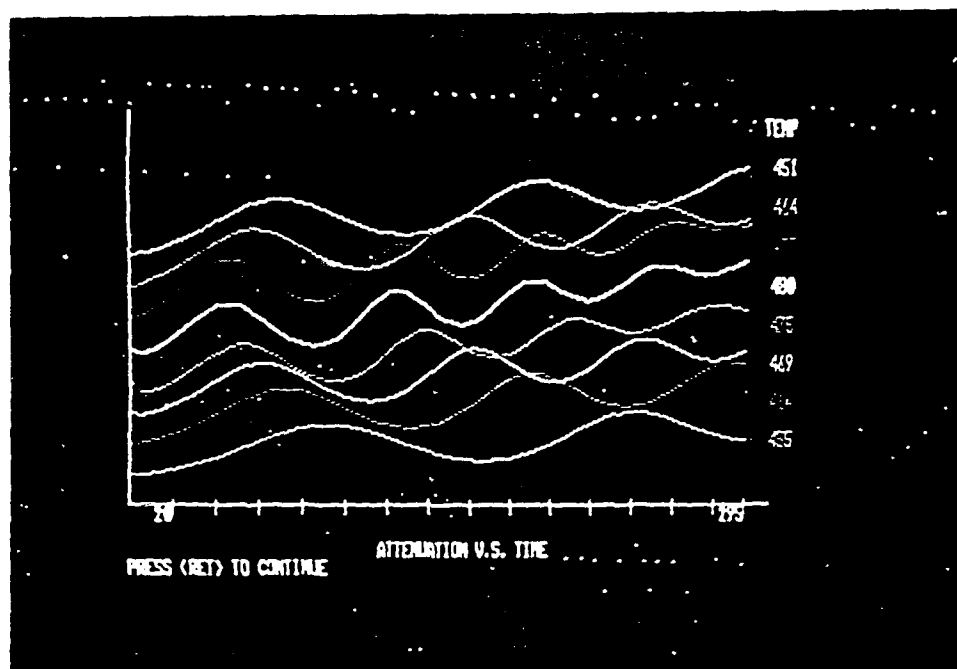
KEY FEATURES OF FIBER OPTIC BASED TUBE DEPOSIT RATER

- DEPOSIT THICKNESS MEASUREMENT BASED ON INTERFERENCE PATTERN OF REFLECTED LIGHT
- FIBER OPTIC SENSORS AND MICROPROCESS OR ACQUISITION/ ANALYSIS YIELD THICKNESS MEASUREMENTS
 - a) Real Time in JFTOT
 - b) Post Test with Scanner
- DATA AT SEVERAL TEMPERATURES OBTAINABLE FROM ONE TEST

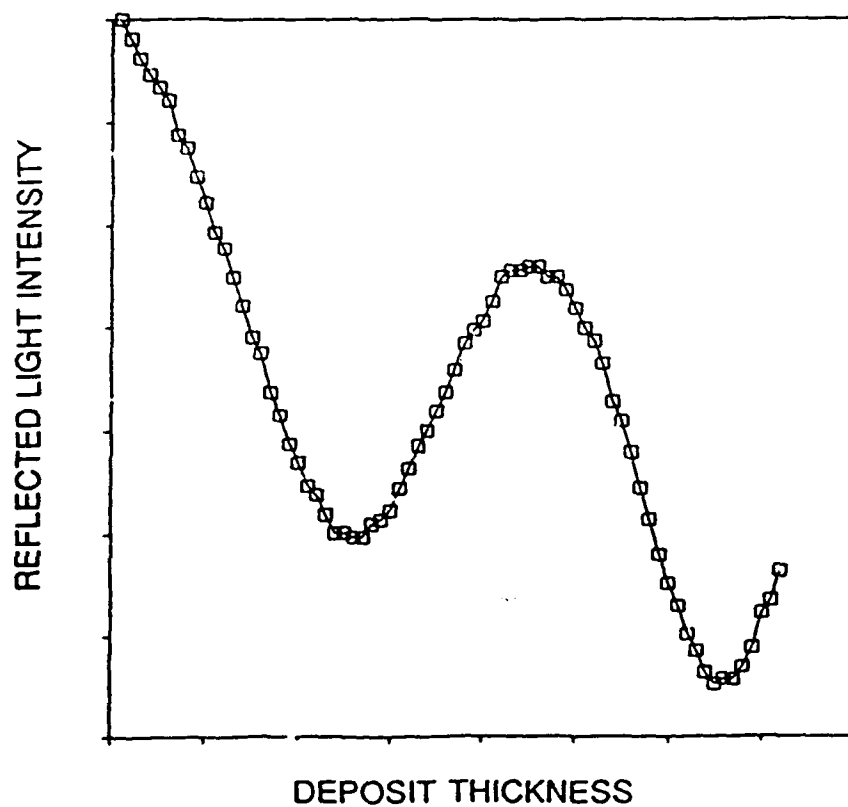
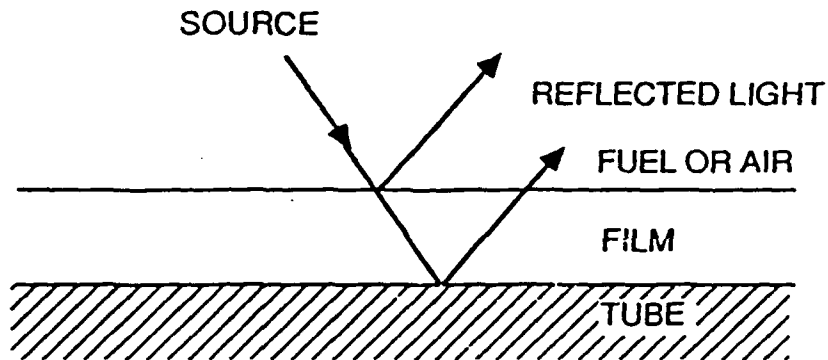






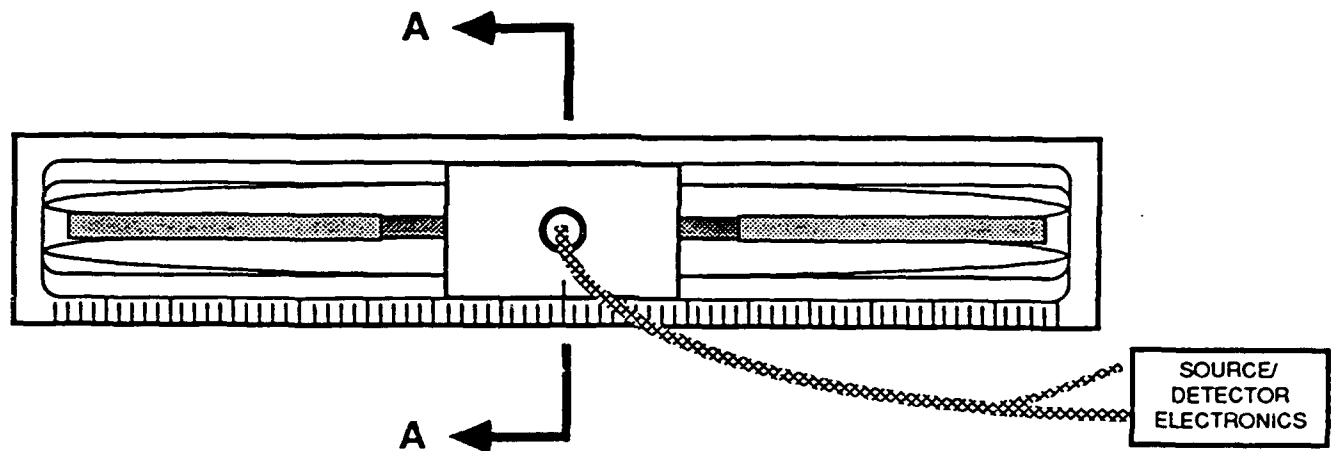


DATA INTERPRETATION

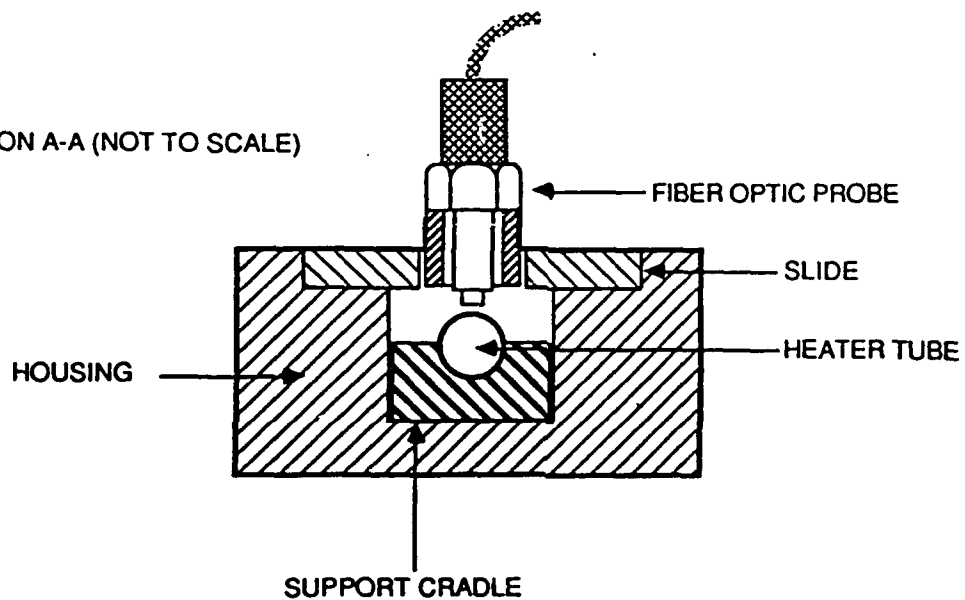


$$d = \frac{m\lambda}{2n_{\text{film}} \cos\theta}$$

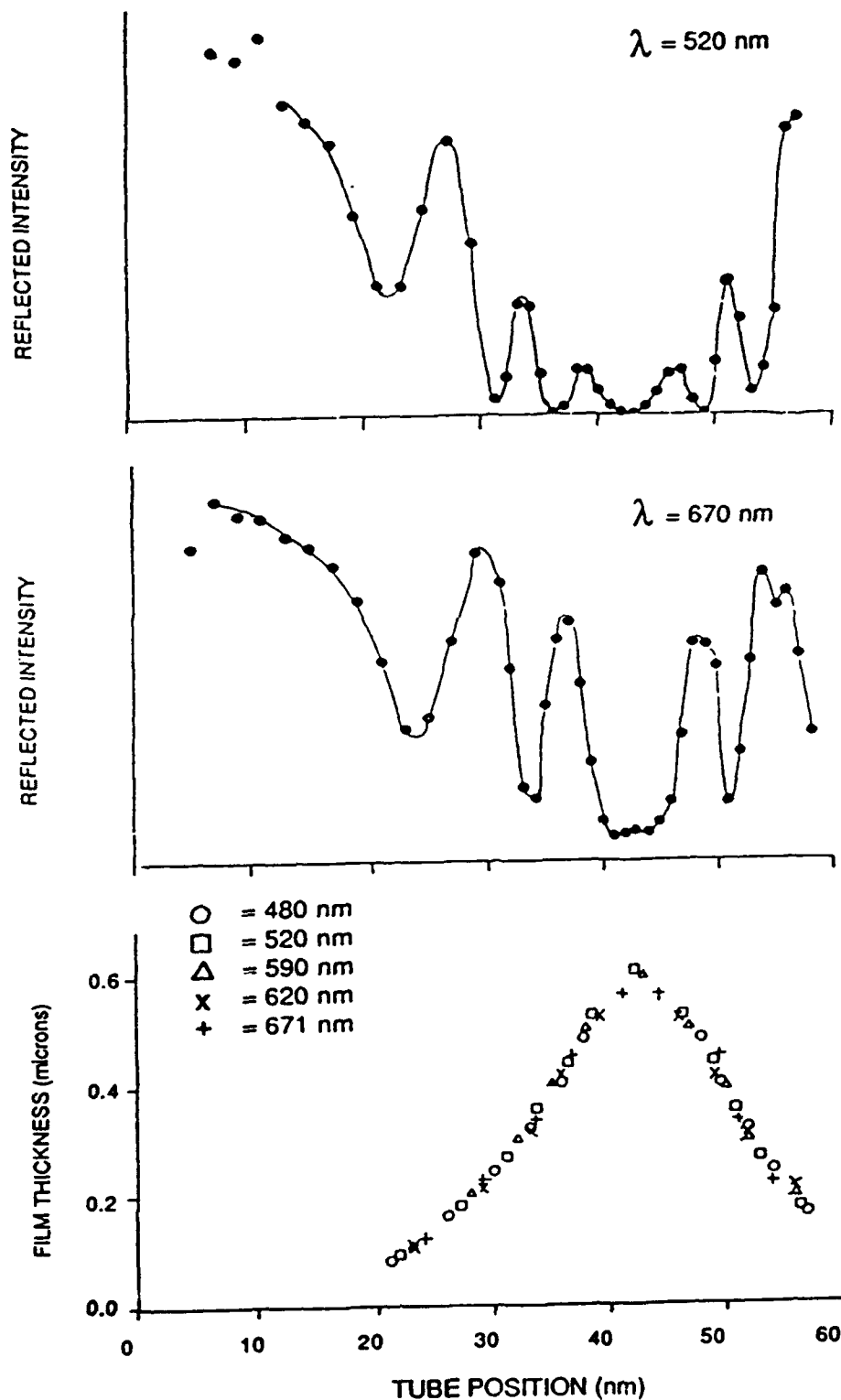
JFTOT TUBE SCANNER



SECTION A-A (NOT TO SCALE)



A COMPARISON OF THICKNESS MEASUREMENTS USING LIGHT OF DIFFERENT WAVELENGTHS





NRL Memorandum Report 6147

Comparison of JFTOT Heater Tube Deposit Rating Methods for the Evaluation of Fuel Thermal Stability

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Chemistry Division*

**Geo-Centers, Inc.*

December 29, 1987

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE			Approved for public release; distribution unlimited.		
4. PERFORMING ORGANIZATION REPORT NUMBER(S) NRL Memorandum Report 6147			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Naval Research Laboratory		6b. OFFICE SYMBOL (If applicable) Code 6180	7a. NAME OF MONITORING ORGANIZATION		
6c. ADDRESS (City, State, and ZIP Code) Washington, DC 20375-5000			7b. ADDRESS (City, State, and ZIP Code)		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Chief of Naval Research		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) 800 Quincy Street Arlington, VA 22217-5000			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO 62233N	PROJECT NO	TASK NO
					WORK UNIT ACCESSION NO
11. TITLE (Include Security Classification) Comparison of JFTOT Heater Tube Deposit Rating Methods for the Evaluation of Fuel Thermal Stability					
12. PERSONAL AUTHOR(S) Morris, Robert E., Hazlett, Robert N., and McIlvaine, C. Linden					
13a. TYPE OF REPORT Interim		13b. TIME COVERED FROM 7/86 TO 6/86		14. DATE OF REPORT (Year, Month, Day) 1987 December 29	
15. PAGE COUNT 18					
16. SUPPLEMENTARY NOTATION Geo-Centers, Inc.					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB GROUP			
			Jet fuels Tube deposit rating methods		
			Thermal oxidation stability JFTOT		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
Quantification of deposits formed of heated metal surfaces is desirable for the evaluation of thermal stability by the JFTOT procedure. Empirical methods widely employed entail either visual comparisons or measurements of reflected light (TDR), both of which are sensitive to deposit color. We have examined these and several other measurement techniques for JFTOT heater tubes and have found that measurements of total carbon content by combustion were the most reliable. Two novel techniques, based on measurements of dielectric strength and interference effects of monochromatic light have been examined. It was found that the dielectric and interference methods correlated well with the combustion analyses and each other, while the TDR often yielded misleading results. The correlations between the various methods will be discussed in addition to the consequence of method choice on the interpretation of experimental data.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT			21. ABSTRACT SECURITY CLASSIFICATION		
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS			UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL R. E. Morris			22b. TELEPHONE (Include Area Code) (202) 767-3845 Code 6180		

GENERAL PAPERS
PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
TORONTO MEETING, JUNE 5-11, 1968

STUDIES ON THE MECHANISM OF H₂S PRODUCTION DURING
THE STEAM STIMULATED RECOVERY OF HEAVY OILS

By

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ABSTRACT

Although the majority of heavy oil now produced in Western Canada is from surface mining operations, most heavy oil is located in subterranean reservoirs, and other methods must be used to exploit these reserves. Steam injection, which raises the formation temperature and pressure, has been studied in numerous field pilots and is being adopted for commercial scale plants. The high reservoir temperatures (150°-350°C) generated by this technique causes chemical breakdown of the organosulfur compounds present in these sulfurous oils (S = 3 - 6 wt%) with the consequence that high levels of H₂S are found in the produced gases. This study reports investigations designed to elucidate the mechanism of these reactions. Two oils, one from the Peace River and the other from the Cold Lake oil sands accumulations were fractionated according to boiling point and each fraction was subjected to conditions observed in steam stimulated reservoirs. Overall, the two oils behaved quite differently and these differences could be related to their general chemical composition.

EFFECTIVENESS OF SELECTED STABILIZER ADDITIVES IN
IMPROVING THE THERMAL OXIDATION STABILITY OF JET FUEL

By

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ABSTRACT

The use of stabilizer additives to improve the ambient storage stability of aviation fuels has raised questions concerning their behavior at elevated temperatures. A hindered phenol, a phenylenediamine, an aliphatic tertiary amine and a metal deactivator were examined during thermal stress in a modified JFTOT apparatus. Experiments were conducted at temperatures up to 310°C. The metal deactivator afforded substantial reductions in insoluble products over the entire temperature range. While all the additives reduced heater tube deposits at 260°C, the effects ranged from innocuous to deleterious at higher temperatures. The phenylenediamine was the most effective in reducing maximum peroxide concentrations, but increased the amounts of insoluble products. The influences of the various additives in terms of heater tube deposits, particulate formation, oxygen consumption and peroxidation will be discussed.

The Effects of Stabilizer Additives on the Thermal Stability of Jet Fuel

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The behavior of several types of fuel stabilizers considered representative of those commonly used was examined during thermal stress of a jet fuel in a modified JFTOT apparatus. A hindered phenol, a phenylenediamine, an aliphatic tertiary amine, and a metal deactivator (MDA) were examined. In experiments conducted at temperatures up to 310 °C, the metal deactivator afforded substantial reductions in insoluble products. All the additives reduced heater tube deposits at 260 °C, but at higher temperatures, the effects of the additives ranged from beneficial for the MDA to deleterious. The phenylenediamine was most effective in reducing maximum hydroperoxide concentrations, but significantly increased the amounts of insoluble products.

The demand for aviation turbine fuel is increasing even as the quality of petroleum crudes is declining. At the same time, new engine designs are putting a greater thermal stress on the fuel as it traverses the aircraft fuel system. This combination of factors has stimulated increased interest and research in fuel stability, the resistance to change in fuel properties.

Two types of stability, low-temperature storage and high-temperature thermal oxidation, are of concern. The first type involves a chemical change, oxidation of fuel molecules to form hydroperoxides (Hazlett et al., 1983; Turner et al., 1986; Watkins et al., 1987). These latter compounds attack elastomers in the fuel system, particularly in the fuel control lines. Hydroperoxides form more readily in fuels produced by hydrocracking or by catalytic cracking followed by hydrotreatment. These refining techniques, which increase the yield of jet fuel, probably remove natural inhibitors which limit hydroperoxide formation by interfering with autoxidation reactions (Smith, 1970).

The second type of fuel stability, thermal oxidation, involves formation of trace amounts of insolubles. Even at the part per million level, insoluble precipitates and gums can be responsible for a variety of problems, which include decreased efficiency of engine heat exchangers, seizing the fuel control valves, and injector fouling. It is known that hydroperoxides play a key role in thermal degradation processes of aviation fuels by initiating a variety of free-radical reactions (Hazlett et al., 1977). Heteroatom (i.e., nitrogen, sulfur, and oxygen) containing species are particularly subject to involvement in this type

of instability (Hazlett and Hall, 1981, 1985).

Additives have been used or considered for addressing these stability problems. In order to prevent the accumulation of hydroperoxides, JP-4 that contains hydrogen-treated blending stocks and all JP-5 produced in accordance with MIL-T-5624 must contain between 17.2 and 24 mg/L of an approved antioxidant. The military specification currently allows the use of various hindered phenols. The ASTM specification (*Annual Book of ASTM Standards*, 1987) for aviation turbine fuels, D1655-82, allows, at a maximum concentration of 24 mg/L, the use of hindered phenols or of a phenylenediamine. A second type of additive, a metal deactivator, is also permitted in military and commercial jet fuels in order to counteract the catalytic effects of active metals, particularly copper, in fuel systems.

In the realm of thermal oxidation stability, several aspects of additive behavior are of concern. First, can additives improve the stability of marginal fuels produced from poorer quality crudes. Second, can additives boost the performance of specification grade fuels to meet the greater thermal requirements of new engine designs. Third, what effect do additives used to control hydroperoxides at low temperatures have on high-temperature stability.

Previous examinations of additive behavior on fuel stability at elevated temperatures have produced mixed results. In the Minex test (Shayeson, 1970), a metal deactivator suppressed insolubles, while phenolic antioxidants did not. At 100 °C and 100 psig of oxygen, reductions in insolubles and hydroperoxides were reported

(Nixon, 1962) in the presence of two different hindered phenols and a phenylenediamine, whereas these same antioxidants were ineffective in long-term storage at atmospheric pressure at 43 °C. Mixed results were obtained with a metal deactivator, also depending on test conditions. Phenolic antioxidants have been used with varying degrees of success, but they have been shown (Henry, 1986; Englin et al., 1976) to be more effective when added during the early months of storage. During storage of hydrotreated jet fuel for 6 months at 50 °C, the addition of as little as 0.01% of two different N,N'-alkylated phenylenediamine antioxidants was found (Englin et al., 1975) to be detrimental to stability. We have also found phenylenediamines to increase insolubles in Naval Distillate fuel in accelerated storage stability tests (Hazlett et al., 1986). In middle distillates and blends containing light cycle oil, insolubles were increased in 12-week 43 °C tests, 2-week 80 °C tests, and 95 °C ASTM D2274-74 stability tests (*Annual Book of ASTM Standards*, 1982). Certain aliphatic amines, either alone or in combination with a metal deactivator, were found to be beneficial.

Thus, the evidence indicates that the effectiveness of any additive is related to its structure and concentration 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. In this study we examined the behavior of selected stabilizer additives in jet fuel by correlating oxygen reactivity and peroxidation with the production of insolubles. The influences that several antioxidants and additives exerted on the thermal stability of jet A were determined by using a jet fuel thermal oxidation tester (JFTOT) apparatus to stress the fuel. The representative antioxidant compounds studied were a hindered phenol and a phenylenediamine. Two commercial additives were examined; FOA-3, which contains a tertiary aliphatic amine as the active ingredient, and FOA-310, which employs the same tertiary amine in combination with a metal deactivator. The metal deactivator was also studied independently. In addition to the measurements of JFTOT heater tube deposits, samples of the stressed fuel were analyzed to determine the levels of peroxidation and amounts of dissolved oxygen consumed.

Experimental Section

JFTOT Stressing Procedure. Fuel samples were thermally stressed in a modified JFTOT apparatus, the operation of which has been described previously (Hazlett et al., 1977). Test samples (1100 mL) were prefiltered through two Gelman Type A/E glass microfiber filters before introduction of the additive. All additives were used at the maximum concentrations allowed in the military specification MIL-T-5624 for Type JP-5 turbine fuel, i.e., 5.8 mg/L for the metal deactivator and 24 mg/L for the other additives. After blending in the additive, the test fuel was placed into a 3-L JFTOT reservoir and sparged with dry air for 15 min. To increase the heated surface area available to the fuel, to reduce the steepness of the tube temperature profile, and to facilitate combustion analysis for total deposit carbon, 304 stainless steel JFTOT heater tubes with 5-in. heated sections were employed. Runs were conducted for 300 min to obtain more deposits, thus affording better statistics on the carbon analysis. Before use, the heater tubes were polished to obtain initial TDR values as low as possible, typically less than eight. Maximum heater tube temperatures of 260, 270, 280, and 310 °C were employed. During the test, pressure differentials across the JFTOT test filter were monitored with a calibrated pressure transducer. In those instances where

appreciable amounts of particulate were formed, the test filter could become plugged, substantially reducing the fuel flow rate below the nominal value of 3 mL/min. This would increase the contact time of the fuel with the heated surface of the heater tube and stress the fuel beyond the normal limits of the test. This possibility of producing misleading quantities of insolubles was avoided by maintaining fuel flow rates at or above 2.5 mL/min by bypassing the test filter when the flow rate dropped below that point. At the completion of each run, the reservoir and fuel lines of the JFTOT apparatus were solvent rinsed and dried.

Tube Deposit Measurements. Tube deposit measurements (TDR) were taken with an Alcor Mark 9 tube deposit during rating device operating in the spinning mode. These optical reflectance readings were taken at every 2 mm along the heater tube length. Δ TDR values were calculated from the differences between the TDR readings before and after stress at each location. The highest Δ TDR value from each tube was taken as the maximum, and the summation of all Δ TDR values on each tube comprised the total Δ TDR.

Total carbon contents of the heater tube deposits were measured by combustion to carbon dioxide with a Perkin-Elmer Model 240 elemental analyzer. The grip ends of each heater tube were removed, and the heated lengths were sectioned axially in half. To eliminate interferences from residual fuel and other organics on both inner and outer walls of the heater tube sections, they were thoroughly rinsed with toluene and dried prior to combustion. After calibration of the analyzer with known compounds, blank carbon values were obtained from unused heater tube sections. All results from used heater tubes were corrected for the blank values.

Fuel Analysis. The JFTOT apparatus was modified to permit sampling of the fuel effluent after passing over the heater tube and before returning to the reservoir (Hazlett et al., 1977). It was found that, when oxygen-depleted fuel was allowed to come in contact with air, the equilibrium concentration of oxygen would be rapidly restored. It was therefore necessary to route JFTOT effluent for oxygen measurements directly to a liquid sampling valve on a gas chromatograph via $1/16$ -in. i.d. stainless steel tubing. The permanent gases were separated from the fuel with 6-ft $\times$ $1/8$ -in. stainless steel 42/60-mesh alumina column, and the permanent gases were resolved by a 6-ft $\times$ $1/8$ -in. stainless steel column packed with 42/60-mesh 5 $\times$ molecular sieves. Column temperatures were maintained at 100 °C. Entrapped organics were periodically removed from the alumina column by backflushing at an elevated temperature. Permanent gases were detected with a helium ionization detector (HID). The helium carrier gas for the HID was purified with a helium diffusion cell in order to attain sufficient oxygen sensitivity.

Samples of the stressed fuel were taken from the liquid sampling valve for peroxide analysis. Hydroperoxides were determined iodometrically in accordance with ASTM D3703-85 (*Annual Book of ASTM Standards*, 1986), with the exception that potentiometric detection was employed using a platinum ring electrode with a Mettler DL-20 automatic titrator.

Materials. The test fuel for all experiments was a commercial jet A. Selected fuel properties, given in table I, were determined to ensure conformance with ASTM Aviation Turbine Fuel Specification D1655-82. All additives were used as received without further purification. The following compounds and additives were examined: 2,6-di-*tert*-butyl-4-methylphenol (Aldrich, 99%); N,N'-

Table I. Test Fuel Properties

property	value	method
acidity, total, mg of KOH/g	<0.01	D663
sulfur, mercaptan, wt %	0.0009	D3227
sulfur, total wt %	0.0325	D2622
aromatics, vol %	16.6	D1319
distillation temp, °F (°C)		D86
10% recovered, temp	364 (184)	
50% recovered, temp	424 (218)	
90% recovered, temp	494 (257)	
final boiling pt, °F (°C)	529 (276)	
distillation residue, %	1.5	
distillation loss, %	1.5	
gravity, °API (sp. gr.) at 60 °F	41.9 (0.816)	D1298
thermal stability at 260 °C		D3241
filter pressure drop, in.Hg	0	
tube deposit rating (TDR)	<2	
copper, ppm	<0.001	ICAP

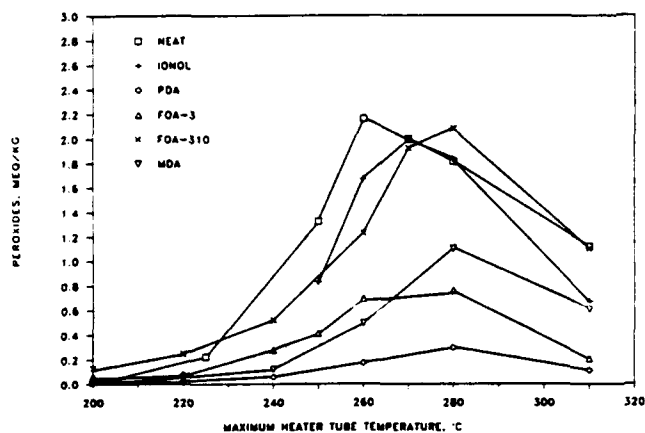


Figure 1. Influences of additives on JFTOT heater tube deposition as determined by combustion analysis.

di-*sec*-butyl-*p*-phenylenediamine (Pfaltz & Bauer); *N,N'*-disalicylidine-1,2-propanediamine (metal deactivator, Pfaltz & Bauer); FOA-3, tertiary aliphatic amine (Du Pont); and FOA-310, tertiary aliphatic amine and metal deactivator (Du Pont).

Results

The effects of the additives on the amounts of heater tube deposits were determined from the quantities of total carbon found on each tube by combustion. When the averages of the total carbon from the two replicate heater tubes are compared (Figure 1), it is apparent that all the additives reduced the amounts of tube deposits at 260 °C with respect to the neat fuel. As the stress temperature was increased, FOA-310 and metal deactivator (MDA) continued to reduce the amounts of heater tube deposits, while the effectiveness of the other additives diminished. FOA-310 contains an aliphatic tertiary amine, *N,N*-dimethylcyclohexylamine, in combination with the metal deactivator, and FOA-3 contains the same aliphatic tertiary amine as its major constituent. Therefore, the aliphatic tertiary amine in FOA-3 was not particularly effective in suppressing deposit formation but in combination with the metal deactivator in FOA-310 did bring about significant reductions. This indicates that the effectiveness of the FOA-310 was attributable to the presence of the metal deactivator. In comparison with the neat fuel, the hindered phenol (IONOL) was essentially innocuous, whereas the phenylenediamine (PDA) often increased the amounts of tube deposits at 270 °C and above, as did FOA-3 at 270 °C.

In comparison of TDR values with carbon contents and two types of nondestructive deposit volume determina-

Table II. JFTOT Heater Tube Deposit Ratings

max heater tube temp. °C	additive*	total ΔTDR		
		1	2	av
260	neat	441	612	527
	IONOL	371	283	327
	FOA-3	433	317	375
	PDA	485	374	430
	FOA-310	362	299	331
	MDA	257	150	204
270	neat	526	594	560
	IONOL	612	634	623
	PDA	570	790	680
	FOA-3	780	685	733
	FOA-310	339	445	392
	MDA	299	355	327
280	neat	727	687	707
	IONOL	698	476	587
	PDA	822	672	747
	FOA-3	897	628	763
	FOA-310	458	419	439
	MDA	380	345	363
310	neat	945	772	859
	IONOL	836	731	784
	PDA	1044	965	1005
	FOA-3	1088	819	954
	FOA-310	836	494	665
	MDA	771	626	699

*MDA added at 5.8 mg/L; all others added at 24 mg/L.

tions, we have shown (Morris et al., 1987) that, although the repeatability of the TDR was good, it was often of limited use as a quantitative measurement. In that study, TDR measurements were found to be influenced by highly colored deposits. This disproportionate response accounts for the indications by the tube deposit ratings (TDR) given in Table II which suggest that the effectiveness of the metal deactivator was less than indicated by the carbon burnoff technique, which is a primary measurement. Furthermore, the TDR indicated FOA-310 and MDA effectiveness decreased as the temperature increased.

The quantities of hydroperoxides found in fuel samples during stressing are a consequence of the differences in the net formation and decomposition rates. While different fuels can peroxidize at different rates under given conditions of stress, comparison of hydroperoxide concentrations in one fuel in the presence of a variety of additives should provide a comparative measure of additive capabilities. The hydroperoxide concentrations measured in JFTOT effluent indicated that the test fuel had a low initial hydroperoxide concentration which increased as it was stressed. Thus, the additive was present during the formation of the peroxides and could react with any free radicals as they formed. Under these conditions, the likelihood of free-radical chain termination is greater, thus increasing the effectiveness of the additive. When the peroxide concentrations are considered as a function of heater tube temperature (Figure 2), they are shown to have accumulated up to a tube surface temperature of approximately 270 °C. Above this temperature, it has been shown (Hazlett et al., 1977) that the hydroperoxides undergo thermal decomposition and their concentration decreases.

Although heater tube deposits were significantly reduced in the presence of FOA-310, levels of hydroperoxides found at temperatures above 260 °C were similar to the neat fuel. When the two components of FOA-310 were tested separately, both the metal deactivator and the FOA-3 significantly reduced hydroperoxides from levels reached in the neat fuel. However, the metal deactivator was very effective in reducing insolubles formation, whereas the FOA-3 was not. The thermal stability of radical-inhibitor

Table III. Oxygen Consumption by Fuel during JFTOT Stressing

tube temp, °C	percentage of initial oxygen consumed					
	neat	IONOL	PDA	FOA-3	FOA-310	MDA
200	1.4	0	0	3.9	0	0
220			1.1	4.1		14.7
225		21.3			0	
240	27.5		2.1	25.1		16.9
250	44.2	45.7		45.1	31.2	
260	89.5	73.8	28.8	94.8	41.7	35.8
270	88.6	98.8	38.1		82.8	
280	98.2	100.0	85.5	100.0	100.0	94.5
310	100.0	100.0	100.0	100.0	100.0	100.0

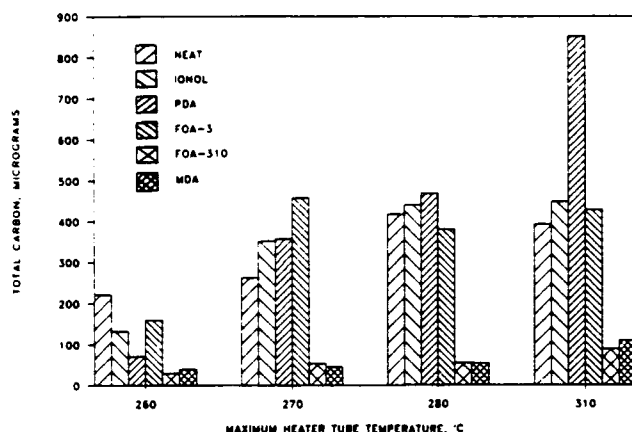


Figure 2. Peroxide concentrations in fuel containing additives after JFTOT stressing.

complexes may play a role in the effectiveness of FOA-3 for controlling hydroperoxide concentrations at elevated temperatures. Although they did not significantly reduce tube deposits, the FOA-3 and particularly the phenylenediamine were effective in suppressing peroxide levels.

Measurements of oxygen content in fuel stressed with JFTOT heater tube temperatures ranging from 21 to 310 °C (Table III) revealed that oxygen consumption was generally in accordance with the observed peroxidation levels. For instance, ionol exerted little effect but PDA, FOA-310, and MDA reduced oxygen consumption. On the other hand, FOA-3 exhibited no reduction in oxygen usage in contrast to the reduction observed for hydroperoxide formation.

In all cases, the quantities of filterable insolubles were indicated by the increases in differential pressure across the standard JFTOT test filter. This was not a quantitative measurement but provided an indication of the magnitude of insolubles produced. The metal deactivator and the FOA-310 were very effective in suppressing filterable insolubles. The effectiveness of the other additives to reduce filterable insolubles decreased with increasing temperature, in accordance with the other measured properties. At higher temperatures, the hindered phenol had no significant effect, while the FOA-3 tended to increase filterable insolubles somewhat. The most rapid filter plugging generally occurred in the presence of the phenylenediamine. When such increases in insolubles were observed previously (Johnson et al., 1970), they were attributed to thermal degradation of the phenylenediamines at 200–230 °C. However, in this study, increases in tube deposits did not occur until 310 °C, whereas filterable insolubles increased dramatically above 270 °C.

Discussion

The additives chosen for study represented several principles of stabilizing action. The Ionol and PDA act as antioxidants to interfere with autoxidation chemistry.

Table IV. Summary of Additive Effects on Fuel Properties during JFTOT Stressing^a

additive	heater tube deposits	filterable insolubles	peroxidation	oxygen consumption
IONOL	0	0	0	0
PDA	+	++	--	--
FOA-3	-	+	-	0
FOA-310	--	--	0	-
MDA	--	--	-	-

^a (o) No or minimal effect, (+/-) significant increase/decrease, (++)/-- large increase/decrease.

These two additives have had extensive use in gasoline and jet fuel as well as military diesel and distillate fuels. MDA is designed to complex copper ions, thus reducing their stimulation of fuel oxidation. It is commonly used in jet, gasoline, and diesel fuels. FOA-3, a tertiary aliphatic amine, counteracts catalysis of sediment formation by fuel acids under low-temperature storage conditions (Hazlett, 1987). This additive is used in commercial diesel and heating oils. FOA-310 combines the functions of MDA and FOA-3.

An overall summary of additive influences on the measured properties of fuels stressed in the JFTOT is given in Table IV. During JFTOT stressing of this particular fuel up to a maximum heater tube temperature of 310 °C, the metal deactivator was the most effective of the additives examined. MDA afforded significant reductions in heater tube deposits and filterable insolubles as well as some control over the rate of oxidation and hydroperoxide concentrations. FOA-310 acted identically with MDA, with the exception of less effect on hydroperoxide concentration. The similarity of these two additives can be attributed to the metal deactivator, alone in MDA but in a mixture with a tertiary amine in FOA-310. Since the copper content of the fuel was found to be less than 1 ppb (Table I), the improvements in thermal stability were not a consequence of copper complexation by the MDA. The tertiary amine, as a single functional additive in FOA-3, exhibited moderate activity except in reducing hydroperoxide concentration. This latter may result from the interaction of the hydroperoxide and FOA-3 to form an amine oxide.

Ionol, the hindered phenol, was mostly innocuous in all properties. Thus, the antioxidant which has demonstrated inhibition of oxidation at low temperatures is not functioning as such in the temperature range used in these tests. The PDA increased insolubles formation in spite of reducing the rate of oxidation and limiting hydroperoxide formation. If thermal decomposition of the phenylenediamine itself was responsible for the formation of insolubles, then loss of the additive would result in marked increases in peroxidation as the temperature increased. Inasmuch as both peroxidation and oxygen consumption were suppressed at all temperatures, it is more likely that the insolubles are a result of thermal decomposition of reaction products of the phenylenediamine with free-rad-

ical species, i.e., phenylenediamine radical adducts or dimers of the additive.

It is recognized that antioxidants, or oxidation inhibitors, can react with free radicals to donate a hydrogen and form a relatively stable inhibitor radical. These inhibitor radicals can then either combine with another fuel component radical or dimerize with another inhibitor radical. The effectiveness of the inhibitor is thus determined by both the lability of the available hydrogen and the stability of the inhibitor-radical complex. Therefore, at elevated temperatures, not only must the thermal stability of the inhibitor itself be considered, but also its ability to remain in a higher energy state after collision with a free radical without rearranging or decomposing to an inactive form. The phenylenediamine and hindered phenol antioxidants examined in this study are capable of stabilization through electron delocalization around an aromatic ring. The resulting inhibitor radicals can then combine with fuel component radicals to terminate free-radical chains. At elevated temperatures, these inhibitor-radical complexes could undergo C-O cleavage, especially if the process is driven by the establishment of aromaticity in the product. Thermal decomposition of soluble inhibitor-radical reaction products is also of concern when evaluating the effectiveness of additives at elevated temperatures.

Conclusions

The most significant reductions in deposits were realized when the metal deactivator was present, either alone or in combination with a tertiary aliphatic amine antioxidant in FOA-310. All the additives exhibited inhibitory effects on insolubles formation and peroxides at lower temperatures, but only those with the metal deactivator remained effective as the temperature increased. The mechanism by which the metal deactivator functions effectively at elevated temperatures is not clear at this time. The tertiary aliphatic amine, FOA-3, was not effective in reducing insolubles at high temperatures, although peroxide levels were suppressed throughout. The phenylenediamine was very effective in reducing peroxidation, but this reduction was accompanied by significant increases in insolubles. The findings do not allow for any distinction to be made as to whether the insolubles were due to thermal decomposition of the phenylenediamine itself or additive-peroxide complexes.

Acknowledgment

The authors thank Naval Air Propulsion Center for providing sulfur and copper analyses and Dr. Charles W. Sink and Dr. J. Brian McKay of Edinboro State University of Pennsylvania for FIA analyses of the base fuel.

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Received for review December 14, 1987

Revised manuscript received March 29, 1988

Accepted April 16, 1988

3rd INTERNATIONAL CONFERENCE ON STABILITY
AND HANDLING OF LIQUID FUELS
London, UK
September 13-16, 1988

COMPARISON OF JFTOT HEATER TUBE DEPOSIT RATING METHODS
FOR THE EVALUATION OF FUEL THERMAL STABILITY

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ABSTRACT

The quantification of deposits formed on heated metal surfaces is used as one measure of thermal stability by the JFTOT procedure. Empirical methods widely employed entail either visual comparisons or measurements of reflected light (TDR), both of which are sensitive to deposit color. We have found that measurements of total carbon content by combustion are more reliable and have compared a number of deposits formed on stainless steel JFTOT heater tubes by the TDR and combustion methods. In addition, two novel techniques based on measurements of dielectric strength and the interference effect produced upon reflectance of monochromatic light have been examined. It was found that the dielectric and interference methods correlated well with the combustion analyses and each other, while the TDR often yielded misleading results. The correlations between the various methods will be discussed in addition to the consequences of method choice on the interpretation of experimental data.

INTRODUCTION

The thermal oxidation of liquid fuels is often accompanied by the formation of insoluble reaction products, either as suspended particulate or as gum which adheres to container surfaces. Modern aircraft engine designs and aerodynamic heating of wing surfaces place more severe thermal stress on the fuel, increasing the likelihood of the formation of insoluble deposits. Aircraft fuel system deposits can be responsible for a variety of problems including decreased efficiency of engine heat exchangers, seizing of fuel control valves and injector fouling.

It is known that thermally initiated fuel degradation is accelerated by the presence of oxygen through autoxidative processes involving free radical chain reactions. The Jet Fuel Thermal Oxidation Tester (JFTOT) is widely used to characterize the thermal oxidation stability of a fuel. In the JFTOT, aerated fuel is pressurized with nitrogen and passed over a heated metal tube so that the fuel is stressed under conditions of high oxygen availability and slowly increasing temperatures. The quantities of insoluble products formed under these conditions constitute a measure of the deposit forming characteristics of the fuel. In accordance with standard ASTM D3241 test procedures [1], the formation of filterable insolubles is detected from

changes in pressure differential across a standard test filter downstream of the heated tube and the adherent insolubles deposited on the hot tube are characterized by visual comparison with color standards. The highly subjective nature of the visual method of rating heater tube deposits was revealed in a round-robin effort conducted by the Coordinating Research Council [2]. The poor precision of visual ratings from unusual and highly colored deposits resulted in random errors which were in excess of the differences between the values, thus eliminating any statistical significance. To increase the reliability of the measurement, the Tube Deposit Rater (TDR) was developed. The TDR is based on the measurement of the attenuation of reflected white light by a photocell; thicker coatings increase the TDR while a clean tube surface gives a reading of zero. From comparisons with measurements of deposit thicknesses by Auger spectroscopy, neither the Visual Rating method nor the TDR were found [3] to be adequate in rating tube deposits. While less subject to operator judgement than the visual rating method, the TDR can be influenced by the optical properties of the deposit.

Quantification of tube deposits by combustion of carbon to carbon dioxide has been investigated, with the assumption that the deposit is composed primarily of carbon. Measurements of total carbon contents per unit area per unit time have been employed [4] to study the influence of dissolved oxygen on the rates of deposit formation from thermally stressed jet fuels on 316 stainless steel tubes. These studies were later extended to examine the effects of trace amounts of sulfur- and nitrogen-bearing compounds [5,6] on deposition rates. Combustion analyses have been utilized [7] to quantify deposition rates from jet fuels stressed under a wide variety of experimental conditions in a special test apparatus. Carbon was determined from deposits on sintered stainless steel filters and from the inner walls of heated 316 stainless steel tubes. A lower limit of 200 micrograms carbon on the tube sections was reported. The precision of combustion analyses conducted on standard JFTOT heater tubes has been shown [8] to be limited by the difficulty with which quantitative removal of carbon from the aluminum surface could be attained. This behavior seems related to the relatively thick porous layer of aluminum oxide which coats aluminum metal surfaces. It had been found [8] that the amount of carbon formed on stainless steel tubes thermally stressed in the JFTOT generally exceeded that from aluminum tubes by a factor of two. In addition, migration of magnesium in 6061 T6 alloy aluminum heater tubes at elevated temperatures has been reported to inhibit deposition. Heater tubes comprised of 304 stainless steel do not form porous oxide coatings, allowing much lower detection limits, nor is magnesium inhibition possible. Besides these limitations associated with the use of aluminum tubes, the tubes are destroyed during the combustion analysis and it provides no detailed information concerning the spatial distribution of the deposit.

Two novel techniques for determining the volumes of heater tube deposits have been developed. One technique [9] is based on measurements of the electrical insulating properties of the deposit. The other method [10] is based on the interference effect produced when monochromatic light is reflected off the tube surface through the deposit. Since these methods are non-destructive, we were able to obtain deposit measurements from the TDR, dielectric, interference and combustion methods on each JFTOT heater tube. The initial findings were described earlier [11] on a limited number of

samples. In this study, the results from the four methods are compared from a greater number of heater tubes and refinements in the use of the optical interferometry apparatus were investigated.

EXPERIMENTAL

Thermal stressing of fuel samples was performed using the modified JFTOT described earlier [12]. The same Jet A fuel was used in all experiments. Five-inch 304 stainless steel heater tubes were employed to achieve a more gradual increase in temperature, greater reactive metal surface area and to facilitate the combustion analysis. In order to ensure sufficient quantities of material for combustion analysis, run times were increased to 300 minutes. Under these conditions, at a maximum fuel flow rate of approximately three milliliters per minute, the residence time of the fuel in the heater tube holder was approximately 28 seconds. Since appreciable amounts of filterable insolubles would substantially reduce the fuel flow rate through the test filter and increase the contact time of the fuel with the heated tube surface, the test filter was bypassed when the flow rate dropped below 2.5 mL/min. Tests were conducted at maximum heater tube temperatures of 260, 270, 280 and 310°C.

Spun TDR measurements were taken with an Alcor Mark 9 tube deposit rating device. The instrument was calibrated in accordance with the manufacturer's instructions, using a calibration tube supplied with the instrument. Readings were taken from heater tubes before and after stressing at 2 mm intervals over the 120 mm heated length. To obtain a measure of the changes in reflectance due to the deposit, differences between the initial and final TDR values at each location were calculated and reported as the delta TDR. The sum of the delta TDR constituted the total delta TDR, which was used as an indication of the total amount of deposit on the tube. The highest spun delta TDR at any one location was taken as the maximum delta TDR.

Volume measurements were performed by Southwest Research, Inc., using their dielectric measuring device. This technique relies on the assumptions that an organic deposit will behave as an electrical insulator and that all "normal" deposits have similar dielectric strengths. When a voltage potential is applied across the tube deposit through a stylus, it will act as an electrical insulator until the potential reaches the point at which the organic material comprising the coating breaks down. The coating then ceases to act as a dielectric insulator and current begins to flow between the heater tube and the stylus. Values for the dielectric breakdown were determined by increasing the voltage potential across the coatings at a controlled rate while monitoring the current. Deposit thicknesses were calculated from an empirically determined [9] proportionality factor, which relates the dielectric breakdown voltage to deposit thickness. The precision of the measurement is reduced with very thin coatings. The dielectric measurements are taken at specific points on the tube, so that spinning cannot be employed to average out variations in thickness around the tube. The side of the tube facing the fuel outlet was taken as a reference point i.e., zero degrees. Measurements were obtained at 2 mm intervals down the tube at 0, 90, 180 and 270 degrees, providing four sets of thickness measurements for each tube. At each location, the readings were averaged and used to define a thickness profile from which the total deposit volume was calculated.

Deposit volumes were determined by Geo-Centers, Inc. with the fiber optic JFTOT tube scanner which they developed. Additional interferometry measurements were taken in our laboratory using a similar instrument, supplied by Geo-Centers. In this method, monochromatic light having a wavelength of 680 nm was directed onto the coated tube in a direction perpendicular to the surface through a fiber optic assembly which contained both the source and detector optics. The intensity of reflected light represents the quantity of light which emerges through the coating after reflecting off the metal tube surface. Since there is a large difference in the refractive indices between the air and the deposit, the reflected light wave undergoes a phase change. As a consequence, the emergent wave interferes constructively or destructively with the incident wave, depending on the thickness of the deposit. As the detector is scanned across a deposit, the light intensity changes periodically as the deposit thickness passes through multiples of the wavelength of the incident light. At thicker deposit thicknesses, absorption of the light by the coating dominates, limiting measurement to thicknesses below approximately two microns. Like the dielectric method, the interference method is also a static measurement which is conducted at four points around the tube circumference, using the side facing the fuel outlet as the reference. The interference measurements are treated as follows. The thicknesses at each tube location are averaged and a table compiled of the locations at which the average coating thicknesses pass through multiples of the incident light wavelength. The deposit depth at each location is then corrected for the refractive index of the deposit and the source-detector geometry. The thickness profiles thus determined are fitted to the appropriate functions and integrated to obtain the deposit volume.

Total carbon contents of the tube deposits were determined after completion of the other measurements. Combustion analyses were performed with a Perkin-Elmer model 240 elemental analyzer. After calibration of the analyzer with known compounds, blank values were obtained from cleaned, unused heater tube sections. The grip ends of the heater tubes were removed and the heated section was cut into two equal lengths, cleaned in toluene, vacuum dried and analyzed.

RESULTS

The quantities of total carbon from each JFTOT heater tube, the TDR values and the deposit volumes from the dielectric breakdown and interference methods are given in Table 1. The scatter plot of TDR values vs total carbon in Fig. 1 illustrates that, although there is a tendency for the heavier deposits to exhibit higher TDR readings, there was a high degree of uncertainty. This illustrates the deficiency of the TDR when used quantitatively in research efforts undertaken with the JFTOT.

A plot of the deposit volumes calculated from the dielectric and interference measurements vs total carbon (Fig. 2), indicates that these quantities are more linearly related to carbon content than the TDR. Light absorption by the thicker deposits limited the useful range of the interference measurements to coatings containing less than 400 micrograms of carbon. There was a tendency for the deposit volumes to be somewhat less by the dielectric method at very thin deposits, i.e., less than 1×10^{-4} cu.mm. This is understandable in light of the fact that the precision of the

dielectric measurements would be expected to decrease on very thin coatings.

Both of these two new non-destructive techniques provide a convenient means of measuring deposit thicknesses at known locations on non-spinning tubes. Such techniques could be employed to determine the relationships between deposit thickness variations and experimental variations. Thickness profiles from interferometry along four sides of a typical heater tube are illustrated in Fig. 3. In this example, the thickness measured at 0° was nearly twice that at 90 and 180°, where the side of the tube having the thickest deposit was designated as 0° and the other profiles were taken by indexing the tube in 90° increments. In those instances where there are large radial variations in thickness, increasing the number of measurements around the circumference would increase the precision of the volume calculation. However, the high degree of correlation with the combustion data indicates that, in these experiments, the precision of the deposit volumes from measurements at four locations was comparable to that of the combustion data.

The agreement between tube deposit measurements from these methods can be quantitatively expressed by performing regression analyses and considering the linear correlation coefficients. From the regression correlation coefficients given in Table 2 the deposit volumes by the dielectric breakdown and the interference methods are shown to correlate extremely well with total carbon contents and with each other. The TDR values did not correlate with any of the other measurements.

Typical TDR profiles from two heater tubes were found to have maximum TDR values of 47 and 28 at the locations of maximum tube temperatures. The TDR scan of the heavier deposit also contained a secondary maximum at approximately 80 mm. Corresponding maximum dielectric breakdown potentials of 828.3 and 17.2 volts were measured from the same two tubes. This illustrates the increased range of the dielectric measurement over the TDR for a case where changes in TDR were not proportional to the actual quantities of tube deposits. Carbon contents of the entire deposits on these two tubes was 381 and 27 micrograms, respectively. The random nature of the correlation between TDR and carbon contents or deposit volumes renders the existence of any systematic non-linear relationship very unlikely. A secondary maximum TDR value at 80 mm was also not apparent from the dielectric measurements. This type of effect may have been caused by light absorption by a thin, highly colored deposit which resulted in an erroneously high TDR. There is also the possibility of interference effects arising from thin coatings with thicknesses in multiples of the dominant wavelength of the incandescent lamps used in the TDR rating device.

The interference measurements were obtained down the length of the heater tube by manually moving the fiber optic probe. The increments between measurements must be reduced in order to sufficiently resolve the point at which the coating thickness passes through a multiple of the incident light wavelength. In order to facilitate interference measurements taken at NRL, the fiber optic probe was fixtured to the photocell transport assembly of our Alcor Mark 9 TDR rater. The probe could be manually positioned in the TDR rater with a resolution of 2.5 mm. In addition, a motor drive was fitted onto the positioning mechanism of the TDR rater and the output signal of the fiber optic probe was applied to a chart recorder, providing a continuous

plot of reflected light intensity vs location. Comparison of plots of intensity vs location from the discrete measurements with the continuous chart recordings revealed that taking readings each 2.5 mm was not sufficient to resolve the coating thickness gradient. It was therefore necessary to obtain the data in a continuous manner. Continuous acquisition of the reflected light intensity was accomplished by input to a suitable analog-digital interface to a desktop microcomputer. The translation rate of the probe across the tube was calibrated to provide a means for determining the position of the probe by the timing of the signal.

A computerized method of converting the raw measurements to deposit volumes would allow for a nearly automated procedure, which would facilitate the use of this technique in routine specification testing. As a first step, a computerized method was applied to fitting the unequally spaced thickness measurements to a smooth curve. Integration of the resulting thickness profile yields the deposit volume. One approach was the application of a cubic spline to fit the data to a smooth curve that passed through all the data points. The curves derived from spatial distributions of deposit thicknesses from dielectric and interference measurements of the same deposit are shown in Figure 4. Good agreement was found between the volumes calculated from the spline fit and the values originally reported. It is not surprising that the volumes calculated from the dielectric data agreed so well, since the dielectric data points are regularly spaced. The agreement between the spline fit and the methods used by Southwest Research and Geo-Center indicates that at least in some cases, automatic measurement and reporting of volumes is possible, providing a means for utilization of these techniques for routine specification testing.

DISCUSSION

Within their respective useful ranges, both non-destructive methods described here provided measurements of deposit volumes which correlated equally well with each other and with measurements of total carbon. Since these measurements are obtained at discrete points, they also describe the distribution of deposits around the heater tube circumference. Comparison of deposit thickness profiles for each quadrant around the tube, it was found that in many cases the deposits were not evenly distributed around the tube circumference. Generally, the thickness was greater on the surface facing the fuel outlet. This unevenness contributed significantly to the uncertainty in the average thicknesses calculated from the four points around the circumference. It may be possible to minimize this unevenness somewhat by reducing the test duration, it may also be necessary in certain instances to increase the number of measurements that are taken around the tube surface to improve the precision of the computed average.

The dielectric method is limited to coatings which are thick enough to electrically insulate the stylus from the tube, thus limiting its use with very thin coatings. A lower limit of 20 volts for the dielectric breakdown potential, which represents a coating 0.05 microns thick, has been indicated by Southwest Research as the point below which the readings can be unreliable. The dielectric method may therefore not be applicable for quantifying very thin deposits produced by aviation fuels when tested in accordance with ASTM D3241 [1]. Lower limits and the correlation with visual ratings would have to be established before it can be determined if the

dielectric method would be suitable for routine specification testing.

The lower limit of detection of the interference method is mainly a function of the wavelength of the incident light. In this work, light with a wavelength of 680 nm was used, theoretically limiting the lower limit to 0.14 microns and the resolution to 0.07 microns. Absorption of light by the coating imposes constraints on the maximum deposit thicknesses that can be measured by the interference technique. The maximum thicknesses of many of the tube deposits generated in this work were beyond the upper limit of the interference technique, but the experimental conditions in this work were formulated to maximize deposit quantities for combustion analysis. Another factor is the distribution of deposit. In the interference method, data points are obtained only at those locations where the deposit thickness passes through multiples of the wavelength of the incident light. The number of data points will therefore be a function of the length of the deposit thickness gradient. A coating which increases in thickness over a short distance may not provide a sufficient number of data points to accurately fit the thickness profile equations. Tube deposits having a long thickness gradient and which appear under white light to have a peacock appearance, will generally yield more data points. Most of the deposits examined in this study provided a sufficient number of data points on the transition between the fuel inlet and the location of the temperature maximum. The heat transfer characteristics of the stainless steel tubes causes the maximum temperature to occur near the fuel outlet and thus, in many cases, the number of data points for the deposit thickness transition between the hot zone and fuel outlet were limited. It would be expected that the use of aluminum JFTOT tubes would alleviate this problem, since the temperature maximum is further from the fuel outlet. In addition, shorter run times would tend to reduce the likelihood of exceeding the upper limit of the measurable thickness. Therefore, the interference technique shows promise as an applicable tool in nondestructively quantifying JFTOT heater tube deposits produced during specification testing.

A limitation that currently exists to the application of the interference method to routine testing of fuels is the methods for data interpretation. The dielectric measurements provide thickness information at regular intervals and therefore, calculation of deposit volume is a relatively straightforward procedure. On the other hand, the interference measurements provide thickness information only at multiples of the incident wavelength, at uneven intervals. Thus, the calculation of deposit volumes is somewhat more complicated and requires some interpretation on the part of the analyst. The use of a computerized technique to obtain the thickness profile would simplify the analysis procedure and eliminate any operator subjectivity. The spline fitting techniques described above show promise as a non-interpretative method for fitting and integrating a thickness profile. However, the accuracy of the fitted thickness profile would still be limited by the number of data points upon which it is based, i.e., the thickness gradient. Future efforts will involve refinement of the mathematical methods to provide automatic reduction of the raw measurements to deposit volumes.

CONCLUSIONS

Excellent agreement was obtained between JFTOT heater tube deposit volumes calculated from measurements of dielectric breakdown and from optical

interference and the total amount of carbon measured by combustion. Within their respective measurement ranges, both the dielectric and interference techniques could be employed to quantitatively determine JFTOT heater tube deposits from the 304 stainless steel tubes. Since the precision of the volume calculations derived from static measurements can be affected by extreme radial variations in deposit thickness in certain instances, it may be necessary to increase the number of measurements taken around the tube circumference. Although the treatment of the regularly spaced dielectric measurement data to calculate deposit volumes is relatively easy, the technique is nevertheless limited to thicker coatings which can be beyond the range of interest in specification testing. The interferometric method will measure thinner deposits, but the accuracy can be compromised in those situations where the thickness gradient is too short to provide for enough data points. The examination of heater tubes prepared in accordance with standard specification test methods by the dielectric and interferometric techniques would be necessary to assess their potential applicability to specification testing. However, automation of the data collection and analysis procedures would seem to be a prerequisite, particularly for interferometry. The use of spline functions to define and integrate the thickness profiles shows promise as a noninterpretive approach towards automating the data analysis procedure.

As practical alternatives to combustion analyses, the dielectric and interference methods may also allow for the use of aluminum JFTOT tubes in quantitative studies. These techniques could also provide a convenient and practical means with which to study the relationships between fuel flow and deposit characteristics and to determine the influence of heater tube composition without resorting to combustion analyses to quantify deposits. The thickness profiles obtained by these two new methods have also demonstrated instances where the TDR values were disproportionately influenced by thin, highly colored deposits. The failure of the spun TDR method to respond proportionately to certain types of deposits poses limitations on its usefulness as a tool for quantitative measurements.

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Table 1. JFTOT Heater Tube Deposit Measurements

Total Carbon, micrograms	Total Delta TDR	Volume, cu.mm.	
		Interferometry	Dielectric Breakdown
876.8	965		0.6365
826.0	1044		0.5405
630.1	822		0.5358
618.6	855		0.5107
587.9	819		0.4570
537.3	628		0.4553
514.9	790		0.4962
513.6	780		
493.5	698		0.5035
456.2	731		0.4129
438.1	836		0.3532
430.8	772		0.4057
415.4	727		0.4325
398.5	685		0.4272
385.2	476		0.4149
381.2	634	0.350	0.3752
370.6	660		0.2883
352.5	945		0.2170
321.8	612	0.310	0.2627
319.7	612		
304.1	672	0.330	0.3493
287.7	526		0.2752
266.9	1088		0.2257
237.6	594	0.260	0.2182
221.6	897		0.1790
196.4	570		
163.4	374	0.190	0.1563
158.4	283	0.110	0.1238
156.5	485		
133.8	771		0.0562
121.2	441		0.0785
112.0	609		0.0942
107.3	745		0.1541
106.0	371		
97.2	706		0.0855
96.7	431		0.1006
92.0	660		0.0805
91.2	494	0.086	0.0545
84.9	836		0.0175
83.6	626		0.0469
80.8	433		
79.2	337		0.0511
66.0	443		0.0607
59.4	317	0.055	0.0237
57.9	458		0.0230
55.8	345	0.067	0.0281
55.4	339		0.1610
52.0	445	0.053	0.0233

Table 1, continued

Total Carbon, micrograms	Total Delta TDR	Volume, cu.mm.	
		Interferometry	Dielectric Breakdown
51.1	304		0.0124
50.8	422		0.1264
50.7	419	0.041	0.0309
50.4	380		0.0197
47.2	365		0.0458
47.0	355	0.041	0.0194
42.8	299		0.0178
39.6	150	0.028	0.0129
37.9	257		0.0700
30.3	362		0.0930
27.2	299	0.016	0.0086
10.3	139		0.013
<10	255		0.0132
<10	244		0.0141

Table 2. Linear Correlation Coefficients from Comparisons of
Tube Deposit Evaluation Methods

Independent Variable		Dependent Variable	Correlation	Observations
Total Carbon		Dielectric Volume	0.929	56
Total Carbon		Optical Volume	0.971	14
Optical Volume		Dielectric Volume	0.970	14
Total	TDR	Total Carbon	0.561	62
Total	TDR	Dielectric Volume	0.473	56
Total	TDR	Optical Volume	0.707	14

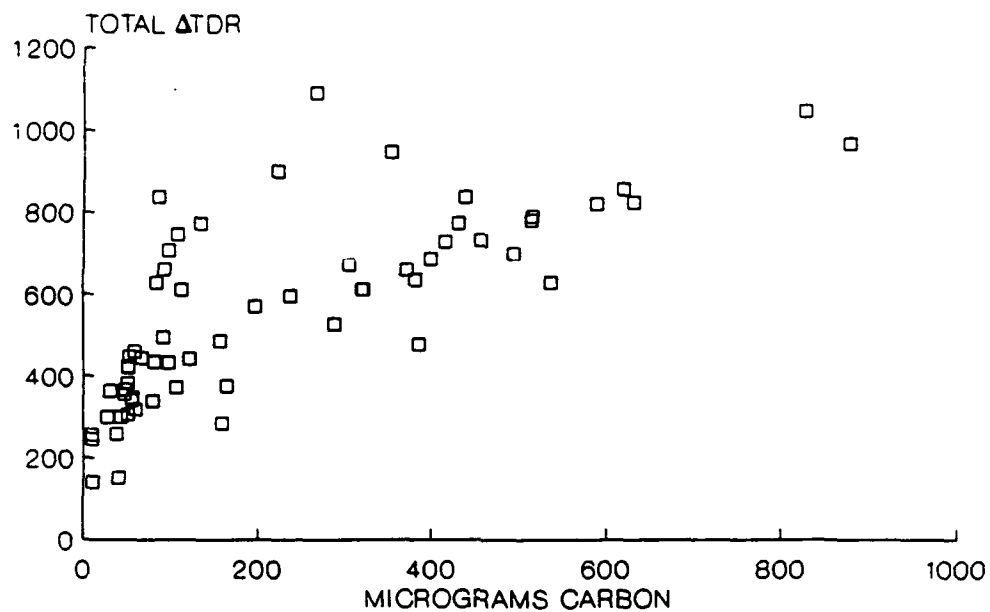


Figure 1. Relationship of TDR values to carbon content.

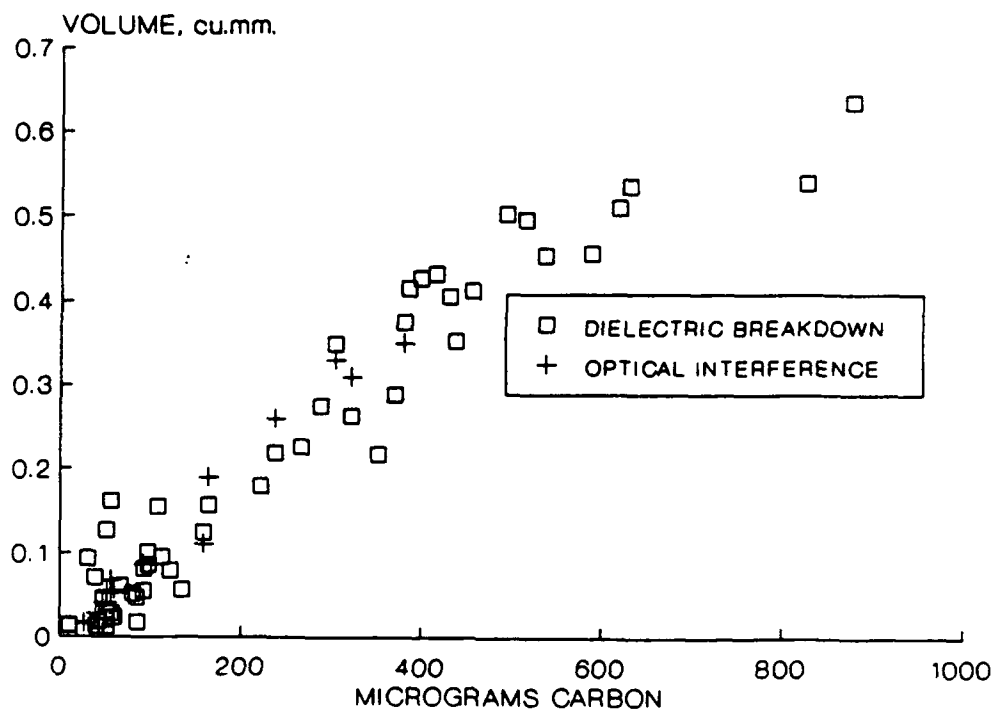


Figure 2. Relationships of deposit volume measurements to carbon content.

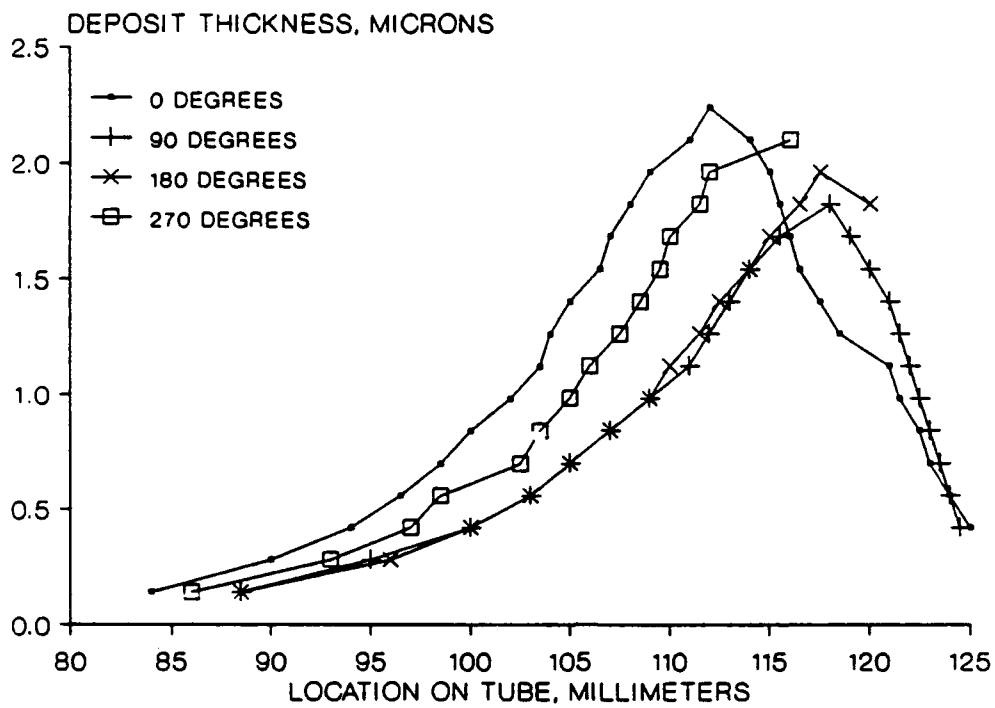


Figure 3. Deposit thickness measurements by interferometry along four sides of heater tube.

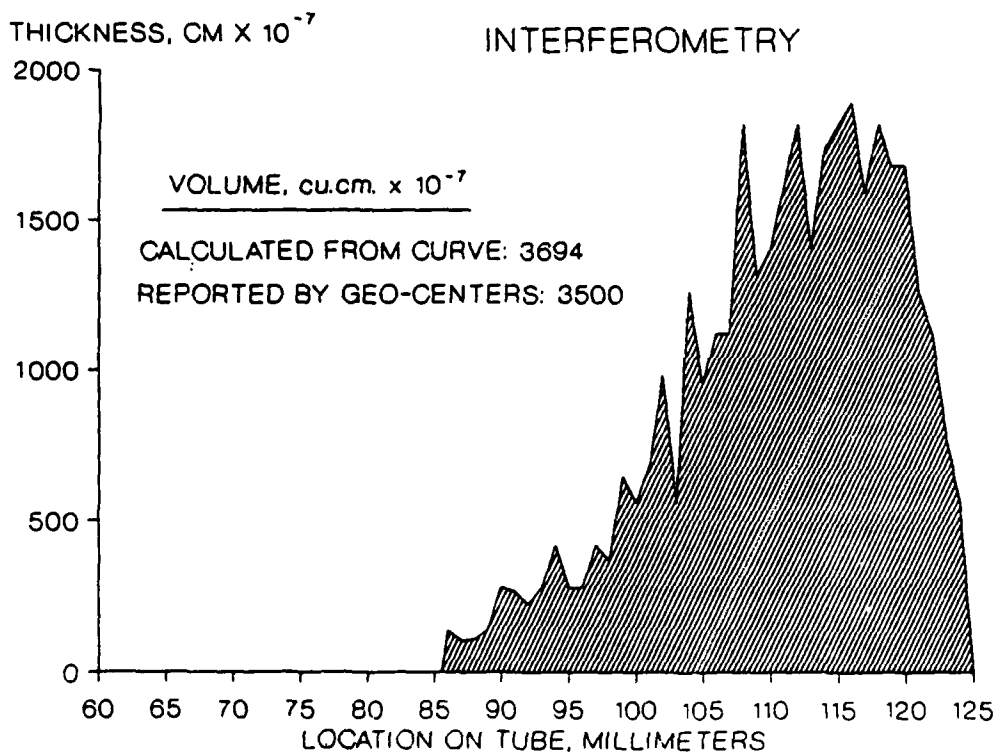
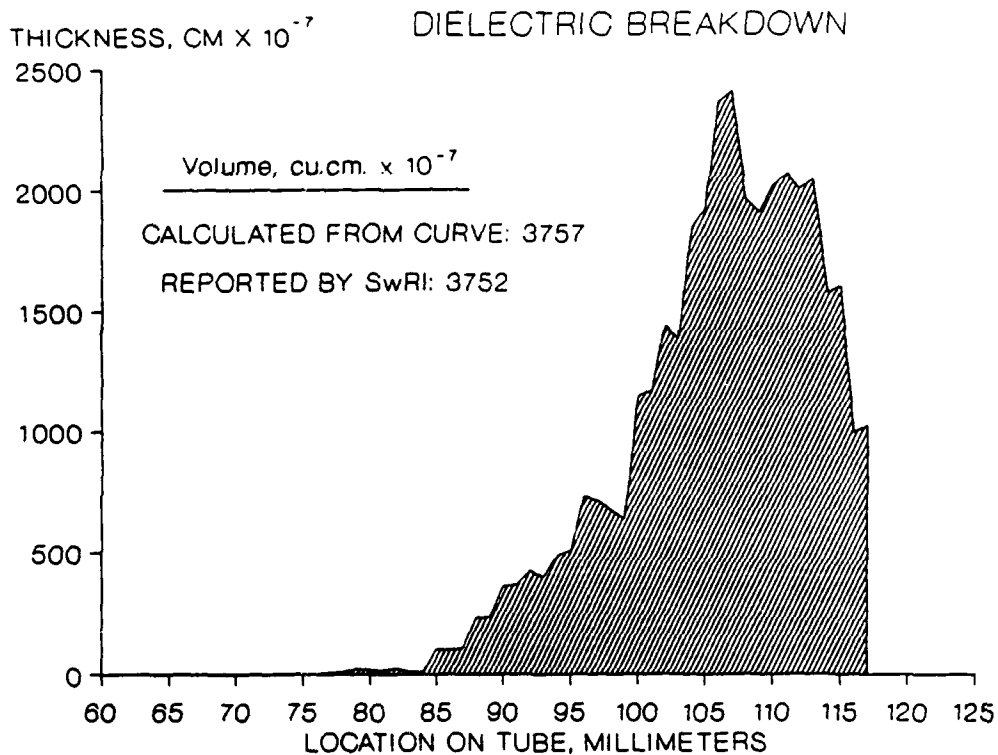


Figure 4. Deposit volumes obtained by integration of thickness profiles derived from cubic spline fitting.

3rd INTERNATIONAL CONFERENCE ON STABILITY
AND HANDLING OF LIQUID FUELS
London, UK
September 13-16, 1988

INFLUENCES EXERTED BY SELECTED STABILIZER ADDITIVES
ON THE THERMAL STABILITY OF JET FUEL

by

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ABSTRACT

The use of additives to improve the ambient storage stability of aviation fuels has created the need to characterize the influences exerted by these additives at the elevated temperatures of an aircraft fuel system. The behavior of several antioxidant compound types considered representative of those commonly used were examined during thermal stress in a modified JFTOT apparatus. The neat compounds 2,6-di-*t*-butyl-4-methylphenol and 2,4-di-isopropylphenylenediamine in addition to a tertiary amine, were blended into Jet A at 24 mg/L. A metal deactivator, N,N'-disalicylidine-1,2-diaminopropane was added at 5.8 mg/L as the pure compound and from a multifunctional additive package which contained both the metal deactivator and a tertiary amine, added at 24 mg/L. From experiments conducted with stainless steel heater tubes at temperatures from 200 to 310°C, measurements of heater tube deposits, particulate formation, oxygen consumption and peroxidation were obtained.

All the additives reduced the quantities of heater tube deposits formed at 260°C, compared to the neat fuel. At higher temperatures, the effects of the additives ranged from innocuous to deleterious, with the exception of the metal deactivator, which afforded substantial reductions in insoluble products at temperatures up to at least 310°C. The phenylenediamine was the most effective in reducing maximum peroxide concentrations, but this reduction was accompanied by increases in insoluble products.

INTRODUCTION

The combination of the increasing demand for aviation fuel and newer engine designs which place greater thermal stress on fuel has increased the interest in fuel stability. Both low temperature storage stability and high temperature thermal oxidation are of concern. Storage stability involves oxidation of fuel constituents to form hydroperoxides [1,2,3], which can attack elastomers in the fuel system. Hydroperoxides form more readily in fuels produced by hydrocracking or catalytic cracking followed by hydrotreatment. These refining techniques, while increasing the yield of jet fuel, probably remove natural inhibitors which limit hydroperoxides produced

through free radical autoxidation reactions [4]. It is known that hydroperoxides play a key role in thermal degradation processes of aviation fuels by initiating a variety of free-radical reactions [5].

Additives have been used or considered for addressing these stability problems. In this context, one of the aspects of additive behavior that is of concern is the effect of stabilizer additives on thermal stability. Previous examinations of additive behavior on fuel stability at elevated temperatures have produced a variety of results. In the Minex test [6], a metal deactivator suppressed insolubles while phenolic antioxidants did not. At 100°C and 100 psig of oxygen, reductions in insolubles and hydroperoxides were reported [7] in the presence of two different hindered phenols and a phenylenediamine, whereas these same antioxidants were ineffective in long-term storage at atmospheric pressure at 43°C. Mixed results were obtained with a metal deactivator, also depending on test conditions. Phenolic antioxidants have been used with varying degrees of success at storage temperatures ranging from 50 to 160°C, but they have been shown [8,9], to be more effective when added during the early months of storage. N,N-alkylated phenylenediamine antioxidants have been found [10] to be detrimental to stability during storage of hydrotreated jet fuel for six months at 50°C.

Thus, the evidence indicates that the behavior of an additive in stability tests is not only influenced by the age and composition of the fuel but also by the nature of the test employed.

EXPERIMENTAL

The test fuels were commercial Jet A fuels which conformed to ASTM Aviation Turbine Fuel Specification D1655-82 [11]. Selected fuel properties are given in Table 1. Fuel samples were thermally stressed with a JFTOT apparatus, which had been modified as described earlier [5] to provide for on-line sampling of the stressed fuel. Test samples (1100 mL) were prefiltered through two Gelman type A/E glass microfiber filters before introduction of the additive. All additives were used at 24 mg/L except the metal deactivator, which was added at 5.8 mg/L, unless stated otherwise. After blending in the additive, the test fuel was sparged with dry air for 15 minutes. Five-inch 304 stainless steel JFTOT heater tubes were employed during runs conducted for 300 minutes. To avoid excessively stressing the fuel in the event that the JFTOT test filter became plugged with filterable insolubles, fuel flow rates were maintained at or above 2.5 mL per minute by bypassing the test filter.

Total carbon contents of the heater tube deposits were measured by combustion to carbon dioxide with a Perkin Elmer model 240 elemental analyzer. After calibration of the analyzer with known compounds, blank carbon values were obtained from unused heater tube sections and subtracted from all deposit measurements.

Oxygen contents in samples of stressed fuel from the JFTOT apparatus were determined as described earlier [5]. Hydroperoxides were determined iodometrically in accordance with ASTM D3703 [12], with the exception that potentiometric detection was employed using a platinum ring electrode with an automatic titrator.

TABLE 1. PROPERTIES OF JET A TEST FUELS

Property	Fuel 8237	Fuel 8711	method
Acidity, total, mg KOH/g	<0.01	<0.01	D 663
Sulfur, mercaptan, wt. %	0.0009	0.0009	D 3227
Sulfur, total wt. %	0.0325	0.0399	D 2622
Aromatics, vol. %	16.6	18.8	D 1319
Distillation temp., °F (°C)			D 86
10% recovered, temp.	364 (184)	363 (184)	
50% recovered, temp.	424 (218)	412 (211)	
90% recovered, temp.	494 (257)	477 (247)	
Final boiling point, °F (°C)	529 (276)	507 (264)	
Distillation residue, %	1.5	2.0	
Distillation loss, %	1.5	0.5	
Gravity, °API (sp gr) at 60°F	41.9 (0.816)	43.7 (0.811)	D 1298
Thermal stability at 260°C			D 3241
Filter pressure drop, inches Hg	0	0	
Tube deposit rating	<2	<2	
Copper, PPM	<0.001	0.004	ICAP

RESULTS AND DISCUSSION

The effects of the additives in fuel 8237 on the amounts of heater tube deposits were determined from the quantities of total carbon found on each tube by combustion. The results from combustion analyses from replicate JFTOT experiments are shown in Fig. 1. When the averages of the total carbon from the two replicate heater tubes are compared, it is apparent that all the additives reduced the amounts of tube deposits at 260°C with respect to the neat fuel. As the stress temperature was increased, FOA-310 and metal deactivator (MDA) continued to reduce the amounts of heater tube deposits, while the effectiveness of the other additives diminished. FOA-310 contains an aliphatic tertiary amine in combination with the metal deactivator and FOA-3 contains the same amine as its major constituent. Therefore, the aliphatic tertiary amine in FOA-3 was not particularly effective in suppressing deposit formation but in combination with the metal deactivator in FOA-310, it did bring about significant reductions. This indicates that the effectiveness of the FOA-310 was attributable to the presence of the metal deactivator. In comparison with the neat fuel, the hindered phenol (ionol) was essentially innocuous. Thus, this antioxidant which has demonstrated inhibition of oxidation at low temperatures was not functioning as such in the temperature range used in these tests. The phenylenediamine (PDA) often increased the amounts of tube deposits at 270°C and above, as did FOA-3 at 270°C.

The measurements of hydroperoxide concentrations in JFTOT effluent, shown in Fig. 2, indicate that fuel 8237 had a low initial hydroperoxide concentration which increased as it was stressed up to a temperature of approximately 270°C. Above this temperature, it has been shown [5] that the hydroperoxides undergo thermal decomposition and their concentration decreases.

Although heater tube deposits were significantly reduced in the presence of FOA-310, levels of hydroperoxides found at temperatures above

260°C were similar to the neat fuel. When the two components of FOA-310 were tested separately, both the metal deactivator and the FOA-3 significantly reduced hydroperoxides from levels reached in the neat fuel. The tertiary amine, as a single functional additive in FOA-3, exhibited moderate activity except it was effective in reducing hydroperoxide concentration. This latter may result from the interaction of the hydroperoxide and FOA-3 to form an amine oxide. The phenylenediamine was the most effective additive in suppressing hydroperoxide accumulation, with a maximum peroxide number of only 0.3 meq/kg measured at 280°C.

Measurements of oxygen content in fuel stressed with JFTOT heater tube temperatures ranging from 21 to 310°C, (Table 2) revealed that oxygen consumption was generally in accordance with the observed peroxidation levels. For instance, ionol exerted little effect but PDA, FOA-310 and MDA reduced oxygen consumption. On the other hand, FOA-3 exhibited no reduction in oxygen usage in contrast to the reduction observed for hydroperoxide formation.

TABLE 2. OXYGEN CONSUMPTION BY FUEL 8237 DURING JFTOT STRESSING

Percent of Initial Oxygen Consumed						
Tube Temp., C.	Neat	IONOL	PDA	FOA-3	FOA-310	MDA
200	1.4	0	0	3.9	0	0
220	-	-	1.1	4.1	-	14.7
225	-	21.3	-	-	0	-
240	27.5	-	2.1	25.1	-	16.9
250	44.2	45.7	-	45.1	31.2	-
260	89.5	73.8	28.8	94.8	41.7	35.8
270	88.6	98.8	38.1	-	82.8	-
280	98.2	100.0	85.5	100.0	100.0	94.5
310	100.0	100.0	100.0	100.0	100.0	100.0

The formation of suspended particulates was monitored by measurement of the pressure differential developed across a standard JFTOT test filter. The metal deactivator and the FOA-310 were very effective in suppressing filterable insolubles. The effectiveness of the other additives to reduce filterable insolubles decreased with increasing temperature, in accordance with the other measured properties. At higher temperatures, the hindered phenol had no significant effect, while the FOA-3 tended to increase filterable insolubles somewhat. The most rapid filter plugging generally occurred in the presence of the phenylenediamine, in spite of reducing the rate of oxidation and limiting hydroperoxide formation. When such an increase in insolubles had been previously observed in the presence of phenylenediamines, [13], it had been attributed to thermal degradation of the PDA itself at 200-230°C. In this study, increases in tube deposits with the PDA did not occur until 310°C, whereas filterable insolubles increased dramatically above 270°C. This indicates that either the reaction of the PDA with a hydroperoxide is a prerequisite to the formation of filterable insolubles or, that thermal decomposition of the PDA below 310°C results in the formation of filterable insolubles.

The effectiveness of the MDA in reducing heater tube deposits in the JFTOT was consistent with the sensitivity of the JFTOT to metal deactivator

reported [14] with aluminum and stainless steel tubes. In order to define the relationship of MDA effectiveness to concentration, a series of JFTOT experiments were conducted with MDA concentrations ranging from 11.6 to 1.5 mg/L at 260, 280 and 310°C in fuel 8711. The reductions in tube deposit volumes were measured by the dielectric measuring device (DMD), which was applicable to the thicker coatings produced in these 5 hour experiments. It has been shown [15] that deposit volumes by DMD correlate well with total carbon by combustion and could be used to compare levels of tube deposition. The maximum effectiveness of the MDA to reduce deposits from fuel 8711 was attained after the addition of 1.5 mg MDA/L (Table 3) at 260° and slightly more at higher temperatures. Further additions of MDA provided no significant further reductions in tube deposits. Addition of the MDA to fuel 8711, which peroxidized to a maximum of 0.7 meq/kg at 280°C, afforded no significant reductions in accumulated hydroperoxides.

Additions of MDA to a 50% by volume blend of Jet A fuel 8711 with a Naval Distillate also produced a strong inhibitory effect on tube deposition, although slightly more MDA was required. The neat Jet A had low initial levels of peroxides but the initial hydroperoxide concentration in the blend was relatively high since the Naval Distillate had an initial peroxide number of 2.6 meq/kg. The effectiveness of the MDA in suppressing tube deposition was therefore not compromised by the presence of fuel peroxides. As with the neat Jet A fuel, the MDA afforded no significant reductions in hydroperoxides of the blend under the various stress tests.

TABLE 3. QUANTIFICATION OF HEATER TUBE DEPOSITS BY DMD MEASUREMENTS

MDA, Addition mg/L	Deposit Volume, cu.cm. x 10 ⁻⁷			%Reduction in Volume by MDA		
	260°C	280°C	310°C	260°C	280°C	310°C
<u>8711 Jet A</u>						
0	1006	2883	5107			
1.5	124	607	1541	87.7	78.9	69.8
2.9	141	1264	855	86.0	56.2	83.3
5.8	132	511	942	86.9	82.3	81.6
11.6	130	458	805	87.1	84.1	84.2
<u>8711 Jet A + 50% ND</u>						
0	1452	1743				
0.5	978	1509			32.6	13.4
1.5		888				49.1
2.9	318	568			78.1	67.4
5.8	365	505			74.9	71.0
11.6	388	621			73.3	64.4

CONCLUSIONS

An overall summary of additive influences on the measured properties of fuels stressed in the JFTOT is given in Table 4. A very significant

reduction (70-85%) in deposits was realized when the metal deactivator was present, either alone or in combination with a tertiary aliphatic amine antioxidant in FOA-310. All the additives exhibited inhibitory effects on insolubles formation and peroxides at lower temperatures, but only those with the metal deactivator remained effective as the temperature increased. The mechanism by which the metal deactivator functions effectively at elevated temperatures is not clear at this time. However, the similar behavior of MDA in fuels with different peroxide levels suggests that one mechanism by which it acts involves the heterogeneous interactions between the fuel and the metal surface of the heater tube rather than as an antagonist for oxidation reactions. However, it would seem that this advantage would be lost as the tube surface becomes coated with an organic deposit and further benefits could then be a result of reactions of the MDA with the fuel and fuel-soluble constituents. Since the copper contents of the jet fuels was very low, complexation of soluble copper was not responsible for the effectiveness of the MDA. The determination of the copper content of the Naval Distillate has yet to be completed, so that copper deactivation cannot be ruled out for the blended fuel.

The tertiary aliphatic amine, FOA-3, was not effective in reducing insolubles at high temperatures, although peroxide levels were suppressed throughout. The phenylenediamine was very effective in reducing peroxidation, but this reduction was accompanied by significant increases in insolubles. The findings do not allow for any distinction to be made as to whether the insolubles were due to thermal decomposition of the phenylenediamine itself or PDA reaction products.

TABLE 4. SUMMARY OF ADDITIVE EFFECTS ON FUEL PROPERTIES AFTER JFTOT STRESSING

Additive	Heater Tube Deposits	Filterable Insolubles	Peroxidation	Oxygen Consumption
IONOL	o	o	o	o
PDA	+	++	—	—
FOA-3	-	+	-	o
FOA-310	—	—	o	-
MDA	—	—	-	-

o: no or minimal effect, +/-: significant increase/decrease, ++/--: large increase/decrease

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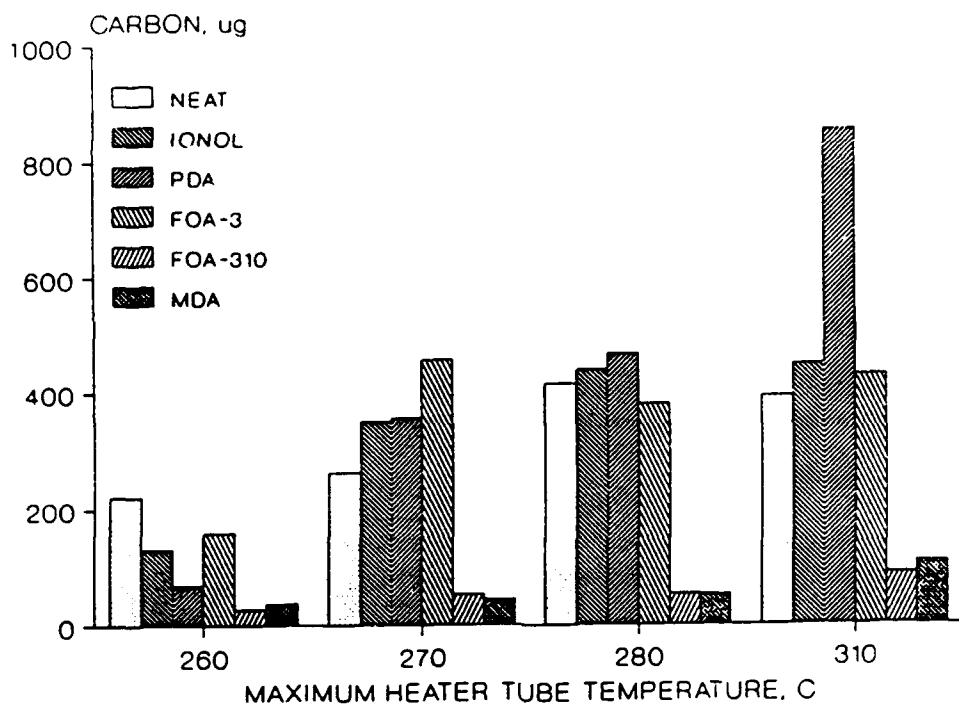


Figure 1. Influences of additives on JFTOT heater tube deposits expressed as total carbon.

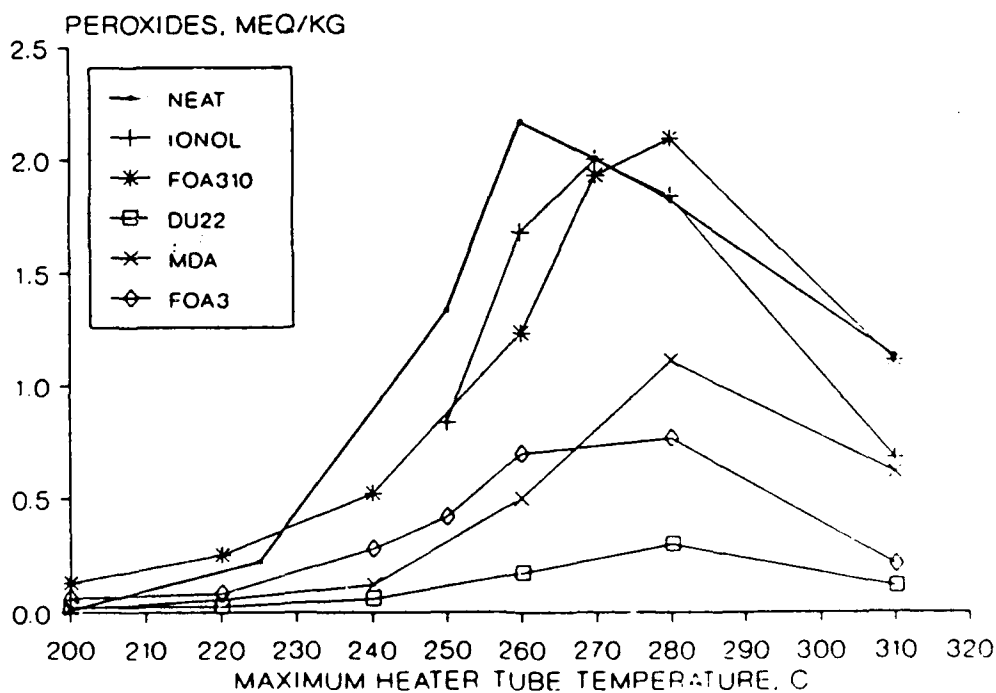


Figure 2. Peroxide concentrations reached in the JFTOT after stressing Jet A fuel 8237 containing stabilizer additives.

THE INTERACTION OF A METAL DEACTIVATOR WITH METAL SURFACES

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Keywords: metal deactivator, thermal stability, JFTOT

INTRODUCTION

In modern aircraft fuel systems, the fuel is used as a heat transfer medium to dissipate heat from the avionics and hydraulic systems. Under these conditions, the fuel can undergo autoxidation. Autoxidation of jet fuel can result in the formation of insoluble gum and sediment which can impair operation of the jet engine. In addition, hydroperoxides which form during autoxidation have been known to attack certain elastomeric fuel system components. Thus, the thermal oxidation stability of the fuel becomes an important consideration. Trace quantities of certain transition metals will catalyze fuel autoxidation. Dissolved copper has been shown to be the most reactive (Pederson, 1949; Smith, 1967). Copper contamination of fuels can and does occur, particularly in shipboard fuel handling systems from contact with copper lines, brass fittings, admiralty metal, and other copper bearing alloys.

Metal deactivator additives (MDA) were developed to counteract the catalytic activity of dissolved metals. These additives (N,N'-disalicylidene-1,2-propanediamine and N,N'-disalicylidene-1,2-cyclohexanediamine) can act as polydentate ligands for copper (Pederson, 1949). Chelate complexes derived from similar hydroxyaromatic Schiff bases are known to be thermally stable (Harvel, et al., 1956). The military specification, MIL-T-5624, allows for the addition of up to 5.8 mg MDA per liter in JP-4 and JP-5, while the ASTM specification for aviation turbine fuels, D1655-85a, (Annual Book of ASTM Standards, 1987) allows up to 5.7 mg per liter.

Laboratory scale tests, such as the Jet Fuel Thermal Oxidation Tester (JFTOT), have been relied upon to evaluate the thermal oxidation stability of aviation fuels. In the ASTM Method for assessing thermal oxidation stability of aviation fuels (Annual Book of ASTM Standards, 1988), the fuel is passed once over the outside of a resistively heated aluminum tube (the heater tube) at a flow rate of approximately three ml/min. In previous work (Morris, et al., 1988; Morris and Turner, in press), we have observed that the addition of a metal deactivator resulted in significant reductions in deposits on 304 stainless steel JFTOT heater tubes from 280 to 310°C.

In tests conducted with an injector feed-arm simulator, metal deactivator reduced deposit formation in two fuels by two and fourteen fold respectively onto clean steel surfaces (Kendall and Earls, 1985). However, after an induction period,

rapid deposition ensued at a rate similar to that observed in the absence of MDA. From this it was concluded that MDA passivated the clean steel surface *couple* thermal deposits, but was ineffective once the surface became coated with an organic deposit (Kendall, et al., 1987). The effectiveness of MDA in JFTOT testing of metal-free hydrotreated fuels was also attributed to passivation of the clean metal surface of the JFTOT heater tube (Clark, 1988).

The strong influence exerted by MDA in JFTOT testing has raised questions about the applicability of the method for ranking fuels with respect to thermal oxidation stability in the presence of metal deactivators. If MDA produces a disproportionately strong inhibition of deposition in the JFTOT, then fuels ranked stable may form insolubles during use. We have thus directed our efforts at ascertaining the various mechanisms by which MDA can act, particularly in accelerated stability testing. One objective of this study was to determine to what extent interactions with metal surfaces of the test apparatus govern the effectiveness of metal deactivators. This paper describes an examination of metal surfaces exposed to MDA solutions to determine under what, if any, conditions metal passivation can occur.

EXPERIMENTAL

X-ray photoelectron spectroscopy (XPS) was used to determine the presence of a continuous layer of MDA on metal surfaces. Analyses were performed using a Surface Science Instruments SSX-100-03 X-ray Photoelectron Spectrometer. Quantitative estimates of the surface composition were obtained using the analysis program supplied with the spectrometer. The base pressure was at least 2×10^{-8} torr for all samples analyzed. Fourier transform infrared spectroscopy (FTIR) was performed with a Digilab FTS-15/90 Fourier transform infrared spectrometer. Secondary ion mass spectroscopy (SIMS) was performed in a static mode with a time of flight instrument constructed at the Naval Research Laboratory (Hues, et al., 1988). A pulsed alkali ion gun with a thermalionic emitting source was used which produced 2-5 ns pulses of 13.0 keV cesium ions, resulting in an impact energy of 8.0 keV for positive ions.

In order to minimize the risk of surface contamination from trace impurities in a fuel, a model fuel consisting of n-dodecane (Phillips 66, Pure grade, 99 mol% min.) was used. XPS analyses were conducted on flat metal coupons exposed to the model fuel and the model fuel containing MDA, N,N'-Disalicylidene-1,2-propylene-diamine (MDA) was obtained from Pfaltz and Bauer and dissolved into the dodecane to obtain a final concentration of 5.8 mg/l. MDA-copper complex was prepared by combining equimolar quantities of MDA and copper(II) ethylacetate in dodecane.

Coupons measuring 2.5 cm $\times$ 1.2 cm consisting of copper, 6061 aluminum and 304 stainless steel were used as substrates. All surfaces were ground to 4000 grit using silicon carbide paper with triply distilled water as the lubricant. Coupon samples used for (FTIR) were further polished with 0.05 micron alumina. The stainless steel samples examined by SIMS were 1 cm $\times$ 1 cm and were prepared as described above. After polishing, the coupons were rinsed with triply distilled water and allowed to air dry in acid cleaned glassware. Samples were immersed in either pure dodecane or dodecane containing MDA at room temperature for two and one half hours. Afterwards the samples were withdrawn from this solution and rinsed with HPLC grade n-heptane, covered with aluminum foil and analyzed

within an hour. Samples that were analyzed by SIMS and FTIR were also rinsed with low residue toluene (Baker).

Stainless steel and aluminum JFTOT heater tubes were also examined by XPS. JFTOT annealing was carried out with dodecane and solutions of MDA at 5.8 mg/l in dodecane at 240°C and 310°C for one hour. The tubes were washed with hexane immediately after a JFTOT experiment.

RESULTS AND DISCUSSION

XPS signal intensity ratios for carbon, nitrogen and oxygen cannot be utilized as a quantitative measure of the amounts of MDA on the surface and can only be used as a qualitative indication of the presence of MDA. Almost any surface that has been exposed to air will have adsorbed oxygen and carbon. It was thus necessary to rely on the intensity of the nitrogen signal alone as the most reliable indication of the presence of MDA on the surface since it is unique to that compound and is not present in the pure dodecane.

An XPS survey scan of the copper-MDA complex demonstrated that the surface binding energies were similar to those reported for a copper-Schiff base analog of MDA (Dillard, et al., 1974). It is clear from analysis of the observed peaks that all the expected elements are present. The nitrogen peak was quite intense relative to both the carbon and oxygen peaks. Although nothing definitive can be said from the spectrum about the relative atomic concentrations, the relative intensities of the carbon, nitrogen and oxygen peaks should give a reasonable indication of the expected intensity ratios for this chelate if it were present as a very thick film. Analysis of signal intensities from high resolution scans of these peaks allowed an estimation of the atomic concentration of the elements present. The calculated copper concentration was a factor of two higher than expected, while the atomic ratios of the other elements were what were expected. Although the exact reason for this discrepancy is not understood, the relative intensities of the peaks should provide a reasonable indication of the amount of MDA present on an uncontaminated surface.

Copper coupons: While it is not practical to attempt to remove all copper-bearing components from shipboard fuel delivery systems, MDA may play a role in inhibiting the dissolution of copper into the fuel. For this reason it was felt that MDA adsorption onto copper surfaces should be studied to provide an insight into the role it may play, if any, in passivating the exposed copper parts. Prepared copper coupons were exposed to dodecane and dodecane containing MDA at 5.8 mg/l for 2.5 hours. The strips were then removed and rinsed with heptane (HPLC grade), mounted onto the XPS carousel and introduced into the vacuum system within two hours using a quick insertion system that is part of the apparatus. The XPS survey scan from the freshly cleaned copper surface, which was mounted as soon as it was air dried, had weak carbon and oxygen peaks and strong copper peaks, indicating that the sample preparation procedure used produced an acceptably clean surface. Exposure to the MDA solution had clearly increased the amount of carbon on the surface but no nitrogen was observed in the broad scan. This indicated that at most there could only be a very thin film of the MDA on this surface. Otherwise, the nitrogen intensity would be comparable with that found in the complex above. High resolution scans of the peaks for each element were obtained and the composition of the surface was estimated. The results of this are shown in Table I for the freshly polished

surface and after exposure to MDA. The carbon and oxygen levels, although still quite high, are small compared with those found from any other cleaning procedures that were tried. As expected, the calculated carbon contents on the surfaces that were exposed to the organic solutions were higher than on the freshly cleaned surfaces. In addition, the quantities of carbon were about the same for the surfaces of both the sample exposed to pure dodecane and to MDA. Nitrogen levels were at or below the detection limit of 1-2 atomic percent. The lack of any nitrogen signal suggests that the formation of an MDA coating on the copper surface was not occurring, since XPS can easily resolve monolayer thicknesses.

Examination of the copper surface by FTIR revealed the presence of an organic acid on all samples exposed to the dodecane. The magnitudes of the C-H and C=O stretches that characterized the surface adsorbed acids were influenced by the MDA concentration. This may indicate some interactive effects between acids adsorbed on metal surfaces and the MDA.

Stainless steel coupons: The results from the XPS examination of 304 stainless steel coupons exposed to dodecane and dodecane containing 5.8 mg MDA/l for 2.5 hours at room temperature are shown in Table I. Higher levels of oxygen were found on the freshly cleaned stainless steel surface than on the copper surface, presumably because of the presence of metal oxides. Nitrogen content was at or below the limit of detection. FTIR analysis of stainless steel strips exposed to dodecane again revealed the presence of a carboxylic acid on the surface, from strong C-H and C=O absorptions. No changes in surface acid concentration were evident, nor was MDA detected on surfaces exposed to dodecane containing 5.8 mg MDA/l. Treatment of the dodecane with silica gel before use was sufficient to eliminate the presence of adsorbed carboxylic acids on the metal surfaces. The presence of a few parts per million of dodecanoic acid was confirmed by HPLC analysis of the base-extractable component of the dodecane. Thus, the acid adsorbed on the metal surface was most likely dodecanoic acid, derived from autooxidation of the dodecane.

In an effort to gain a more sensitive measure of the presence of MDA on the surface, SIMS analysis was performed on a stainless steel surface which had been exposed to neat dodecane and a dodecane solution of 5.8 mg MDA/l for 2 hours at room temperature. The positive secondary ions thus formed showed that indeed some MDA was present on the surface, while none was detected on the neat dodecane exposed blank. Since the surface had been rinsed with toluene, it is assumed that the MDA present was tightly bound to the surface. However, a more intense signal was obtained at 52 Daltons higher than the MDA peaks, suggesting that most of the MDA was bound to chromium. These findings demonstrate that after exposure of 304 stainless steel to a solution of MDA at room temperature, some MDA will be bound to the surface, predominantly at chromium sites. However, the coating is far from complete and would not significantly alter the surface reactivity towards deposition.

Stainless steel JFTOT heater tubes: While 6061 aluminum is the material most commonly used in the construction of JFTOT heater tubes, 304 stainless steel is often employed in research efforts involving the JFTOT apparatus. Furthermore, many fuel system components are constructed from stainless steel. XPS analyses were performed on selected areas of stainless steel JFTOT heater tubes used to stress samples of dodecane with and without 5.8 mg MDA/l in the JFTOT apparatus for one hour. Nitrogen on heater tubes heated at 260°C was near the detection

limit. The metal contents (i.e., Fe, Cr, Mn, etc.) on the tube surfaces were very low (Table II). Chromium levels were at or below the detection limit of 1 atomic percent, compared to a nominal level of 18% in the base metal. This indicates multilayer deposit formation was taking place regardless of whether MDA was present or not. At 310°C in the presence of MDA, similar results were obtained except that the carbon levels were higher. These findings demonstrate that within one hour of JFTOT testing, it is possible to produce multilayer coatings of carbonaceous thermal oxidation products on the stainless steel JFTOT heater tube surface from a relatively unreactive "fuel", i.e., dodecane.

Aluminum JFTOT heater tubes: XPS examinations of 6061 aluminum JFTOT heater tubes tested at 260°C for one hour in dodecane and dodecane with 5.8 mg MDA/l revealed that, in both cases, carbon levels were lower than on the stainless steel tube surfaces (Table III). There was no evidence of multilayer structure of thermally degraded dodecane over the full length of the tube. This substantiates earlier reports that while the liquid-phase chemistry is identical for both tube materials (Hazlett, et al., 1977), heavier deposits tend to form on stainless steel heater tubes (Faith, et al., 1971; Kendall, et al., 1987). Nitrogen was at or below the detection limit in both cases, however, slightly more nitrogen was evident on tubes heated in the MDA solution.

CONCLUSIONS

Surface analyses of copper, aluminum and stainless steel exposed to MDA in static solutions and in JFTOT testing, point towards a different mechanism than what would be expected if the surface were deactivated towards deposition by a contiguous layer of MDA. While these findings suggest that the surface contains some MDA, it is sparsely distributed. In addition, there may be some interactive effects between MDA and surface bound carboxylic acids. On stainless steel, it appears that the MDA is predominantly bound to chromium sites on the surface but this coating is also a fraction of a monolayer and thus would not significantly change the surface activity. There was no evidence that MDA was coating a pure copper surface.

In the JFTOT, there was more deposition onto the 304 stainless steel tubes than on the 6061 aluminum. If surface passivation was responsible for the strong response of the JFTOT to the presence of MDA, then one would expect to observe at least a monolayer of MDA on the tube surface over the entire test duration of two and one half hours. However, in this study, multilayer thermal oxidation deposits were produced on 304 stainless steel JFTOT tubes after only one hour of JFTOT testing at the specification test temperature, 260°C. Therefore, the time required for monolayer deposition of thermal oxidation products onto stainless steel heater tubes during JFTOT testing was well within the limits of the test.

While it does not seem likely that surface passivation is occurring in the JFTOT, there is still no doubt that MDA exerts a powerful inhibiting influence on thermal deposition and the question of validity of the JFTOT results in the presence of MDA remains to be answered. Measurements of oxidation of JFTOT effluent have shown inhibition by MDA in some cases and none in others. This suggests the possibility that the effects exerted by MDA in the JFTOT may be a consequence of interactions in the liquid-phase.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. Stephen M. Hues of the Naval Research Laboratory, Chemistry Division, Code 6170 for conducting the SIMS analyses and Mr. Bruce Black of Geo-Centers, Inc. for the determination of acid in the dodecane. This work was funded by the Office of Naval Research and the Naval Air Propulsion Center.

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Table I. Composition of Films Formed on Polished Flat Coupons Exposed to Dodecane and 5.8mg MDA/l Dodecane in Atomic Percent

Condition	Copper			Cu		
	C	O	Fe	C	O	Fe
Freshly Polished	39	27	35			
Dodecane, 2.5 hrs	63	23	12			
MDA/dodecane, 2.5 hrs	54	28	18			

304 Stainless Steel

Condition	C	O	Fe
Freshly Polished	21	58	14
Dodecane, 2.5 hrs	46	37	8
MDA/Dodecane, 2.5 hrs	35	49	11

Table II. Composition of Films Formed on Stainless Steel JFTOT Tubes in Atomic Percent after Stressing for 1 Hour

Temp. (°C)	Dodecane, 260°C			Fe		
	C	O	Al	C	O	Al
174-208	57	38	3			
208-238	41	49	7			
238-257	52	40	5			
257-260	78	20	1			
5.8 mg MDA/l in Dodecane, 260°C						
174-208	56	38	2			
208-238	43	46	4			
238-257	48	42	4			
257-260	82	18	0			
5.8 mg MDA/l in Dodecane, 310°C						
212-253	40	45	11			
253-287	56	38	4			
287-305	82	14	0			
305-310	93	6	0			

Table III. Composition of Films Formed on Aluminum JFTOT Tubes in Atomic Percent after Stressing for 1 Hour

Temp. (°C)	Dodecane, 260°C			Al		
	C	O	Al	C	O	Al
141-193	31	47	20			
193-232	29	47	21			
232-256	32	46	18			
256-260	28	48	19			
5.8 mg MDA/l in Dodecane, 260°C						
141-193	31	45	19			
193-232	33	43	18			
232-256	34	43	19			
256-260	44	36	17			

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EVALUATION OF COMMERCIAL STABILITY ADDITIVES FOR NAVAL DISTILLATE FUEL

By

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ABSTRACT

This paper summarizes the effectiveness of nine commercial stabilizer additives in nine freshly refined fuels tested under a wide variety of test conditions. The tests included bottle tests between 43 and 80°C, ASTM D2274 and oxygen overpressure tests between 43 and 90°C. In addition to these gravimetric tests, some evaluation of additive effectiveness by a light scattering technique were made. This work emphasized the usefulness of additives added within 24 hours of fuel production. The control fuels exhibited a wide range of storage instability and were selected from U.S. refineries utilizing a wide range of crude sources and processing. The fuels contained a range of catalytically cracked stock from less than 10 percent up to 40 percent.

The results of the accelerated storage stability tests will be discussed. Taken as a whole, it is possible to identify several of the commercial additives as routinely effective and the bulk of the remainder as being innocuous at the concentration range studied in this work (24 to 50 mg/liter). In addition to the additives' effect on storage stability,

their effects on other selected fuel properties will also be discussed.

INTRODUCTION

Naval distillate fuel (MIL-F-16884H; NATO F-76) is frequently stored for several years in strategic reserves. Over these extended periods of time, fuels tend to degrade forming insoluble products. Stability is a measure of a fuel's resistance to the formation of insoluble material. These fuel degradation products can plug fuel system filters and engine nozzles. Naval distillate fuel stability, with respect to fuel purchases is measured by an ASTM accelerated storage test, D2274, which stresses the sample at 95°C for 16 hr with bubbling oxygen. The maximum amount of insolubles allowed by D2274 in MIL-F-16884H is 1.5 mg/100 ml [1]. With freshly refined fuels containing catalytically cracked light cycle oil (LCO) stocks above 10% v/v, this test frequently assesses potentially unstable fuels as quite stable.

Strategic storage stability of F-76 has been of modest concern for fuels refined by straight run distillation. However, increasing quantities of crudes are being produced in refineries using catalytic cracking processes to increase the yield of middle distillate fuels. The cracked products are blended into straight run streams. The unstable components, although diluted by the blending, still exert a strong influence on instability behavior, particularly for long storage periods.

One approach to long term storage problems of this nature is to monitor fuel quality and to adopt remedial action as necessary. Such action might involve immediate use of deteriorating stock or stabilizing the product with a suitable additive. The latter course is normally the preferred choice providing additives with adequate performance are at hand.

Additive manufacturers have indicated that immediate addition of stabilizer additives (less than 24 hours after production of the fuel) ensures the best protection against insolubles formation in any given fuel. This paper builds on previous work assessing the usefulness of five commercial stability additives in four aged diesel stocks of varying degrees of instability [2]. This study concluded that several of the commercial additives offered a significant improvement in oxidation stability of the aged fuels and recommended a program of evaluating more commercial additives in freshly refined fuels.

In order to properly evaluate the efficacy of the additive, several freshly refined fuels were used. This is necessary because additives do not behave the same in all fuels [3]. This paper contains storage stability and fuel characterization data for several different sets of fuel blends containing LCO stocks. These studies show that two additives delayed degradation in the majority of fuels studied and did not cause any statistically significant degradation. When they were ranked in comparison with the other additives, they were consistently among the most

effective. Neither of them caused a fuel to go outside the tolerances allowed by Military Specification MIL-F-16884H. Therefore, they could be expected to be reliably beneficial when used in Naval Distillate fuels.

EXPERIMENTAL

Additives

Nine different additive manufacturers provided additives that were used in the test fuels. The amount of active ingredient (percent of actual antioxidant) in these additive packages varied from 15 to 100%; most contained 70% or greater active ingredient.

The additives were solicited from the commercial sector and are coded in Table 1. A generic chemical description provided by the manufacturers is given and six of the nine additives contain strong organic bases (secondary or tertiary amines). These were blended into the test fuels at the refinery usually within 24 hours of fuel production and blending. Details of this procedure are available [3].

Fuels

Five of the nine fuel blends are shown in Table 2 which codes the fuels and gives their physical/chemical properties. All of the fuels shown contain 30% v/v catalytically cracked LCO in a straight run (SR) distillate (70% v/v). Most MIL specification requirements are thereby met except cetane number/index. The relatively high proportion of cracked stock was both an attempt to simulate possible worst case future fuels and an attempt to simulate a wide range of storage instabilities to effectively test the stability additives. The resultant fuel stabilities are given in Table 3 which indicates for five fuels that the desired range of relative instabilities was achieved.

Accelerated Storage Stability Tests

ASTM D2274 test procedure at 95 degrees C was followed exactly. Adherent gums were determined by evaporating the solvent on a hot plate in place of the D381 steam jet gum method.

Bottle tests at 43, 65 and 80°C used a modification of a method described by Cooney et al [4]. Test fuels were prefiltered through double glass fiber filters (Gelman, Type A/E 47 mm) contained in a Buchner funnel. Triplicate fuel samples (300 ml each) were dispensed into tared 500 ml amber borosilicate bottles with teflon lined caps. Fuels samples were then stored in ovens at 43°C for 18 weeks, 65°C for 8 weeks, or 80°C for 2 weeks. During accelerated storage, the bottles were loosely capped to provide venting. After storage, stressed fuel samples were filtered through tared Buchner funnels containing a glass fiber filter. Bottles and filtered sediment contained in funnels were rinsed with three 50 ml portions of hexanes. Bottles and funnels were dried overnight at 120°C in a vacuum oven, cooled, removed, then weighed to the nearest 0.1 mg. Two weight measurements (filtered sediment and insoluble adherent gum) were obtained and corrected for blanks and summed to give a total weight of insolubles. An alternative procedure to determine adherent gums consisted of dissolving the gums in 1:1:1 methanol:acetone:toluene and

gently evaporating the solvent to dryness in a tared beaker or aluminum weighing dish on a hot plate. No significant differences in total insolubles by either method was noted.

Tests at 90°C were run by a new oxygen overpressure method in which 100 ml samples of filtered fuel in 125 ml borosilicate bottles were placed in a low pressure reactor (LPR). The reactor was sealed and pressurized with 99.5% pure oxygen to 700kPa (100 psig). The samples were stressed, under pressure, for 16 hrs at 90°C. At the end of the stress period, the pressure was released slowly and the samples were removed and cooled. The amount of filterable sediment and adherent gum were determined gravimetrically and reported as total insoluble sediment weight. Samples were run in triplicate and the average values are given in mg/100ml [5].

Fuel Physical Property Characterization

Military specifications require that the fuel used as NDF meet certain bulk property requirements. Therefore, the control fuels used in these studies were analyzed for all of the specified properties and results are reported elsewhere [3,6,7].

Because an additive could have an effect on certain key properties such as demulsibility, copper corrosion and flash point, additive blends at 24 ppm were subjected to these tests. Details are reported elsewhere [3,6,7] but general conclusions are discussed in the next section.

RESULTS AND DISCUSSION

None of the additives had any significant effect on fuel acid number, ash, copper corrosion, flash point or carbon residue at the 24 ppm level. Additives 4, 5 and 7, however, failed to meet salt water demulsibility test specifications.

Typical gravimetric results are shown in Tables 4 and 5 for two unstable fuels. Neat denotes the additive-free fuel blend. The additives are ranked by insolubles formation by the lowest temperature test (43°C). Table 4 indicates that in a very unstable fuel all of the additives at 50 ppm exhibited some beneficial effect at both 43 and 65°C. Five of the nine are generally assessed to be quite a bit more effective. The failure of D2274, the current US Navy MIL specification test to correctly assess this unstable fuel is typical [3]. The test correctly assessed the stability of only two of the nine test fuel blends. Furthermore, the test is not at all useful in assessing the relative effectiveness of the nine additives. When test times are considerably extended (to about 40 hours), this test exhibits good correlation to lower temperature results and also is useful in evaluating the relative effectiveness of additives.

Table 5 shows typical results for a slightly unstable fuel. In general, fewer of the additives show an improving effect at all test temperatures. The usefulness of a high temperature oxygen overpressure test (100 psig oxygen) at short times is clearly demonstrated. The low pressure reactor (LPR) test assessed the additive-free fuel correctly in

addition to evaluating the additives when compared with the lower temperature tests. Additives 4 and 7 are noteworthy exceptions, indicating the need to possibly extend LPR test times to exceed reaction induction times.

CONCLUSIONS

The overall summary of results is listed in Table 6. Table 6 shows the number of times each additive made a statistically significant change in fuel quality. These changes met the 95% confidence level in the Student-T test. Each additive was subjected to 26 fuel/test method trials. The importance of Table 6 is not in the individual lines of data but in the continuing trends. Additives 2 and 3 continue to delay degradation in the majority of test fuels, while remaining innocuous in fuels they do not improve. All other additives caused fuel to degrade in at least one test. Obviously, this table does not account for the fact that some test methods are more accurate than others, and that some of the fuels are better for testing additives than others. However, it does give an indication of the overall efficacy of an additive in typical Naval distillate fuels.

One factor neglected in Table 6 is the extent of solids reduction of one additive when compared with another. A slight decrease in sediment which is statistically significant is given the same weight as a major decrease. Therefore, Table 7 lists the number of times an additive is included in the top three in reducing sediment. This table shows that samples 2 and 3 are most often among those reducing sediment to the greatest extent. For these reasons it is possible to recommend either mandatory or optional use of these two commercial additives in US Naval distillate (NATO F-76) fuels at concentrations of about 50 ppm. In general, significant increases in fuel storage stability should result from the use of these amine type additives.

The ASTM D2274 storage stability test has traditionally been an acceptable method for predicting the quality of distillate fuels. However, it does not appear to be accurate in differentiating the quality of additive-free fuels containing LCO stocks above 10 or 15% v/v. The test was even less useful in evaluating the usefulness of the stability additives in this study.

Finally it is important to note that a new storage stability test involving oxygen overpressure, the LPR, is also potentially very useful in quickly and accurately evaluating stability additives for use in mid distillate diesel fuels.

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Table 1

DESCRIPTION OF TEST ADDITIVES (STORAGE STABILIZERS)

ADDITIVE CODE	% ACTIVE INGREDIENT	CHEMICAL DESCRIPTION
1	70	UNKNOWN
2	100	TERTIARY AMINE
3	80	AMINE (PROPRIETARY)
4	70	AMINE + DISPERSANT + CORROSION INHIBITOR
5	15	TERTIARY AMINE + METAL DEACTIVATOR + DISPERSANT
6	82	SECONDARY AMINE + METAL DEACTIVATOR
7	46	UNKNOWN + DISPERSANT + CORROSION INHIBITOR
8	50	UNKNOWN
9	70	SECONDARY AMINE

Table 2

SPECIFICATION TEST FOR SOME REPRESENTATIVE TEST FUELS

TEST	UNITS	REQUIREMENT	GULF COAST FUEL (2143)	WEST COAST SINGLE CRUDE (2225)	WEST COAST MIXED CRUDE (2246)	MIDCONTINENT FUEL (2422)	LOUISIANA FUEL (3006)
ACID NUMBER	mg KOH/g	0.30 MAX	0.05	0.06	0.28	0.02	0.20
CETANE INDEX, D976	—	46 MIN	46.2	42.7	45.4	41.3	38.8
D86 DISTILLATION							
IBP	°C	—	198	223	208	187	207
10%	°C	RECORD	228	252	246	207	232
50%	°C	RECORD	265	285	274	232	277
90%	°C	357 MAX	317	325	305	290	311
END POINT	°C	385 MAX	345	345	324	339	348
RESIDUE	PCT	3.0 MAX	1.2	1.4	1.3	0.9	0.2
SPECIFIC GRAVITY	—	RECORD	0.8521	0.8873	0.8660	0.8407	0.8850
SULFUR	WT PCT	1.00 MAX	0.3	0.8	0.2	0.2	0.5
VISCOSITY AT 40°C	CST	1.7-4.3	2.8	3.5	2.8	2.0	2.8

Table 3

CONTROL (ADDITIVE-FREE) FUEL STORAGE STABILITY RESULTS

TEST	TOTAL SEDIMENT, mg/100 ml					
	PASS/FAIL CRITERIA	GULF COAST FUEL (2143)	WEST COAST SINGLE CRUDE (2225)	WEST COAST MIXED CRUDE (2246)	MIDCONTINENT FUEL (2422)	LOUISIANA FUEL (3006)
43° C/18-WK	4.0	2.9	6.0	11.3	8.9	6.0
65° C/8-WK	6.1	4.3	7.0	13.0	17.8	9.0
80° C/2-WK	6.0	3.6	—	9.8	—	—
95° C/16-HR	1.5	0.7	—	0.6	0.8	0.6

Table 4

**GRAVIMETRIC RESULTS FOR ACCELERATED STORAGE STABILITY TESTS
FUEL FROM US MIDCONTINENT REFINERY
NEAT FUEL (2422) - 30% LCO/70% STRAIGHT RUN**

SAMPLE ID	43°C/18WK BOTTLE	65°C/8WK BOTTLE	95°C/16HR 2274
2	1.5	6.3	0.6
6	1.7	7.1	0.3
4	1.7	5.9	0.1
3	2.1	4.6	0.1
9	2.3	7.0	0.3
8	3.8	11.3	0.3
7	4.0	9.1	0.4
5	5.6	13.8	0.3
1	5.6	13.5	0.4
NEAT	8.9	17.8	0.8
PASS/FAIL	4.0	7.0	1.5

Table 5

**GRAVIMETRIC RESULTS FOR ACCELERATED STORAGE STABILITY TESTS
FUEL FROM U.S. GULF COAST REFINERY
NEAT FUEL (3006) - 30% LCO/70% STRAIGHT RUN**

SAMPLE ID	43°C/18WK BOTTLE	65°C/8WK BOTTLE	95°C/16HR 2274	90°C/16HR LPR
2	1.9	2.8	0.2	0.7
3	2.8	3.8	0.2	1.1
4	3.9	5.2	0.1	1.3
9	4.3	5.3	0.4	3.1
6	4.5	7.3	0.3	2.8
8	4.7	5.1	0.2	2.4
1	5.2	6.4	0.2	3.4
5	5.6	6.8	0.3	3.1
7	5.6	5.6	0.2	1.4
NEAT	6.2	9.0	0.6	4.5
PASS/FAIL	4.0	7.0	1.5	3.0

Table 6

**A SUMMARY OF STATISTICALLY SIGNIFICANT CHANGES IN THE
STORAGE STABILITY OF FUEL BLENDS CAUSED BY
INTRODUCTION OF ADDITIVES 1-9 TESTED IN 26 TRIALS**

ADDITIVE NO.	DELAYS DEGRADATION	INNOCUOUS	INCREASES DEGRADATION
1	8	15	3
2	18	8	0
3	19	7	0
4	11	13	2
5	7	14	5
6	12	9	5
7	8	15	3
8	11	11	4
9	17	7	2

Table 7

NUMBER OF TIMES EACH ADDITIVE WAS LISTED IN THE TOP THREE IN REDUCING SEDIMENT GENERATION

ADDITIVE	FIRST	SECOND	THIRD	TOTAL
1	0	0	1	1
2	11	3	1	15
3	2	6	5	13
4	2	0	2	4
5	0	1	0	1
6	0	0	2	2
7	0	0	0	0
8	0	0	1	1
9	1	3	1	5

Third International Conference on Stability
and Handling of Liquid Fuels

London, U.K.

September 13-16, 1988

STABILITY MEASUREMENTS OF MILITARY AND COMMERCIAL MARINE FUELS
FROM A WORLDWIDE SURVEY

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ABSTRACT

As a part of a continuing U.S. Navy mobility fuels flexibility program, the storage stabilities of 22 military (NATO F-76) fuels and 26 commercial marine fuels from a worldwide survey taken in 1986 were evaluated. The commercial fuels were marine gas oils (MGO) which are very similar to current use F-76 fuels. Accelerated storage stability tests included 43°C bottle tests, ASTM D 2274 and a new low pressure reactor test at 90°C and 100 psig overpressure of oxygen. Results from all three stability tests on both categories of fuel will be presented along with conclusions based on fuel type and geographical location.

INTRODUCTION

The U.S. Navy marine fuels have a specification that requires each lot to pass a minimum accelerated storage stability test. The test method utilizes the procedure outlined in ASTM D2274, which subjects the test fuel to a temperature of 95°C for 16 hours while oxygen is bubbled through the fuel. This specification requires that a fuel shall not generate a total weight of fuel insoluble sediment and gum greater than 1.5 mg/100 ml. This concern for long term storage stability of Naval Distillate (NATO F-76) fuel comes from the need to store large reserves of fuel in strategic locations around the world for up to three years at ambient conditions.

One of the tasks in the U.S. Navy's mobility fuels flexibility program initiated in 1980 was the survey of critical fuel properties of commercially available marine fuels for possible future Navy use as shipboard mobility fuels. This task was accomplished by procuring, during 1982, samples of commercial marine fuels from a variety of locations around the world which combined the Naval needs of strategic location and the possibility of local problems in supply of specification grade fuel. In all, stability data for 36 samples were generated at a variety of accelerated test conditions and at temperatures ranging from 43°C to 95°C. In comparing the data obtained for the different accelerated storage stability tests, remarkable agreement was obtained with regard to the pass/fail designations. It was noted that the higher temperature stability tests were more stringent in failing possibly acceptable fuels on the basis of their inherent storage stability. The combination of these data and other property data led to recommendations that additional commercial samples be collected to substantiate and extend the data base begun in this work, that more emphasis should be placed on MGOs and HMGOS and that the sample collection regions should be enlarged to include more South American, Mediterranean, African and Far Eastern ports/depots [1].

Because of these recommendations, a second worldwide fuel survey was undertaken in 1986. Samples of commercial marine fuels (MGOs) and of Naval Distillate (NATO F-76) were procured and submitted for stability testing. Stability data for 26 MGOs and for 22 F-76 fuels were obtained. The accelerated test conditions are outlined in the Experimental Section of this paper. The test temperatures ranged from 43°C to 95°C. All results are tabulated in gravimetric form in mg of total insoluble sediment per 100 ml of fuel.

EXPERIMENTAL

The fuels used in this work are coded in simple numerical order in each of the two fuel types, commercial marine gas oil (MGO) and naval distillate (NATO F-76) and the geographical regions of fuel collection are shown in Figure 1. The fuels were obtained in 1986 in epoxy lined 5 gallon cans and distributed for stability testing in 1987 in epoxy lined

one gallon cans. Actual stability testing was done in late 1987 and early 1988.

The 43°C tests were standard bottle tests using 300 ml of filtered fuel which was stored in brown borosilicate bottles for 18 weeks at 43°C. The filterable sediment and adherent insoluble gum were determined gravimetrically and added together for a total insoluble sediment weight. Samples were run in duplicate and the average of the two values are reported in mg/100 ml. Details of the method are given in the literature [2].

Tests at 90°C were run by a new oxygen overpressure method in which 100 ml samples of filtered fuel in 125 ml brown borosilicate bottles were placed in a low pressure reactor (LPR). The reactor was sealed and pressurized with 99.5% pure oxygen to 700kPa (100psig). The samples were stressed, under pressure, for 16 hrs at 90°C. At the end of the stress period the pressure was released slowly and the samples were removed and cooled. The amount of filterable sediment and adherent gum were determined gravimetrically and reported as total insoluble sediment weight. Samples were run in triplicate and the average values are given in mg/100ml. Details of the method and construction of the low pressure reactor (LPR) are given in another paper in this symposium [3].

The 95°C tests utilized the procedure outlined in ASTM D2274, which subjects the test fuel to a temperature of 95°C for 16 hours while oxygen is bubbled through the fuel.

RESULTS AND DISCUSSION

The results for the three storage stability tests for 26 commercial MGOs are presented in Table 1. From these data it can be seen that these fuels met the pass/fail criteria set by the Naval Research Lab of 4.0 mg per 100 ml of fuel for the 43°C bottle tests [4] and 90°C oxygen overpressure tests with one exception. The 95°C D2274 test showed good agreement with the lower temperature tests when the pass/fail limit was considered. The 95°C test did give one false fail while the LPR test did not give any but neither one of the tests gave any false passes. MGO 26 failed in all three tests so it is possible that this fuel was mistakenly categorized as an MGO.

Table 2 gives the results of the three storage stability tests for the 22 military F-76 fuels. These results show that these fuels are quite stable and passed both the 43°C and the 90°C tests, with one exception, but they appear to be slightly more unstable than the commercial MGOs. The 95°C D2274 test was in general agreement with the lower temperature tests but it did give more false fails than the LPR test but there were no false passes when compared to the lower temperature tests. It is possible that the higher temperature tests are generally more stringent in assessing possible long term storage problems. The F-76 fuel No.22 failed all three of the storage tests.

Fuel color was determined according to ASTM D1550 on all the fuels before and after the 43°C/18 week bottle tests. It was determined that there was no correlation between the color and the instability of the fuel.

CONCLUSIONS

By comparing the results of the stability tests for the 26 commercial MGOS, it is apparent that they are quite storage stable worldwide and that they appear to be more stable than the fuels from the 1982 worldwide survey. This may be because of a faster rotation of the fuel stocks, the possibility that stability additives have been added to the fuels and/or because it is not necessary to blend in as much cracked stock because of the current abundance of available crudes. The military F-76 fuels are also quite stable worldwide but were not be as stable as the commercial MGOS.

In comparing the pass/fail results for all 48 samples using the three different accelerated storage stability test, there is very good interlab and intertest agreement as was observed in the 1982 survey. Comparing the results of the 95°C D2274 with the lower temperature results indicated that the test gave some false fails but gave no false passes. It therefore appears that the D2274 test correctly assesses the stability of aged fuels or fuels that contain no LCO. However the results of new LPR test indicate that it also correctly assesses the stability of aged fuels. In addition, the LPR test also is a good predictor of the stability of fuels containing LCO. It was also noted that the higher temperature stability tests were more stringent in failing possibly acceptable fuels on the basis of their inherent storage stability. This was particularly true of the F-76 diesel fuels.

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Table 1

COMMERCIAL MGO WORLDWIDE FUEL SURVEY

Results of Three Storage Stability Tests in mg/100 ml

Code No	Sample Location	Bottle 43°C/18 WK	LPR 90°C/16 HR	D2274
1	Pakistan	0.0	0.9	0.1
2	France	0.1	0.9	0.1
3	Japan	0.1	1.3	0.1
4	Venezuela	0.2	2.6	0.1
5	Egypt	0.2	2.2	0.2
6	U.A.E.	0.2	2.8	0.2
7	Malaysia	0.2	0.8	0.3
8	India	0.3	0.6	0.3
9	Sweden	0.3	0.7	0.1
10	Australia	0.4	0.8	0.2
11	Italy	0.4	1.2	0.2
12	Kenya	0.4	1.3	0.5
13	Belgium	0.6	1.1	0.4
14	Indonesia	0.6	2.0	0.5
15	Peru	0.6	1.7	0.6
16	Brazil	0.7	1.2	0.2
17	Malta	0.7	1.0	0.5
18	Senegal	0.8	1.0	0.6
19	Greece	0.8	1.3	0.7
20	Thailand	0.8	0.8	0.5
21	Singapore	0.9	2.2	0.4
22	England	1.0	1.4	0.5
23	Greece	1.1	1.0	0.3
24	Singapore	1.2	2.3	0.4
25	Saudi Arabia	1.4	1.4	1.9*
26	Netherlands	18.0*	12.4*	2.8*
Pass/Fail		4.0	4.0	1.5

* Values indicate a fuel fails this particular test as indicated by the pass/fail criterion at the bottom of each column

Table 2

NAVY DISTILLATE (NATO F-76) WORLDWIDE FUEL SURVEY

Results of Three Storage Stability Tests in mg/100 ml

Code No	Sample Location	Bottle 43°C/18 WK	LPR 90°C/16HR	D2274
1	Scotland	0.2	0.2	0.1
2	Panama	0.2	1.1	0.4
3	Japan	0.2	1.8	0.8
4	Philippines	0.3	3.0	1.8*
5	Iceland	0.5	0.7	0.5
6	Scotland	0.4	1.8	0.4
7	England	0.5	1.2	0.8
8	Turkey	0.6	1.1	1.1
9	Scotland	0.7	0.5	0.7
10	Japan	0.7	1.3	1.1
11	Guam	0.8	2.0	1.2
12	Diego Garcia	0.8	1.0	0.9
13	Japan	0.9	3.0	1.5*
14	Cuba	1.1	0.7	0.4
15	Spain	1.1	1.7	1.0
16	Japan	1.1	2.1	1.7*
17	Bermuda	1.2	1.4	0.3
18	Azores	1.4	2.4	0.7
19	Spain	1.6	1.8	0.8
20	Crete	1.6	3.1	1.8*
21	Portugal	1.7	1.2	1.0
22	Puerto Rico	3.9*	3.9*	2.9*
Pass/Fail		4.0	4.0	1.5

* Values indicate a fuel fails this particular test as indicated by the pass/fail criterion at the bottom of each column.

LOCATION OF FUEL SAMPLES 1986 WORLDWIDE SURVEY

STARRED CIRCLES ARE 22 NAVAL DISTILLATE NATO F-76 FUELS
SOLID CIRCLES ARE 26 COMMERCIAL MGO FUELS

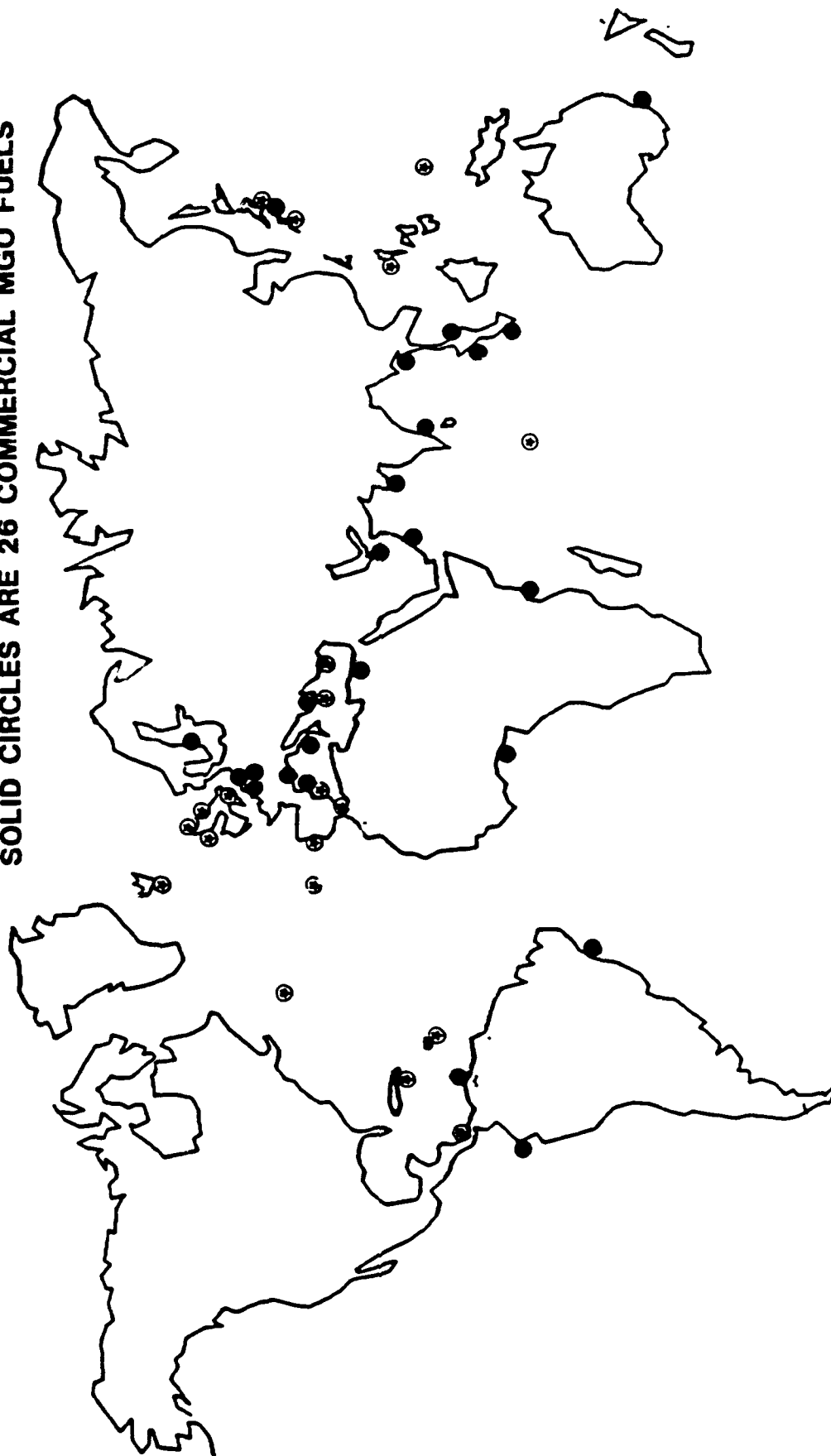


Figure 1

Third International Conference on Stability
and Handling of Liquid Fuels

London, U. K.

September 13-16, 1988

ASSESSING DISTILLATE FUEL STORAGE STABILITY BY OXYGEN OVERPRESSURE

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ABSTRACT

This paper describes a new method for determining a distillate fuel's tendency for forming deleterious fuel insoluble products during ambient storage. Oxygen is forced into solution in the fuel at pressures up to 700 kPa (100 psi) at temperatures up to 80°C for up to 96 hours in order to accelerate the reactions which take place at ambient pressure and temperature in the field or laboratory. The method then makes use of gravimetric determination of the total insolubles formed. The method is predictive for up to three years of ambient conditions, and it is rapid and very precise. It has been used to rank additive free fuels over a wide range of storage stabilities and has also been useful in assessing the relative effectiveness of middle distillate fuel stabilizer (antioxidant) additives.

Details of the new method will be given along with data comparing traditional bottle type tests at various temperatures with results from the new technique. At any given temperature for any given fuel, the data indicate a significant acceleration of insoluble sediment formation. Thus, the test has considerable usefulness, both in quality assurance and as a research tool to investigate autoxidation chemistry.

INTRODUCTION

Currently utilized methods for assessing storage stability of middle distillate fuels suffer a variety of drawbacks. Lower temperature bottle tests are generally the best indicators of storage stability of a particular fuel, but meaningful results require storage at 40 to 50°C for between 12 and 18 weeks. At temperatures of 80°C and above bottle storage tests can usually be completed in a reasonably short time, as little as 24 hours, but these tests are generally poor indicators of actual ambient fuel reactions leading to insoluble products.

One test widely used in both the commercial and military sectors for a rapid assessment of fuel storage oxidative stability is the ASTM D2274 method [1]. This test has several major problems. It is not a good predictor of storage stability for freshly refined middle distillate fuels which contain any catalytically cracked stocks. Another problem is the fact that the recommended fuel incubation time of 16 hours is too short for many fuels. This leads to two further related problems. The total amount of insolubles formed is very low and quite difficult to quantify. Second, and more important, it allows a potentially unstable fuel to pass the test. Recent attempts to circumvent this second problem in the military have been to lower the pass criterion (rather than increase the incubation test time). In the past six years the military procurement specification maximum has been lowered from 2.5 to 1.5 mg/100ml of fuel. The primary effect of this has been a worsening of the precision of replicate analyses both within the laboratories and between laboratories.

The present method evolved from attempts to measure oxygen uptake in middle distillate fuels using an ASTM D525 oxidation bomb apparatus at elevated pressures of pure oxygen. During these experiments, it was apparent that the actual chemically involved oxygen uptake leading to insoluble production was too small to measure by this technique and further work in this area was abandoned. Other very interesting effects were noted however. Oxygen solubilization in the fuel occurred very slowly, large amounts of insolubles formed in short times and good precision was obtained for replicates when the insolubles were gravimetrically determined. This led to the development of a procedure to purposely accelerate the instability reactions by oxygen overpressure and to attempt to relate this new procedure to traditionally accepted tests run at atmospheric pressure and close to ambient temperatures.

EXPERIMENTAL

Sample containers were borosilicate glass bottles capable of holding 100ml of sample but not greater than 150ml total volume. A top closure of aluminum foil with small holes for oxygen exchange was used. A reactor was constructed from a 1A air cylinder (9 inches in diameter) by cutting off a section about 10 inches long and welding a bottom plate of half inch stainless steel. The top was a half inch stainless steel plate about 10 inches in diameter fitted with a bellows isolation valve and an adjustable pressure relief valve along with a small pressure gauge. The reactor was sealed with a neoprene o-ring which was placed in a groove machined into the top of the reactor. The top plate was held in place with nuts threaded onto eight 5/8 inch steel rods which were welded into the bottom plate. The entire vessel was pressure tested hydrostatically at 200psig. The relief valve was set for 120 psig. Other reactor designs have also been used successfully.

The reactor was placed in either a water/ethylene glycol bath or an explosion proof oven. The source oxygen was 99.5% purity. The hydrocarbon solvent was hexane. Adherent insolubles solvent was an equal volume mixture of acetone, toluene, and methanol. All solvents were CP grade. Filtration medium for the gravimetric determination of suspended insolubles was Gelman type A/E glass fiber filters with a nominal 1.2 micron porosity.

Sample bottles were initially rinsed with adherent insolubles solvent followed by water. They were then washed in a mildly alkaline or neutral pH laboratory detergent, rinsed with distilled water and dried. Aluminum weighing dishes used in the determination of adherent insolubles were first cleaned in adherent insolubles solvent for several minutes and allowed to dry. One dish was placed within a second dish for each sample replicate to be run.

Each sample replicate was prefiltered through Gelman type A/E glass fiber filters and 100ml aliquots were placed in the cleaned bottles using a graduated cylinder. Each blank and sample bottle was placed in the reactor which was capable of holding up to 22 individual sample containers. A minimum of three replicates for each sample and blank was used. The reactor was slowly pressurized to about 800 kPa (100psia). Then the pressure was slowly released. The reactor was then pressurized and depressurized again. The third and final time, the pressure was adjusted to 700kPa and recorded. The isolation valve was closed and the reactor placed in the thermostated bath or oven.

After the incubation period at temperature, the pressure was slowly released and the sample bottles removed and allowed to cool in the dark to room temperature for a minimum of four hours. The samples were not exposed to light until immediately prior to filtration.

Two filters for each sample and blank replicate were weighed together to the nearest 0.1mg. The weighed filters were placed in a vacuum filter funnel and rinsed with 50ml of hexane. This was followed by filtration of the contents of a sample bottle. The bottle was rinsed with 50ml of hexane and the rinse poured through the filter. The filter holder was washed down with hexane from a rinse bottle.

The bottle was then carefully rinsed with two 15ml portions of adherent insolubles solvent. The entire inner surface of the bottle was in contact with this solvent. The solvent was poured into an aluminum weighing dish assembly which had been weighed to the nearest 0.1 mg. This was placed on a hot plate at low heat to slowly evaporate just to dryness. This procedure was also followed for each of the blank correction bottles.

The sample and blank filters and adherent insolubles weighing dish assemblies were placed in a drying oven at 120°C and dried for at least four hours. They were removed from the oven and allowed to cool to ambient for about four hours. Each filter and weighing dish assembly was weighed to the nearest 0.1mg. Total insolubles were computed by summing the weight gain of the filter plus the weighing dish with appropriate corrections for filter blanks and weighing dish blanks. The average of the replicates was calculated along with the standard deviation of a single determination

RESULTS AND DISCUSSION

Development Of The Oxygen Overpressure Protocol. Two test temperatures were initially chosen to span a range of low temperature, long time bottle test methods (43°C) and high temperature, shorter time bottle test methods (80°C). A well characterized diesel fuel containing 30% catalytically cracked stock was chosen to test effects of varying the oxygen partial pressure and the total pressure. In addition, the effect of time at constant temperature and pressure was investigated.

Four pressures of oxygen were run at 80°C for 64 hours; 25, 50, 75 and 100 psia. The results are given in Table I and depict a linear dependence of gravimetrically determined total insoluble production as a function of oxygen pressure. A second series of experiments was run at 100 psia total pressure but using oxygen/nitrogen mixtures at partial oxygen pressures of 25, 50 and 75 psia. These data in Table I indicate that it is the molar amount of oxygen present rather than an increase in oxygen dissolution that is controlling the reaction leading to fuel insoluble products. This is ascribed to the equilibrium of the insolubles producing reactions being forced to the right and not an increase in the rate of insoluble formation at a given temperature and reaction time. By forcing the equilibrium of these insolubles forming reactions that would proceed at ambient temperatures, the test time can be considerably reduced at any given temperature.

Previous work on bulk distillate fuel storage stability has clearly demonstrated a linear Arrhenius relationship in the temperature range between about 20 and about 40°C where total fuel insolubles doubles for each 10°C rise in temperature [2,3]. This means that a laboratory stability test run at 40°C for 13 weeks approximates testing at 20°C for 1 year. This is the basis for an ASTM D 4625 bottle test regimen at 43°C (110°F). A continuation of this type of argument with increasing temperature gives a testing time at 60°C for 3 weeks or at 80°C of 6 days which should approximate 1 year of 20°C storage. Assuming from the data in Table 1 that the effect of oxygen on insolubles formation is linear, a 30-fold increase in oxygen availability by substituting pure oxygen at 100 psia for air at 15 psia would mean about 5 hours at 80°C would approximate total insolubles formation at 20°C for 1 year. Since the test is meant to be predictive, 15 hours at 80°C would approximate 3 years at 20°C. Since the theoretically possible maximum acceleration is not reached in reality, it is generally necessary to increase the test time at a given temperature. This will be discussed in a subsequent section of this paper.

Relative Evaluation Of Middle Distillate Fuel Storage Stability. Five middle distillate fuels were chosen to evaluate the oxygen overpressure method. The five fuels have been well characterized [4] and have undergone numerous different time/temperature accelerated storage stability tests at atmospheric pressure. The fuels spanned a range of predicted storage stability from very stable to very unstable as ranked by bottle tests at 43°C (slight variation of ASTM 4625) [5].

Two test temperatures were chosen. The first was 43°C for 4 weeks at an oxygen pressure of 100 psia and the second was 80°C for 64 hours at an oxygen overpressure of 100 psia. The results for the lower temperature test are shown in Table 2 along with atmospheric pressure bottle test data for the fuels at 43°C for 18 weeks. The results for the higher temperature test are shown in Table 3 along with the data for these fuels tested in bottle tests at atmospheric air pressure and 80°C for two weeks. The relative stability rankings in both temperature cases is identical over the wide range of total insolubles formed in both the lower and higher pressure cases. If a ratio of total insolubles is calculated as in Table 2, it can be seen that the results at higher pressures and shorter times range between 1 and 1.9 for the five fuels. This indicates that the time acceleration of 4.5 (= 18wks/4wks) at higher pressures is actually about 1.5 times greater or about a seven fold increase. In Table 3, the ratio for 80°C is higher, ranging between 2 and 3. This shows that the time acceleration of about 5 (=186hrs/64hrs) at higher pressures is actually about 2.5 times higher or about a 12 fold acceleration.

The Effect of Pressure and Time at Pressure for Various Fuels. The effect of pressure on the five test fuels was examined at two temperatures, 43°C and 80°C, over a range of 3 to 100 psia of oxygen. The results are given in Figure 1 for 80°C and in Figure 2 for the 43°C regimen. At the higher temperature the test time was held constant at 64 hours. In general, all fuels showed an increase of insolubles with increasing oxygen

pressure. The more unstable fuels showed greater dependence of insolubles formation on oxygen pressure. At the lower temperature the test time was held constant at 4 weeks. In this case, the effect of pressure was much less than at the higher temperature, especially for the more stable fuels. The more unstable fuels showed an apparent oxygen independence above 50 psia.

If the partial pressure, or molar concentration, of oxygen is high relative to reactive insoluble precursors at 43°C, the precursors essentially become the limiting reagent in the reaction pathway and further elevation of oxygen pressure would not increase the amount of insolubles formation (Figure 2). As the temperature is raised, more reactive insolubles precursors and pathways to insolubles formation become available and so insoluble products increase with increasing pressure as shown in Figure 1.

It is significant that the five fuels are ranked identically at both temperatures and at all oxygen pressures. This means that by judiciously selecting higher temperatures and oxygen pressures, one may conveniently shorten the time of oxidation without sacrificing the chemical equivalence of the ambient oxidation. Figure 3 shows results for five fuels spanning a broad range of stability when tested at 43°C for 18 weeks in atmospheric air bottle tests. The five fuels were also tested at 43°C for 4 weeks at 100 psia oxygen. A linear least squares correlation, R^2 , gives 0.98 for these two tests (Figure 3). The correlation between 43°C/4wks/100psia oxygen and 80°C/64hrs/100psia oxygen is 0.97 for these same five fuels. This is a clear indication that a combination of increased temperature and increased oxygen pressure together should be quite useful to predict ambient storage stability for most mid-distillate fuels.

Figures 4 and 5 show the effects at 80°C and 43°C of varying the time at 100 psia oxygen for five fuels. In Figure 4, the major effect is the greater ability to differentiate between fuels at the longer test time (96 hours). If there is no need to finely differentiate fuels, the test time could be reduced to 32 hours. At 43°C (Fig. 5) the same effect is noted. At 2 weeks, one is effectively predicting storage stability at ambient conditions of about 14 months.

Evaluation of Stabilizer Additives in Mid-Distillate Fuels. In addition to testing mid-distillate fuels to assess their relative stabilities, the test method should be able to differentiate the relative effectiveness of various stabilizer (antioxidant) additives added to a particular fuel to control insolubles formation. For this work, two relatively unstable fuels were chosen. Up to twelve different commercial stabilizer additives were blended into each fuel. Fuel A was tested at 43°C for 18 weeks at atmospheric pressures and at 43°C for 4 weeks at 100 psia oxygen. The results are given in Table 4 and the data is ranked on the basis of the additives effect in reducing insolubles in the atmospheric test. Two conclusions are evident. There is remarkable agreement in the ranking of

additive effectiveness. Second, the oxygen overpressure test is about one-third more stringent than the bottle test, i.e., the overpressure test could have been shortened to about 3 weeks to yield the same amount of insolubles.

The results for Fuel B are given in Table 5. This fuel was tested at 43°C for 18 weeks in atmospheric pressure bottles and at 65°C for 7 days at 100 psia oxygen. The R^2 values given in both Table 4 and Table 5 indicate excellent correlation between the accepted 43°C bottle tests and the oxygen overpressure tests.

CONCLUSIONS

Analytically, the advantages of this new method over previous methods are its greatly reduced test times and its excellent precision for replicate samples. Chemically, the advantages are its excellent correlations with lower temperature bottle tests, its good discrimination of stability between fuels and most importantly, its ability to accurately predict insolubles formation of various fuels during ambient storage. Systematic extension of the test to higher temperatures and shorter times will be the subject of a subsequent report.

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ACKNOWLEDGEMENTS

The authors wish to thank the US Navy Energy R and D Office and David Taylor Research Center for financial support of this work.

Table 1
Effect of Oxygen Pressure on Total Insolubles Formed
at 80°C for 64 hrs. Test Fuel: Blend of
30% Catalytically Cracked Light Cycle Oil and
70% Straight Run Distillate

<u>PSIA</u>		
<u>Partial Oxygen Pressure</u>	<u>Total Pressure</u>	<u>Insolubles Formed(mg/100ml)</u>
25	25	1.5
50	50	4.2
75	75	5.9
100	100	8.3
25	100*	3.0
50	100*	4.4
75	100*	6.2

*Brought to total indicated pressure using Nitrogen.

Table 2

Comparison of Total Insolubles Generated at 43°C for Five Fuels
Atms refers to bottle tests at atmospheric air pressure
100 psia refers to oxygen overpressure tests

<u>Fuel Code</u>	<u>Total Sediment, mg/100ml</u>		<u>Ratio</u>
	<u>43°C/18wk/atms</u>	<u>43°C/4wk/100psi</u>	
1	1.0	0.9	1.0
2	2.2	2.9	1.5
3	4.4	5.2	1.2
4	7.1	13.8	1.9
5	15.3	24.3	1.8

Table 3

Comparison of Total Insolubles Generated at 80°C for Five Fuels
 Atms refers to bottle tests at atmospheric air pressure
 100 psia refers to oxygen overpressure tests

Fuel Code	Total Sediment, mg/100ml		Ratio
	80°C/2wk/atms	80°C/64hrs/100psia	
1	1.0	1.9	2.0
2	2.0	4.8	2.4
3	4.0	9.8	2.5
4	6.7	16.1	2.4
5	11.8	36.4	3.0

Table 4

Total Insolubles Generated in Fuel A By Two Different Test Methods
 Each sample number is the identical base fuel with 12 different additives
 Standard Deviation refers to triplicate determinations
 $R^2 = 0.80$

Sample Number	43°C/18wks	STD	43°C/4wks	STD
	bottle, mg/100ml	DEV	100 psia Oxy, mg/100ml	DEV
2	6.6	0.1	9.5	0.1
10	7.6	0.3	9.9	0.4
11	8.2	0.3	12.1	0.7
12	8.4	0.1	12.5	0.7
3	8.5	0.2	12.2	1.1
8	10.5	0.1	13.2	0.3
6	10.7	0.6	12.4	0.4
9	10.8	0.1	13.4	0.2
1	10.9	0.4	15.0	0.2
5	11.0	0.2	13.1	0.9
4	11.2	0.4	14.4	0.2
Neat	11.3	0.4	14.6	0.1
7	11.5	0.5	14.3	1.3

Table 5

Total Insolubles Generated in Fuel B by Two Different Test Methods
 Each Sample Number is the Identical Base Fuel with 10 Different Additives
 Standard Deviation Refers to Triplicate Determinations
 $R^2 = 0.92$

Sample Number	43°C/18wks bottle, mg/100ml	STD DEV	65°C/7days 100 psia Oxy, mg/100ml	STD DEV
2	1.9	0.2	0.8	0.1
10	2.5	0.1	0.9	0.5
3	2.8	0.1	2.5	0.6
4	3.9	0.2	4.4	0.1
9	4.3	0.0	4.8	0.8
6	4.5	0.0	4.0	0.5
8	4.7	0.2	4.8	0.1
1	5.2	0.1	6.1	0.7
5	5.6	0.1	6.5	0.2
7	5.6	0.2	5.3	0.1
Neat	6.2	0.2	6.5	0.5

**80°C FOR 64 HOURS LPR DATA
 PSIA VS TOTAL INSOLUBLES
 AVERAGE OF TRIPPLICATE RUNS**

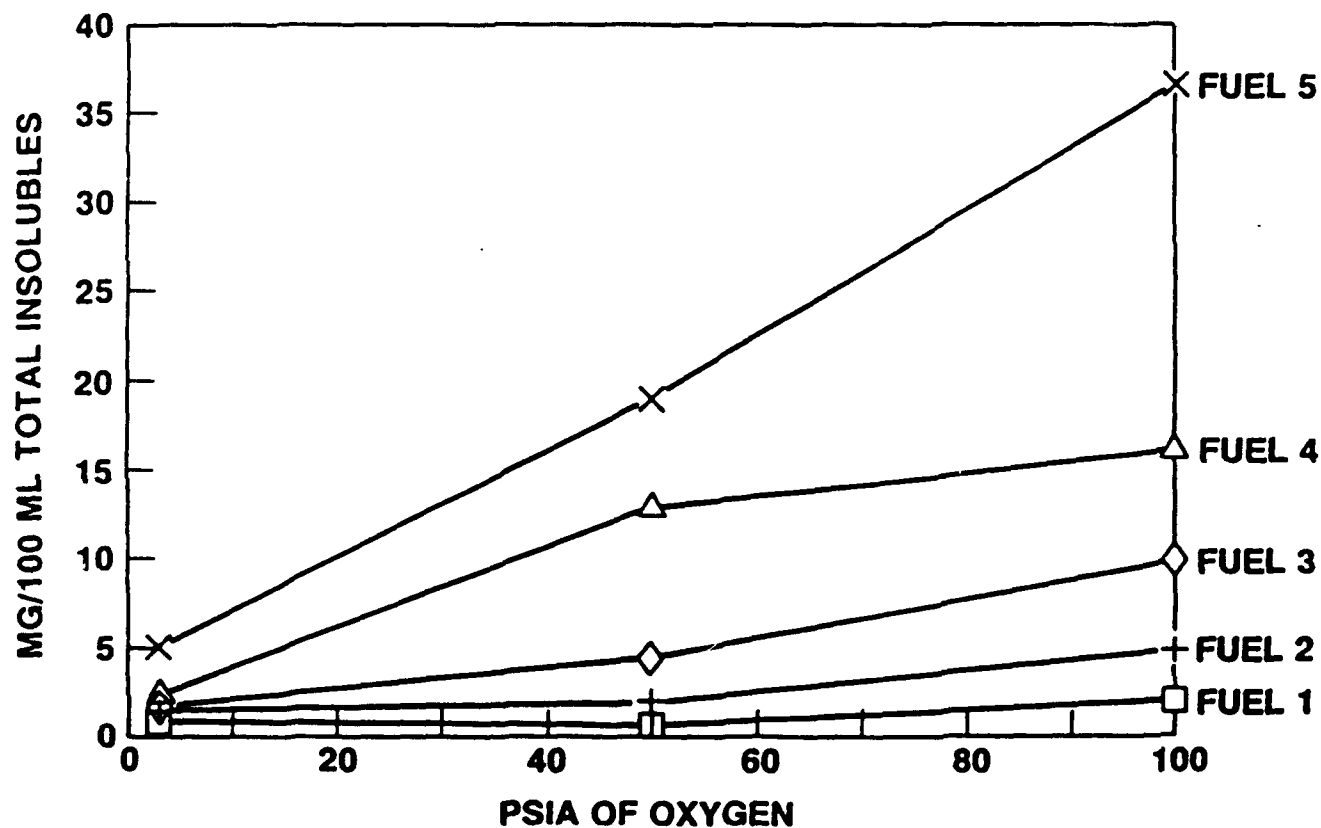


Figure 1

**43°C FOR 4 WEEKS LPR DATA
PSIA VS TOTAL INSOLUBLES
AVERAGE OF TRIPPLICATE RUNS**

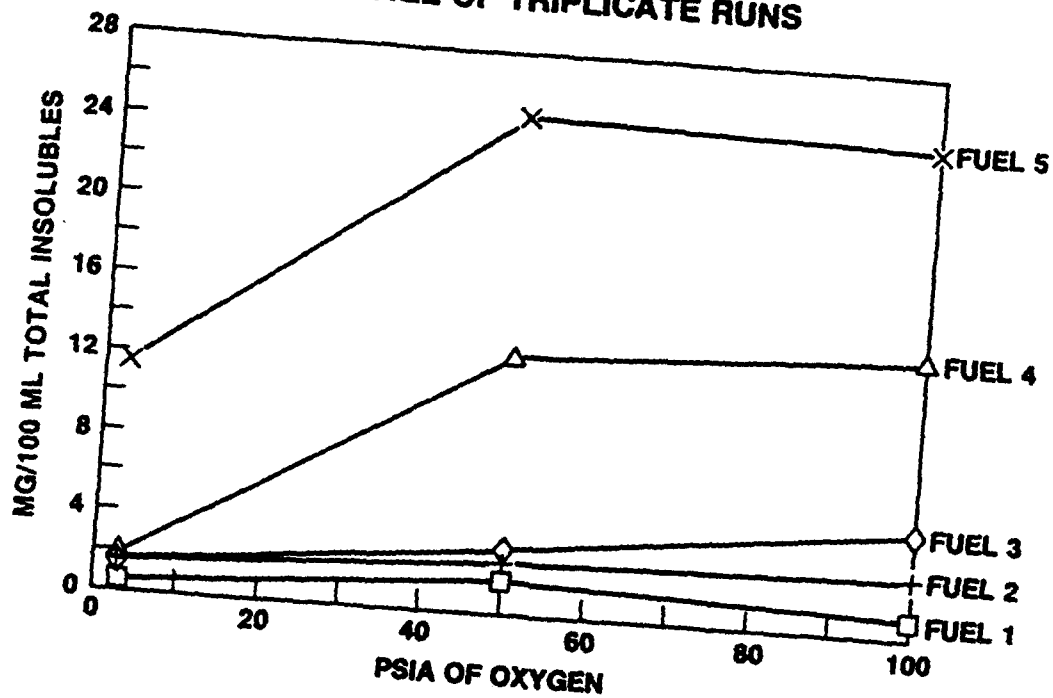


Figure 2

**COMPARISON OF 43°C 18 WEEK BOTTLE TESTS
WITH
43°C 4 WEEK LPR TESTS**

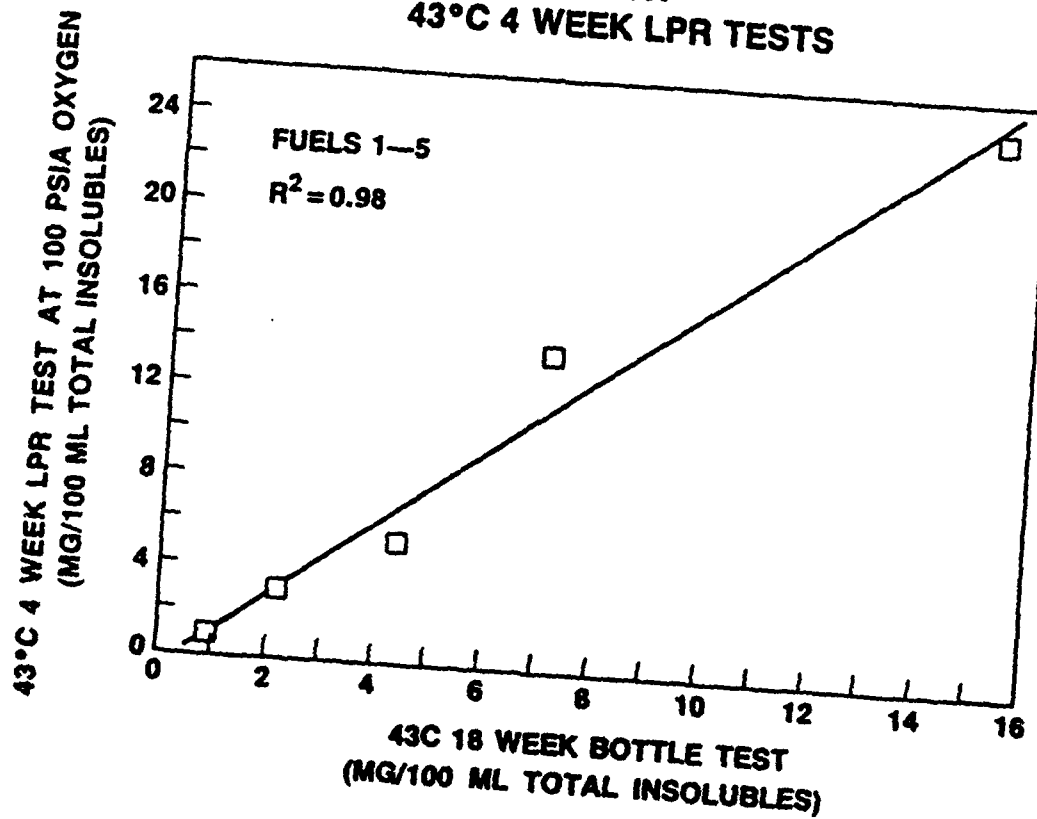


Figure 3

80°C AT 100 PSIA LPR DATA
HOURS VS TOTAL INSOLUBLES
AVERAGE OF TRIPPLICATE RUNS

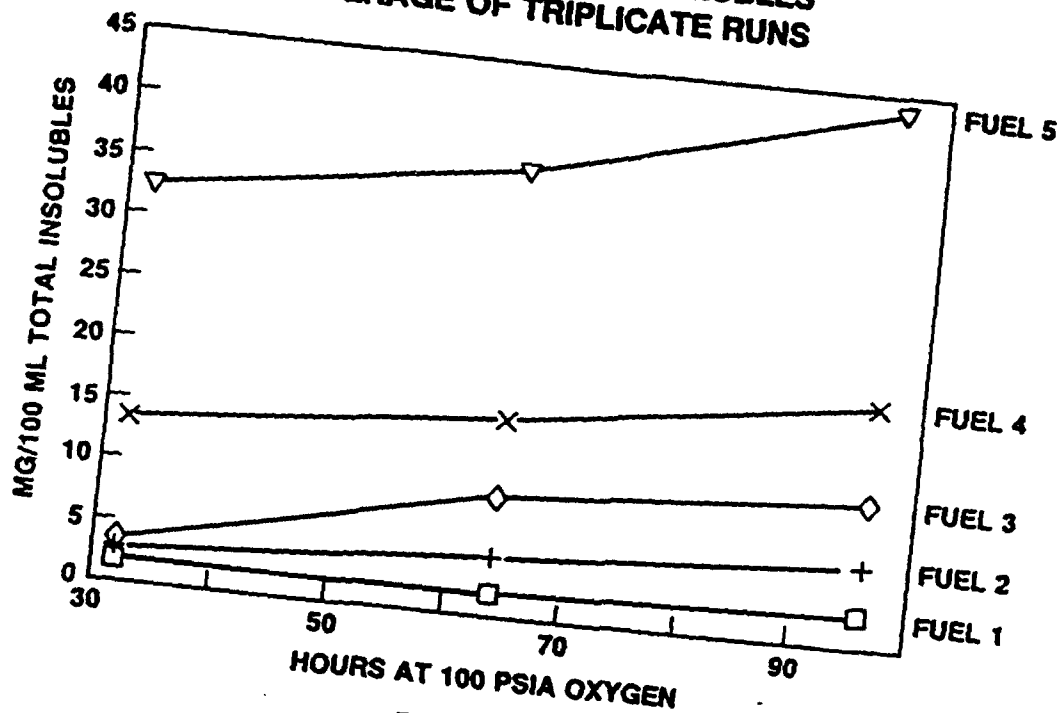


Figure 4

43°C AT 100 PSIA LPR DATA
WEEKS VS TOTAL INSOLUBLES
AVERAGE OF TRIPPLICATE RUNS

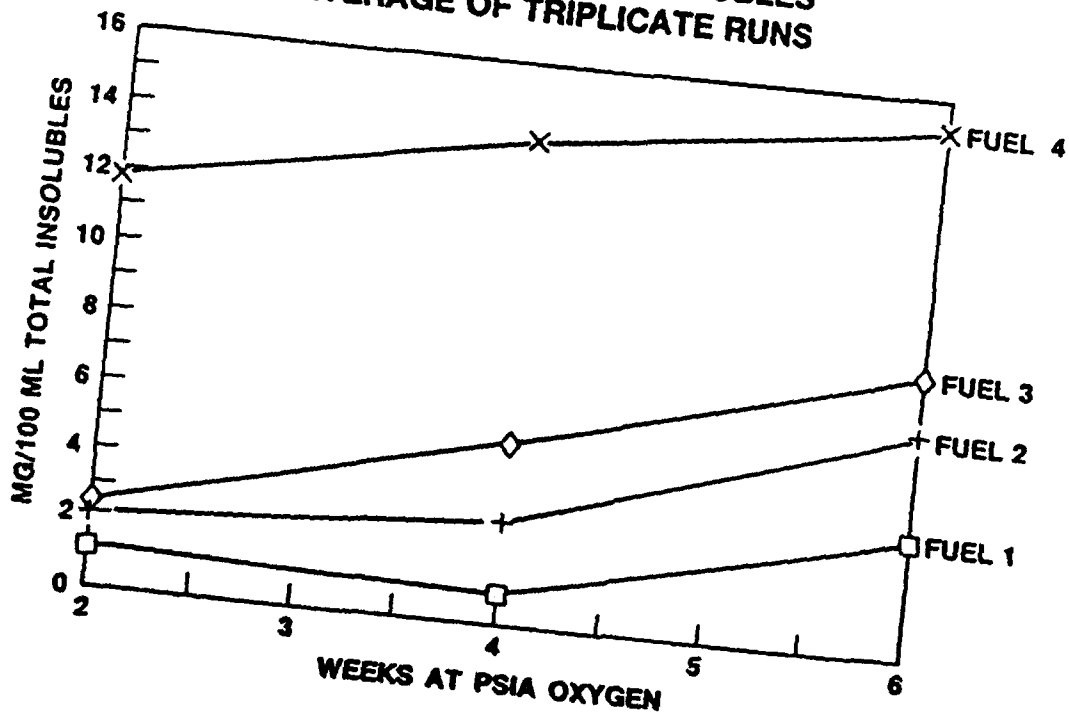


Figure 5

CHEMICAL FACTORS AFFECTING INSOLUBLES FORMATION
IN SHALE DERIVED DIESEL FUEL

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ACKNOWLEDGEMENT

The authors thank the Department of Energy for sponsoring this work under contract number DE-IA-81BC10525. References to brand names were made for identification only and do not imply endorsement by DOE.

ABSTRACT

Detrimental changes in fuel properties with time have been a continuing problem in the use of middle distillate fuels. Instability of diesel fuels is usually defined by the formation of insoluble sediments and gums. Gravimetric stability tests have been conducted at 43°C and 80°C, respectively, using three model nitrogen heterocycles, 2-methylpyridine, 2,6-dimethyl quinoline, and dodecahydrocarbazole, as dopants in an otherwise stable shale diesel fuel. Potential interactive effects have been defined for these three model nitrogen heterocycles in the stable fuel in the presence of a second model dopant, t-butyl hydroperoxide. 2-Methyl pyridine and 2,6-dimethyl quinoline were inactive and only 2-methyl pyridine showed slight positive interactive effects. Dodecahydrocarbazole formed large amounts of insolubles by itself and exhibited positive interactive effects.

INTRODUCTION

As petroleum crudes continue to increase in price and decrease in quality, refinery feedstocks are getting heavier with increasing quantities of metals and heteroatoms present, particularly sulfur and nitrogen. As a consequence, refineries are using new and more severe processing techniques. This current trend toward using lower grade petroleum crudes coupled with the tremendous potential for the near future use of synfuels (shale, coal, and tar sands) has created a pressing need for investigation into the fundamental nature of liquid fuel instability.

Changes in fuel composition with time has been a continuing problem to the utilization of middle distillate fuels. Problems associated with the storage instability of diesel fuels include the formation of insoluble sediments and gums as well as the production of peroxides and color bodies (Frankenfeld et. al., 1982, 1983a-c; Goetzinger, et. al., 1983; Cooney et. al., 1984; Dahlin et. al., 1981).

Present knowledge has suggested that for some fuels, nitrogen heterocycles may play a causative role in the formation of insoluble sediments and gums under conditions of ambient and accelerated storage. In particular, nitrogen containing aromatics (pyrroles, pyridines, indoles, etc.) appear to be very harmful (Frankenfeld et. al., 1982; Daniel, 1983; Hazlett et. al., 1983). Nitrogen heterocyclic compounds which commonly occur in middle distillate fuels include

alkylated pyridines, quinolines, tetrahydroquinolines, indoles, pyrroles, and carbazoles. Currently, it appears that relatively non-basic nitrogen heterocycles, particularly those which contain alkyl groups in certain positions, may be the most troublesome (Mushrush, et. al., 1986). However, in other fuels and under different test conditions, basic nitrogen compounds may play a significant role (Cooney et. al., 1984). While the oxidation reactions of these heterocycles have been well studied (Jones and Bean, 1977; Newkome and Paudler, 1982), present knowledge is very limited regarding the chemistry of their autoxidation in the complex fuel media. Correlation of model dopant studies with results obtained from actual unstable fuels has indicated that the autoxidation processes are usually not isolated reactions but are sensitive to the presence of other fuel constituents (Cooney, 1984; Frankenfeld et. al., 1982; Worstell and Daniel, 1981). Little is known about the chemical mechanisms of such interactive effects in fuel instability.

In our effort to address the instability of shale-derived diesel fuel, we have conducted gravimetric accelerated storage stability tests at 43°C and 80°C using three model nitrogen compounds, 2-methyl pyridine (MP), 2,6-dimethylquinoline (DMQ), and dodecahydrocarbazole (DDC), as dopants in an otherwise stable shale diesel fuel, DFM. Also, information about potential interactive effects has been defined for these three model nitrogen compounds in the stable fuel in the presence of a second model dopant, t-butyl hydroperoxide (tBHP).

EXPERIMENTAL

Storage Test Technique

The accelerated storage stability test method used has been described in detail (Cooney et. al., 1983). In summary, 300 ml samples of filtered fuel (doped and undoped) were thermally stressed at 43° and 80°C in the dark in 500 ml screw-cap borosilicate Erlenmeyer flasks with teflon-lined caps. After the appropriate stress period, the test flasks were allowed to cool to room temperature before the contents were filtered under slight vacuum through a double layer of Gelman, Type A/E, 47mm glass fiber filters. The residue in the flasks was then rinsed with n-heptane, with additional sediment being collected on the filter paper. The precipitate was then rinsed with additional heptane to remove adsorbed fuel. The flasks and filter holders were heated at 120°C for 12 h under vacuum, allowed to equilibrate at room temperature for 4 h, and weighed on an analytical balance. Appropriate blank flask-filter holder corrections were applied. Filterable sediment values were obtained from the corrected net weight change of the filter holder with adherent gum values determined from the weight change of the test flask.

In this paper, fuel stability is generally defined as the amount of total insoluble material formed as a result of thermal stress. This quantity was equal to the sum of filterable sediment and adherent gum values and is presented in the data tables in units of mg/100mL of fuel. All samples were

run in duplicate or triplicate. Noted tests were accomplished by using modified screw caps which were drilled to hold 6 mm glass tubing (with glass wool plugs). Peroxide values were determined in stressed fuel samples following filtration through glass fiber filter paper by a standard iodometric titration procedure (ASTM D-1583-60). Duplicate titrations were conducted for each sample of filtered fuel.

Base Fuel

The base fuel was a diesel fuel marine (DFM) refined from Paraho crude shale oil by SCHIO. This fuel was produced in the Navy's Shale-II demonstration and is well characterized (Cooney et. al., 1983; Waslik and Robinson, 1981; Affens et. al., 1981; White, 1981). It was available with, D-11, and without, D-1, antioxidant added. The antioxidant, 2,4-dimethyl-6-tertiary butyl phenol (AO-30), was originally present at the 24 mg/liter level in fuel D-11. No other additives were present in either sample. All compounds used as dopants were pure by NMR, combined capillary GC/MS, and/or melting point.

Reagents

2-Methyl pyridine was supplied by Aldrich Chemical Co. and the 2,6-dimethyl quinoline and dodecahydrocarbazole were supplied by Pfaltz & Bauer. The purity of each reagent was checked by capillary column GC. Purity of each was >99% and they were used without further purification. t-Butyl hydroperoxide, 90%, Aldrich Chemical Co. was purified by low pressure distillation. Caution note on the purification of t-butyl hydroperoxide. Low pressure distillation of 15 ml

quantities of the tBHP proceeded smoothly. A pressure such that the distillation temperature did not rise above 30°C was used. However, when the distillation was scaled up to 100ml, a potentially dangerous situation occurred. The temperature started to rise drastically in the reaction vessel. The reaction was quenched by liquid nitrogen and no further distillation attempt was made at this volume.

RESULTS AND DISCUSSION

In earlier studies, nitrogen-rich fractions of marginally stable shale-derived fuels were extracted and used as dopants to show that these fractions can induce instability behavior in both D-1 and D-11 stable fuels (Mushrush, et. al., 1986; Cooney et. al., 1985). Attempted correlation of the composition of the heterocyclic extracts with their activity in both sediment formation and hydroperoxide interaction was complicated by the complexity of the extracts. These extracts were as active as dimethyl pyrrole in inducing instability. Results indicated that the type of nitrogen compound rather than the quantity of nitrogen was the controlling factor in fuel degradation. In addition, the presence of obscure but significant interactive effects between fuel components could not be analyzed in a dopant that was so complex. The extracts consisted of a complex mixture of alkyl pyridines, alkyl quinolines and hydrogenated carbazoles. Over 300 specific isomers were identified in these extracts. Specific compounds included

short alkyl chain mono and disubstituted pyridines, short-chain alkyl disubstituted quinolines, and carbazoles such as dodecahydrocarbazole.

In the present study, accelerated storage stability tests were conducted at temperatures of 43° for 70 and 140 days, and 80°C for time periods ranging from 7 to 14 days using three model nitrogen compounds as dopants in a stable shale-derived diesel fuel. The three model compounds, 2-methylpyridine (MP), 2,6-dimethylquinoline (DMQ) and dodecahydrocarbazole (DDC) were added to either D-1 or D-11 at concentrations of 0, 45, 135, 270 and 450 ppm N(w/v). Runs were conducted both in the non-vented and vented mode. Vented runs were conducted with 45 and 450 ppm N respectively.

Tables I, II, and III give the total insolubles observed for the MP, DMQ and DDC dopants respectively. The amount of total insoluble material reported in these Tables is the mean value for duplicate experimental runs. The insoluble material consisted primarily of filterable sediment with a smaller amount of adherent gum. The hydroperoxides formed during the time-temperature matrix are given in parentheses. Hydroperoxide values reported are the average of two runs. The results in Table I and II indicate that 2-methyl pyridine and 2,6-dimethylquinoline were inactive in sediment promotion for all temperatures, times and concentrations employed. In all instances, the total insolubles formed never exceeded 2 mg/ 100 ml or 1 mg/100 ml when MP or the DMQ, respectively, were

TABLE I

Total Insolubles for Fuel D-11 with Added 2-Methyl Pyridine

ppm N (w/v)	Total Insolubles (mg/100ml)**			
	80°C 7 days	80°C 14 days	43°C 70 days	43°C 140 days
0	0.0	0.2(3.9)**	0.4(0.8)	-0.4(1.2)
45	-0.2	-0.2(4.1)	0.3(0.5)	0.4(0.7)
45*	-0.3	-0.1(4.6)	0.1(0.5)	0.4(0.6)
135	-0.4	-0.1(4.3)	0.2(0.4)	1.2(0.5)
270	0.0	-0.2(3.7)	0.1(0.4)	1.9(0.6)
450	-0.1	-0.1(3.5)	0.2(0.3)	-0.1(0.5)
450*	0.0	0.1(3.1)	-0.1(0.4)	-0.1(0.5)

* Flasks Vented

** Average of Duplicates

*** Peroxide numbers in parentheses (meq of active oxygen/kg fuel)

TABLE II

Insolubles for Fuel D-11 with added 2,6-Dimethyl Quinoline

ppm N (w/v)	Total Insolubles (mg/100ml)**			
	80°C 7 days	80°C 14 days	43°C 70 days	43°C 140 days
0	-0.1	0.1(4.2)**	0.2(0.8)	0.2(3.4)
45	0.2	0.1(24.6)	0.6(0.8)	0.2(2.5)
45*	0.2	0.1(42.8)	0.4(1.1)	0.0(3.8)
135	0.2	0.3(42.6)	0.5(1.1)	0.1(7.4)
270	0.1	0.3(48.5)	0.5(1.2)	0.3(5.3)
450	0.1	0.4(46.9)	0.4(1.0)	-0.3(2.9)
450*	0.0	-0.3(69.8)	0.5(1.2)	-0.2(3.1)

* Flasks Vented

** Average of Duplicates

*** Peroxide numbers in parentheses

TABLE III

Total Insolubles with Added Dodecahydrocarbazole
For Fuels D-1 and D-11

ppm N (w/v)	Total Insolubles (mg/100ml)**			
	Fuel	D-11	D-1	D-11
	80°C 7 days	80°C 14 days	43°C 70 days	43°C 140 days
0	0.2	1.0(47.2)***	-0.4(0.7)	0.1(1.1)
45	46.6	38.5(8.8)	26.1(15.6)	49.6(20.3)
45*	42.4	51.7(12.9)	1.1(63.8)	6.1(192.4)
135	75.3	102.7(2.7)	61.2(38.9)	88.9(109.1)
270	158.7	177.2(2.7)	193.0(7.4)	128.5(44.0)
450	322.9	267.8(0.8)	328.4(11.8)	244.9(15.2)
450*	220.8	271.0(2.4)	99.9(28.9)	140.8(56.9)

* Flasks Vented

** Average of Duplicates

*** Peroxide numbers in parentheses

added. Venting of the flasks did not significantly change the total insolubles observed for these two dopants. The similarities in behavior of MP and DMQ are reasonable since they are both heterocyclic tertiary amines of comparable base strength. Another possible factor for MP is that D-11 contains a free radical chain breaking antioxidant, AO-30. Earlier nitrogen surveys showed MP to be innocuous in D-11, yet it was mildly reactive in fuel D-1 which contained no additives.

Dodecahydrocarbazole, DDC, a saturated cyclic secondary amine effected significant insolubles formation in earlier work (Cooney et.al., 1986). The results for the full matrix of

concentration, time and temperature presented in Table III support the earlier finding. Large amounts of insoluble sedimenta were formed when DDC was added as a dopant to the shale DPM. For the trials at 43° with D-11, the table shows mixed results at lower ppm of added nitrogen (up to 135). The results show increasing sedimentation as added nitrogen is increased. At 270 and 450ppm N respectively, the sedimentation increases with time. However, the longer stress period results in an unexpected lower quantity of insolubles. This shows that insoluble formation alone is not just a function of added nitrogen.

Vented trials compared to the non-vented runs at 80°C resulted in both more insolubles and higher peroxide numbers as shown in Table III. However, at 43°C the results for the vented trials showed less insolubles and much higher peroxide numbers. At 45 ppm added nitrogen, 70 days, only 1.1 mg/100ml of insolubles was formed and the peroxide number was 63.8 meq/kg fuel. For the same concentration and a 140 day stress the insolubles were 6.1 mg/100ml while the peroxide number was 192.4 meq. At 450 ppm added nitrogen, the same trends were noted, i.e., lower insolubles than the non-vented runs and much higher peroxide numbers. The increase in insolubles was less than first order in DDC concentrations, except for the 43°C - 70 day experiment. The 43°C - 140 day set gave a reaction order of about 0.6. The explanation for the lowered insolubles and the higher peroxide values observed is not readily apparent. For D-11 the peroxide concentration is initially low,

but increases markedly up to 135 ppm of added nitrogen and then the peroxide number decreases as the dopant is increased in concentration. One trial, 80°C for 14 days, was conducted with D-1. The fuel, as expected, peroxidized readily, 47.2 meq/kg fuel. This trial also resulted in significant formation of insolubles. In the non-vented trials for D-1, the peroxide value is initially high and decreases markedly with increasing concentration of DDC. Since large amounts of insolubles formed in this as well as the other sets using D-11, we conclude that NO-30 did not have a significant effect on the instability induced by DDC. Thus, DDC performs quite differently from the other two heteroaromatic amines of this study.

Interactive Effects

The interaction study involved the addition of a model nitrogen compound to fuel D-11 together with an active oxidant, a hydroperoxide, as a co-dopant. The hydroperoxide selected was t-butyl hydroperoxide, tBHP, since it is relatively stable and easily purified by low pressure distillation. The tBHP can be quantitated by either a titration procedure or capillary column GC. The goal of the experiments was to survey the importance of the accumulation of hydroperoxides in a complex fuel in influencing the formation of insolubles during stress when a particular class of nitrogen heterocycles was present.

These studies were conducted in duplicate, both in vented and closed test flasks, where both additives were present at a concentration of $3.21 \times 10^{-2} M$. This is a concentration that corresponds to 450 ppm N (w/v) for the nitrogen compounds. In

addition to the interaction flasks, appropriate blanks were tested in duplicate with undoped fuel, fuel doped with MP, DMQ, or DDC, and fuel doped with just the co-dopant tHHP.

Table IV shows the extensive matrix that was conducted for the MP and tHHP co-dopant studies. Both a "Lo" and "High" concentration were used which corresponded to MP at two levels: Lo MP = 135 ppm N(w/v), equivalent to $9.64 \times 10^{-3}M$; and Hi MP = 450 ppm N($3.21 \times 10^{-2}M$). The levels of the co-dopant, tHHP, corresponded to the same molar concentrations.

With tHHP, the results in Table IV indicate that in the presence of this hydroperoxide, MP is able to weakly induce the formation of solids in the fuel. Although venting of the flasks uniformly led to increased instability (when the concentrations of MP and tHHP were held constant), there was no clear-cut increase in deterioration when raising the concentration levels (i.e., from Lo to Hi) of either the tHHP or the MP. A maximum of 2.1 mg/100ml of total insolubles was attained for the Hi tHHP/Lo MP vented flasks, indicating that a weak synergism was present. In this interactive experiment, the MP and tHHP reacted to yield more ROOH compared to the Lo and Hi tHHP blanks as shown in Table IV. Vented samples were higher in ROOH than the unvented ones.

Results for the DMQ/tHHP and DDC/tHHP co-dopant interactions are given in Table V. The dopants were added at a concentration equivalent to $3.21 \times 10^{-2}M$. The tHHP/DMQ co-dopants interacted in a manner similar to the tHHP/MP couple. Similarity included: the maximum quantity of

TABLE IV

Total Insolubles For Fuel D-11 with Co-Dopants 2-Methyl Pyridine and t-Butyl Hydroperoxide at 80°C for 14 days

Sample	Total Insolubles(mg/100ml)**
Blank Fuel	-0.1 (5.8)***
Lo tHHP Blanks	0.1 (60.0)
Lo tHHP/Lo MP	0.8 (89.0)
Lo tHHP/Lo MP*	1.2 (112.0)
Lo tHHP/Hi MP	0.4 (56.4)
Lo tHHP/Hi MP*	0.5 (67.9)
Hi tHHP Blanks	0.3 (65.2)
Hi tHHP/Lo MP	0.6 (79.7)
Hi tHHP/Lo MP*	2.1 (113.4)
Hi tHHP/Hi MP	0.8 (81.4)
Hi tHHP/Hi MP*	1.6 (115.9)

* Vented

** Average of duplicates

*** Peroxide numbers in parentheses

insolubles was obtained for a vented run with both dopants present; and the ROOH concentration increased for the vented runs. This indicated a weak synergism in operation for the tHHP/DMQ system.

The tHHP/DDC co-dopants exhibited completely different behavior than the other two systems. Total insolubles, Table V, for the interactive studies were similar to the trials in which DDC was the lone dopant. For this matrix, the most insolubles were observed in the unvented runs. Table V shows a dramatic increase of total insolubles at 450 ppm N at 80°C for the unvented runs. This is similar to the results in Table III for fuel D-11 at 80°C and for the same fuel at 43°C.

TABLE V

Total Insolubles For Fuel D-11 with t-Butyl Hydroperoxide and Co-Dopants DMQ or DDC at 80°C for 14 days

Sample	Total Insolubles (mg/100ml)*	
	DMQ	DDC
Blank Fuel	0.2 (4.9)**	0.0 (8.0)
tBHP Blanks	1.3 (60.4)	2.8 (102.0)
Dopant Trials	0.4 (32.7)	168.5 (10.4)
tBHP/Dopant (unvented)	1.3 (84.0)	310.4 (15.3)
tBHP/Dopant (vented)	1.5 (96.4)	176.4 (16.4)

* Dopant concentration: $3.21 \times 10^{-2}M$

** Peroxide numbers in parentheses

The results in Table III for fuel D-1 are not comparable, but this was expected because of the presence of AO-30 in D-11. DDC reduced the ROOH concentration significantly (ca. 102 to 16 peroxide numbers) after 14 days at 80°C in fuel D-11 as shown in Table V. In fact, DDC was more effective in reducing ROOH concentration than 2,5-dimethyl pyrrole, a very effective peroxide reducer (Cooney et. al., 1986).

CONCLUSIONS

Model compound dopant studies show that the 2-methyl pyridine, MP, and the 2,6-dimethylquinoline, DMQ, were inactive as sediment producers by themselves and in the presence of a co-dopant, t-butyl hydroperoxide, tBHP. The maximum insolubles produced for MP was 1.9 mg/100ml and 0.5 mg/100ml for DMQ. In the interactive studies with tBHP, MP gave 2.1 mg/100ml and DMQ

yielded 1.5 mg/100ml of total insolubles for fuel D-11. This indicated that a weak synergism was present. Similarities in behavior of these two compounds is reasonable since they are both tertiary amines of comparable base strength.

Dodecahydrocarbazole, DDC, a saturated cyclic secondary amine performs quite differently from the other two amines. In fact, DDC triggered instability behavior comparable to the most active pyrroles on a nitrogen concentration basis. The amount of insolubles always increased in unvented runs as the nitrogen concentration increased. The maximum insolubles observed was 322 mg/100ml for fuel D-11 at 80°C with 450ppm of N (DDC) in an unvented trial. In the interactive studies with tBHP, the greatest amounts of total insolubles were formed in the unvented tests with almost a two-fold increase over the vented trials and over the runs where only DDC was present.

The ROOH concentration data exhibited few consistent patterns with respect to chemical structure, insolubles formation, or other experimental parameters. For example, MP had little effect on D-11 peroxidation. In contrast, DMQ formed much ROOH at 80°C/14d but little at 43°C/140d even though these two compounds are closely related structurally. The DDC consistently stimulated peroxide formation at 43°C, but inhibited formation of or decomposed ROOH at 80°C. The stimulation of ROOH formation at 43°C was greatest at a low DDC concentration (45 ppm N) under vented conditions.

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RECEIVED: February 22, 1988 ACCEPTED: March 23, 1988

Assessing Distillate Fuel Storage Stability by Oxygen Overpressure

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Received August 5, 1988. Revised Manuscript Received October 20, 1988

This paper describes a new method for predicting distillate fuel's tendency for forming deleterious fuel insolubles during ambient storage. Oxygen is forced into solution in the fuel at pressures up to 794 kPa (100 psig). The fuel is stressed under conditions of accelerated storage. The method then makes use of gravimetric determination of the total insolubles formed. This rapid and precise method is predictive for up to 3 years of ambient conditions. It has been used to rank additive-free fuels over a wide range of storage stabilities and has also been useful in assessing the relative effectiveness of middle-distillate fuel stabilizer (antioxidant) additives.

Introduction

Currently utilized methods for assessing storage stability of middle-distillate fuels suffer a variety of drawbacks. Lower temperature bottle tests are generally the best indicators of storage stability of a particular fuel, but meaningful results require storage at 40–50 °C for between 12 and 18 weeks. At temperatures of 80 °C and above, bottle storage tests can usually be completed in a reasonably short time, as little as 24 h, but these tests are generally poor indicators of actual ambient fuel reactions leading to insoluble products.^{1,2}

One test widely used in both the commercial and military sectors as a rapid assessment of fuel storage oxidative stability is the ASTM D 2274 method.³ This test has several major problems. It is not a good predictor of storage stability for freshly refined middle-distillate fuels that contain any catalytically cracked stocks. Another problem is the fact that the recommended fuel incubation time of 16 h is too short for many fuels.^{1,2} This leads to two further related problems. The total amount of insolubles formed is very low and quite difficult to quantify. Second, and more important, it allows a potentially unstable fuel to pass the test. Recent attempts to circumvent this second problem in the military have been to

lower the pass criterion (rather than increase the incubation test time). In the past 6 years the military procurement specification maximum has been lowered from 2.5 to 1.5 mg/100 mL of fuel. The primary effect of this has been to worsen the precision of replicate analyses both within the laboratories and between laboratories.

The present method evolved from attempts to measure oxygen uptake in middle-distillate fuels using an ASTM D 525 oxidation bomb apparatus at elevated pressures of pure oxygen. During these experiments, it was apparent that the actual chemically involved oxygen uptake leading to insoluble production was too small to measure by this technique and further work in this area was abandoned. Other very interesting effects were noted however. Oxygen solubilization in the fuel occurred very slowly, large amounts of insolubles formed in short times, and good precision was obtained for replicates when the insolubles were gravimetrically determined. This led to the development of a procedure to purposely accelerate the reactions leading to the formation of fuel insoluble sediments

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by oxygen overpressure and to attempt to relate this new procedure to traditionally accepted tests run at atmospheric pressure and close to ambient temperatures.

Experimental Section

Sample containers were borosilicate glass bottles capable of holding 100 mL of sample but not greater than 150 mL total volume. A top closure of aluminum foil with small holes for oxygen exchange was used. A reactor was constructed from a 1A air cylinder (9 in. in diameter) by cutting off a section about 10 in. long and welding a bottom plate of $1/2$ -in. stainless steel. The top was a $1/2$ -in. stainless-steel plate about 10 in. in diameter fitted with a bellows isolation valve and an adjustable pressure relief valve along with a small pressure gauge. The reactor was sealed with a neoprene o-ring, which was placed in a groove machined into the top of the reactor. The top plate was held in place with nuts threaded onto eight $5/8$ -in. steel rods, which were welded into the bottom plate. The entire vessel was pressure tested hydrostatically at 1484 kPa (200 psig). The relief valve was set for 932 kPa (120 psig). Other reactor designs have also been used successfully.

The reactor was placed in either a water/ethylene glycol bath or an explosion-proof oven. The source oxygen was of 99.5% purity. The hydrocarbon solvent was hexane. Adherent gum solvent was an equal volume mixture of acetone, toluene, and methanol. All solvents were CP grade. Filtration media for the gravimetric determination of suspended insolubles were Gelman type A/E glass fiber filters with a nominal 1.2- μ m porosity.

Sample bottles were initially rinsed with adherent gum solvent followed by water. They were then washed in a mildly alkaline or neutral pH laboratory detergent, rinsed with distilled water, and dried. Aluminum weighing dishes used in the determination of adherent insolubles were first cleaned in adherent gum solvent for several minutes and allowed to dry. One dish was placed within a second dish for each sample replicate to be run.

Each sample replicate was prefiltered through Gelman type A/E glass fiber filters and 100-mL aliquots were placed in the cleaned bottles by using a graduated cylinder. Each blank bottle and sample bottle were placed in the reactor, which was capable of holding up to 22 individual sample containers. A minimum of three replicates for each sample and blank was used. The reactor was slowly pressurized to about 794 kPa (100 psig). Then the pressure was slowly released. The reactor was then pressurized and depressurized again. The third and final time, the pressure was adjusted to 794 kPa and recorded. The isolation valve was closed and the reactor placed in the thermostated bath or oven. The oxygen pressure was continually monitored by an attached pressure gauge. A final pressure of about 828–897 kPa (105–115 psig) was attained depending upon the incubation temperature. No measurable pressure decrease was ever observed. Separate sets of experiments were performed to test the effects of sample stirring on total sediment production. No measurable effect was noted.

After the incubation period at temperature, the pressure was slowly released and the sample bottles removed and allowed to cool slowly in the dark to room temperature for a minimum of 4 hours. The samples were not exposed to light until immediately prior to filtration.

Two filters for each sample and blank replicate were weighed together to the nearest 0.1 mg. The weighed filters were placed in a vacuum filter funnel and rinsed with 50 mL of hexane. This was followed by filtration of the contents of a sample bottle. The bottle was rinsed with 50 mL of hexane and the rinse poured through the filter. The filter holder was washed down with hexane from a rinse bottle.

The bottle was then carefully rinsed with two 15-mL portions of adherent gum solvent. The entire inner surface of the bottle was in contact with this solvent. The solvent was poured into an aluminum weighing dish assembly that had been weighed to the nearest 0.1 mg. This was placed on a hot plate at low heat to slowly evaporate just to dryness. This procedure was also followed for each of the blank correction bottles.

The sample and blank filters and weighing dish assemblies were placed in a drying oven at 120 °C and dried for at least 4 hours. They were removed from the oven and allowed to cool to the

Table I. Effect of Oxygen Pressure on Total Insolubles Formed at 80 °C for 64 h for a Test Fuel^a

pressure, ^b psia		
partial oxygen pressure	total pressure	insolubles formed, mg/100 mL of fuel
25	25	1.5
50	50	4.2
75	75	5.9
100	100	8.3
25	100 ^c	3.0
50	100 ^c	4.4
75	100 ^c	6.2

^a The test fuel is a blend of 30% catalytically cracked light-cycle oil and 70% straight run distillate. ^b 100 psia = 690 kPa. ^c Brought to total indicated pressure by using nitrogen.

ambient temperature for about 4 hours. Each filter and weighing dish assembly was weighed to the nearest 0.1 mg. Total insolubles were computed by summing the weight gain of the filter (the so-called filterable insolubles formed) plus the weight gain of the weighing dish (the so-called adherent gum insolubles formed) with appropriate corrections for blanks. The average of the replicates was calculated along with the standard deviation of a single determination.

Results and Discussion

Development of the Oxygen Overpressure Protocol.

Two test temperatures were initially chosen to span a range of low-temperature, long-time bottle test methods (43 °C) and high-temperature, shorter time bottle test methods (80 °C). A well-characterized diesel fuel containing 30% catalytically cracked stock was chosen to test effects of varying the oxygen partial pressure and the total pressure. In addition, the effect of time at constant temperature and pressure was investigated.

Four pressures of oxygen were run at 80 °C for 64 h: 173, 346, 518, and 690 kPa (25, 50, 75, and 100 psia). The results are given in Table I and depict a linear dependence of gravimetrically determined total insoluble production as a function of oxygen pressure. A second series of experiments was run at 690 kPa (100 psia) total pressure but using oxygen/nitrogen mixtures at partial oxygen pressures of 173, 346, and 518 kPa (25, 50, and 75 psia). These data in Table I indicate that it is the molar amount of oxygen present rather than an increase in oxygen dissolution that is controlling the reactions leading to fuel-insoluble products. This is ascribed to the equilibrium of the insolubles-producing reactions being forced to the right and not an increase in the rate of insoluble formation at a given temperature and reaction time. By forcing of the equilibrium of these insolubles-forming reactions that would proceed at ambient temperatures, the test time can be considerably reduced at any given temperature.

Previous work on bulk distillate fuel storage stability has clearly demonstrated a linear Arrhenius relationship in the temperature range between about 20 and 40 °C where total fuel insolubles double for each 10 °C rise in temperature.⁴⁵ This means that a laboratory stability test run at 40 °C for 13 weeks approximates testing at 20 °C for 1 year. This is the basis for an ASTM D 4625 bottle test regimen at 43 °C (110 °F). A continuation of this type of argument with increasing temperature gives a testing time at 60 °C for 3 weeks or at 80 °C of 6 days which should approximate 1 year of 20 °C storage. A 30-fold increase in oxygen availability by substituting pure oxygen at 690 kPa for air at 104 kPa (15 psia) would mean about 5 h at 80 °C would

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Table II. Comparison of Total Insolubles Generated at 43 °C for Five Fuels*

fuel code	total sediment, mg/100 mL of fuel		ratio
	43 °C/18 weeks/atms	43 °C/4 weeks/100 psia	
1	1.0	0.9	1.0
2	2.2	2.9	1.5
3	4.4	5.2	1.2
4	7.1	13.8	1.9
5	15.3	24.3	1.8

* Atms refers to bottle tests at atmospheric air pressure. 100 psia refers to oxygen overpressure tests. 100 psia = 690 kPa.

Table III. Comparison of Total Insolubles Generated at 80 °C for Five Fuels

fuel code	total sediment, mg/100 mL of fuel		ratio
	80 °C/2 weeks/atms	80 °C/64 h/100 psia	
1	1.0	1.9	2.0
2	2.0	4.8	2.4
3	4.0	9.8	2.5
4	6.7	16.1	2.4
5	11.8	36.4	3.0

* Atms refers to bottle tests at atmospheric air pressure. 100 psia refers to oxygen overpressure tests. 100 psia = 690 kPa.

approximate total insolubles formation at 20 °C for 1 year. Since a desirable test should be predictive, 15 h at 80 °C would approximate 3 years at 20 °C. Since the theoretically possible maximum acceleration is not reached in reality, it is generally necessary to increase the test time at a given temperature. This will be discussed in a subsequent section of this paper.

Relative Evaluation of Middle-Distillate Fuel Storage Stability. Five middle-distillate fuels were chosen to evaluate the oxygen overpressure method. The five fuels have been well characterized⁶ and have undergone numerous different time/temperature accelerated storage stability tests at atmospheric pressure. The fuels spanned a range of predicted storage stability from very stable to very unstable as ranked by bottle tests at 43 °C (slight variation of ASTM D4625).⁷

Two test temperatures were chosen. The first was 43 °C for 4 weeks at an oxygen overpressure of 690 kPa (100 psia) and the second was 80 °C for 64 h at an oxygen overpressure of 690 kPa (100 psia). The results for the lower temperature test are shown in Table II along with atmospheric pressure bottle test data for the fuels at 43 °C for 18 weeks. The results for the higher temperature test are shown in Table III along with the data for these fuels tested in bottle tests at atmospheric air pressure and 80 °C for 2 weeks. The relative stability rankings in both temperature cases are identical over the wide range of total insolubles formed in both the lower and higher pressure cases. If a ratio of total insolubles is calculated as in Table II, it can be seen that the results at higher pressures and shorter times range between 1 and 1.9 for the five fuels. This indicates that the time acceleration of 4.5 (=18 weeks/4 weeks) at higher pressures is actually about 1.5 times greater or about a 7-fold increase. In Table III, the ratio for 80 °C is higher, ranging between 2 and 3. This shows that the time acceleration of about 5 (=336 h/64

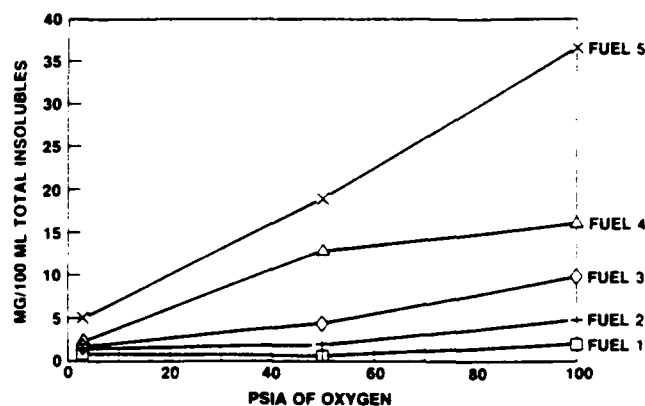


Figure 1. Effect of pressure on the five fuels: LPR data, 80 °C for 64 h; psia (100 psia = 690 kPa) vs total insolubles. For the average of triplicate runs, the standard deviation is <1.0.

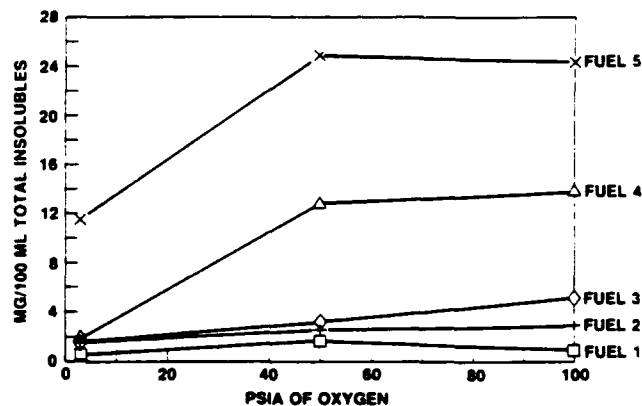


Figure 2. Effect of pressure on the five fuels: LPR data, 43 °C for 4 weeks; psia (100 psia = 690 kPa) vs total insolubles. For the average of triplicate runs the standard deviation is <1.5.

h) at higher pressures is actually about 2.5 times higher or about a 12-fold acceleration.

Effect of Pressure and Time at Pressure for Various Fuels. The effect of pressure on the five test fuels was examined at two temperatures, 43 and 80 °C, over a range of 21–690 kPa (3–100 psia) of oxygen. The results are given in Figure 1 for 80 °C and in Figure 2 for the 43 °C regimen. At the higher temperature the test time was held constant at 64 h. In general, all fuels showed an increase of insolubles with increasing oxygen pressure. The more unstable fuels showed greater dependence of insolubles formation on oxygen pressure. At the lower temperature the test time was held constant at 4 weeks. In this case, the effect of pressure was much less than at the higher temperature, especially for the more stable fuels. The more unstable fuels showed an apparent oxygen independence above 345 kPa (50 psia).

If the partial pressure, or molar concentration, of oxygen is high relative to reactive insoluble precursors at 43 °C, the precursors essentially become the limiting reagent in the reaction pathway and further elevation of oxygen pressure would not increase the amount of insolubles formation (Figure 2). As the temperature is raised, more reactive insolubles precursors and pathways to insoluble products become available, and so insoluble products increase with increasing pressure as shown in Figure 1.

It is significant that the five fuels are ranked identically at both temperatures and at all oxygen pressures. This means that by judiciously selecting higher temperatures and oxygen pressures, one may conveniently shorten the time of oxidation without sacrificing the chemical equivalence of the ambient oxidation. Figure 3 shows results for five fuels spanning a broad range of stability when

(6) Brinkman, D. W.; Stirling, K. Q. *NIPER-222*; National Institute for Petroleum and Energy Research: Bartlesville, OK, 1987.

(7) *Distillate Fuel Storage Stability at 43 °C (110 °F)*; ASTM D 4625-86; American Society for Testing and Materials: Philadelphia, PA, 1986.

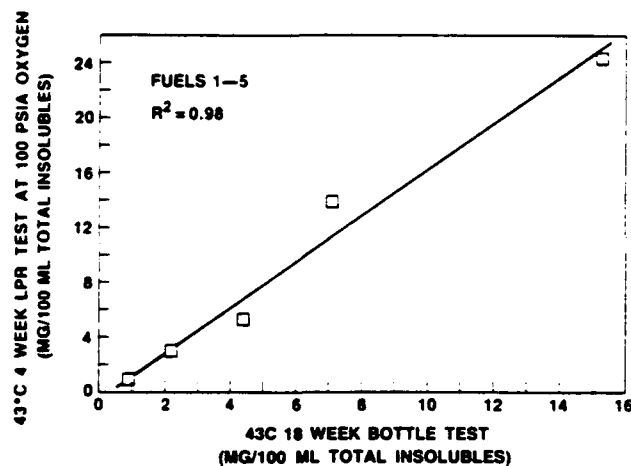


Figure 3. Comparison of 43 °C/18 weeks bottle tests with 43 °C/4 weeks LPR tests. 100 psia = 690 kPa; std dev < 1.5.

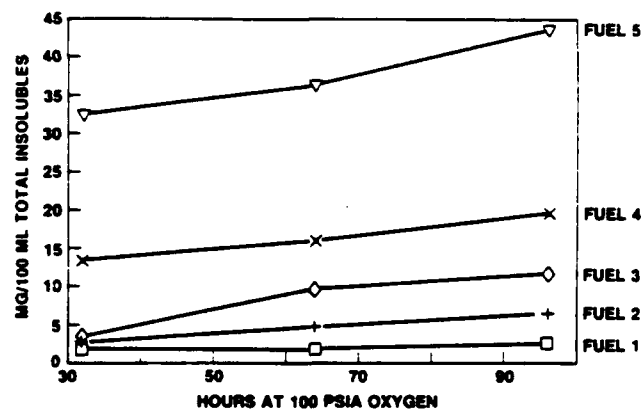


Figure 4. Effect of varying the reaction time on the five fuels: LPR data, 80 °C at 100 psia (690 kPa); hours vs total insolubles. For the average of triplicate runs the standard deviation is <1.0.

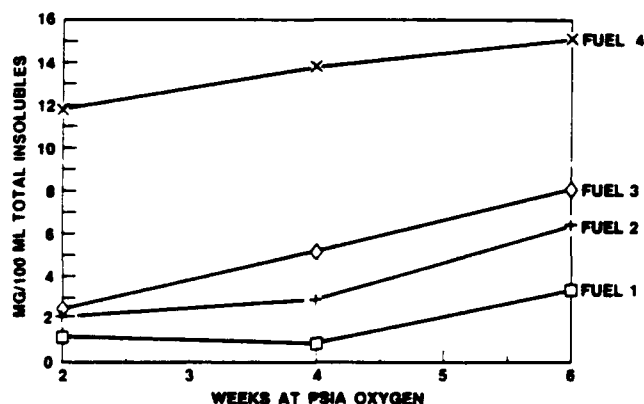


Figure 5. Effect of varying the reaction time on the five fuels: LPR data, 43 °C at 100 psia (690 kPa); weeks vs total insolubles. For the average of triplicate runs the standard deviation is <1.5.

tested at 43 °C for 18 weeks in atmospheric air bottle tests. The five fuels were also tested at 43 °C for 4 weeks at 690 kPa (100 psia) oxygen. A linear least squares correlation, R^2 , gives 0.98 for these two tests (Figure 3). The correlation between 43 °C/4 weeks/690 kPa of oxygen and 80 °C/64 h/690 kPa of oxygen is 0.97 for these same five fuels. This is a clear indication that a combination of increased temperature and increased oxygen pressure together should be quite useful to predict ambient storage stability for most middle-distillate fuels.

Figures 4 and 5 show the effects at 80 and 43 °C of varying the time at 690 kPa oxygen for five fuels. In Figure 4, the major effect is the greater ability to differentiate

Table IV. Total Insolubles Generated in Fuel A by Two Different Test Methods*

sample no.	total insolubles (43 °C/18 weeks, bottle), mg/100 mL of fuel	std dev	total insolubles (43 °C/4 weeks, 690 kPa of O ₂), mg/100 mL of fuel	std dev
2	6.6	0.1	9.5	0.1
10	7.6	0.3	9.9	0.4
11	8.2	0.3	12.1	0.7
12	8.4	0.1	12.5	0.7
3	8.5	0.2	12.2	1.1
8	10.5	0.1	13.2	0.3
6	10.7	0.6	12.4	0.4
9	10.8	0.1	13.4	0.2
1	10.9	0.4	15.0	0.2
5	11.0	0.2	13.1	0.9
4	11.2	0.4	14.4	0.2
neat	11.3	0.4	14.6	0.1
7	11.5	0.5	14.3	1.3

* Each sample number is the identical base fuel with 12 different additives. Standard deviation (std dev) refers to triplicate determinations. $R^2 = 0.80$.

Table V. Total Insolubles Generated in Fuel B by Two Different Test Methods*

sample no.	total insolubles (43 °C/18 weeks, bottle), mg/100 mL of fuel	std dev	total insolubles (65 °C/7 days, 690 kPa of O ₂), mg/100 mL of fuel	std dev
2	1.9	0.2	0.8	0.1
10	2.5	0.1	0.9	0.5
3	2.8	0.1	2.5	0.6
4	3.9	0.2	4.4	0.1
9	4.3	0.0	4.8	0.8
6	4.5	0.0	4.0	0.5
8	4.7	0.2	4.8	0.1
1	5.2	0.1	6.1	0.7
5	5.6	0.1	6.5	0.2
7	5.6	0.2	5.3	0.1
neat	6.2	0.2	6.5	0.5

* Each sample number is the identical base fuel with 10 different additives. Standard deviation (std dev) refers to triplicate determinations. $R^2 = 0.92$.

between fuels at the longer test time (96 h). If there is no need to finely differentiate fuels, the test time could be reduced to 32 h. At 43 °C (Figure 5) the same effect is noted. At 2 weeks, one is effectively predicting storage stability at ambient conditions of about 14 months.

Evaluation of Stabilizer Additives in Middle-Distillate Fuels. In addition to testing middle-distillate fuels to assess their relative stabilities, the test method should be able to differentiate the relative effectiveness of various stabilizer (antioxidant) additives added to a particular fuel to control insolubles formation. For this work, two relatively unstable fuels were chosen. Up to 12 different commercial stabilizer additives were blended into each fuel. Fuel A was tested at 43 °C for 18 weeks at atmospheric pressures and at 43 °C for 4 weeks at 690 kPa of oxygen. The results are given in Table IV, and the data are ranked on the basis of the additives effect in reducing insolubles in the atmospheric test. Two conclusions are evident. There is remarkable agreement in the ranking of additive effectiveness. Second, the oxygen overpressure test is about one-third more stringent than the bottle test; i.e., the overpressure test could have been shortened to about 3 weeks to yield the same amount of insolubles.

The results for Fuel B are given in Table V. This fuel was tested at 43 °C for 18 weeks in atmospheric pressure bottles and at 65 °C for 7 days at 690 kPa of oxygen. The R^2 values given in both Tables IV and V indicate excellent correlation between the accepted 43 °C bottles tests and

the oxygen overpressure tests.

Conclusions

Analytically, the advantages of this new method over previous methods are its greatly reduced test times and its excellent precision for replicate samples. Chemically, the advantages are its excellent correlations with lower temperature bottle tests, its good discrimination of stability between fuels, and, most importantly, its ability to accu-

ately predict insolubles formation of various fuels during ambient storage. Systematic extension of the test to higher temperatures and shorter times will be the subject of a subsequent report.

Acknowledgment. We thank the U.S. Navy Energy Research and Development Office and David Taylor Research Center for financial support of this work.

Registry No. Oxygen, 7782-44-7.

GENERAL PAPERS (POSTER SESSION)
PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
MIAMI BEACH MEETING, SEPTEMBER 10 - 15, 1989

ASSESSING DISTILLATE FUEL STORAGE STABILITY BY OXYGEN
OVERPRESSURE AT HIGHER TEMPERATURES

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INTRODUCTION

As available petroleum crudes continue to decrease in quality and the amount of catalytically cracked stock used in middle-distillate fuels increases, there is a need for an accelerated stability test which is capable of reliably assessing the long term storage stability of diesel fuels. Currently used methods for storage stability assessment suffer from a variety of drawbacks. Lower temperature bottle tests are generally the best indicators of storage stability of a particular fuel; however, meaningful results require storage at 43°C for between 12 and 18 weeks. Bottle storage tests at temperatures of 80°C and above can be completed in a reasonably short time but these tests are generally poor indicators of actual ambient fuel reactions leading to insoluble products (1).

One test widely used as a rapid assessment of fuel storage oxidative stability is the ASTM D2274 method (2). It is not a good predictor of storage stability for freshly refined middle-distillate fuels that contain any catalytically cracked stocks. The recommended fuel incubation time of 16 hours is too short for many fuels and leads to very small amounts of total insolubles which are hard to quantify. Most importantly, this test allows a potentially unstable fuel to pass the test.

A new oxygen overpressure method has been used to purposely accelerate the reactions leading to insoluble sediments formation by forcing oxygen into solution in the fuel at a pressure of 100 psig and then stressing the fuel under conditions of accelerated storage at various temperatures from 43 to 100°C. The method makes use of gravimetric determination of the total insolubles formed. This method is rapid and precise and is predictive for up to 3 years of ambient conditions. Work at 43°C for up to 4 weeks at 100 psia and at 80°C for up to 64 hours at 100 psia shows very good correlation with bottle tests done at 43°C (slight variation of ASTM D4625) (3). In an attempt to make the test shorter, recent work has been done at 90°C for 16 hours at 100 psig.

In order to test the reliability of this higher temperature method, a mini-round robin was conducted using five middle-distillate fuels tested at four different laboratories at the same 90°C/16 hr/100 psig conditions. Also, stability data for 26 MGOs and for 22 F-76 fuels from a world-wide fuel survey were obtained. Results from the higher temperature oxygen overpressure test are compared to results obtained from other standard tests. All results are tabulated in gravimetric form in mg of total insoluble sediment per 100 ml of fuel.

EXPERIMENTAL

Four of the fuels used for the mini-round robin were blends of 30% catalytically cracked light cycle oil and 70% straight run fuel. The fifth sample was a naval distillate (NATO F-76) fuel.

The fuels from the world-wide survey are coded in simple numerical order in each of the two fuel types, commercial marine gas oil (MGO) and naval distillate (NATO F-76).

Tests at 90°C were run by a new oxygen overpressure method in which 100 ml samples of filtered fuel in 125 ml brown borosilicate bottles were placed in a low pressure reactor (LPR). The reactor was sealed and pressurized with 99.5% pure oxygen to 700 kPa (100 psig). The samples were stressed, under pressure, for 16 hours at 90°C. At the end of the stress period the pressure was released slowly and the samples were removed and cooled. The amount of filterable sediment and adherent gum were determined gravimetrically and reported as total insoluble sediment weight. Samples were run in triplicate and the average values are given in mg/100 ml. Details of the method and construction of the low pressure reactor (LPR) have been described (3).

The 43°C tests were standard bottle tests using 300 ml of filtered fuel which was stored in vented brown borosilicate bottles for 18 weeks at 43°C. The filterable sediment and adherent insoluble gum were determined gravimetrically and added together for a total insoluble sediment

weight. Samples were run in duplicate and the average of the two values are reported in mg/100 ml. Details of the method are given in the literature (4).

The 95°C tests utilized the procedure outlined in ASTM D2274, which subjects the test fuel to a temperature of 95°C for 16 hours while oxygen is bubbled through the fuel.

RESULTS AND DISCUSSION

Table I shows the results obtained by four different laboratories using the oxygen overpressure method to test five middle-distillate fuels. Comparison of these data shows very good inter-laboratory agreement. When the pass/fail criteria is considered, the method correctly assessed the storage stability with the exception of one fuel.

TABLE I
MINI-ROUND ROBIN

Average of Triplicate Samples in mg/100 ml					
Fuel Code	Lab 1	Lab 2	Lab 3	Lab 4	Average
1	1.1	1.7	0.9	1.0	1.2
2	1.7	1.4	1.9	1.0	1.5
3	2.8	3.7	3.3	4.0	3.5
4	3.4	5.1	3.2	5.1	4.2
5	10.9	14.0	12.8	11.6	11.6

Pass/Fail 4.0 mg/100 ml

The results for the three storage stability tests for 26 commercial MGOs are presented in Table II. From these data it can be seen that these fuels met the pass/fail criteria set by the Naval Research Lab of 4.0 mg per 100 ml of fuel for the 43°C bottle tests (5) and 90°C oxygen overpressure tests with one exception. The 95°C test showed good agreement with the lower temperature tests when the pass/fail limit was considered, however, all of these fuels were aged fuels and the D2274 test does appear to correctly assess the stability of aged fuels that contain no cracked stock. The 95°C test did give one false fail while the LPR test did not give any but neither one of the tests gave any false passes. MGO 26 failed in all three tests so it is possible that this fuel was mistakenly categorized as an MGO.

Table III gives the results of the three storage stability tests for the 22 military F-76 fuels. These results show that these fuels are quite stable and passed both the 43°C and the 90°C tests, with one exception, but on an average they appear to be slightly more unstable than the commercial MGOs. The 95°C D2274 test was in general agreement with the lower temperature tests but it did give more false fails than the LPR test but there were no false passes when compared to the lower temperature tests. In general, the higher temperature tests are more stringent in assessing possible long term storage problems. The F-76 fuel No. 22 failed all three of the storage tests.

In comparing the pass/fail results for all 48 samples using the three different accelerated storage stability tests, there is very good interlaboratory and intertest agreement. Comparing the results of the 95°C D2274 with the lower temperature results indicated that the test gave some false fails but gave no false passes. It therefore appears that the D2274 test correctly assesses the stability of aged fuels or fuels that contain no LCO. However, the results of new LPR tests indicate that it also correctly assesses the stability of aged fuels. In addition, the LPR test also is a good predictor of the stability of fuels containing LCO.

CONCLUSIONS

The advantages of this new method over previous methods are its greatly reduced test times and its excellent precision for replicate samples. Results obtained with this method show excellent correlation with the lower temperature bottle tests. It also shows good discrimination of stability between fuels and, most importantly, it accurately predicts insolubles formation of various fuels during ambient storage.

TABLE II
COMMERCIAL MGO WORLD-WIDE FUEL SURVEY

Code No.	Sample Location	Results of Three Storage Stability Tests in mg/100 ml		
		Bottle 43°C/18 wk	LPR 90°C/16 hr	D2274
1	Pakistan	0.0	0.9	0.1
2	France	0.1	0.9	0.1
3	Japan	0.1	1.3	0.1
4	Venezuela	0.2	2.6	0.1
5	Egypt	0.2	2.2	0.2
6	U.A. E.	0.2	2.8	0.2
7	Malaysia	0.2	0.8	0.3
8	India	0.3	0.6	0.3
9	Sweden	0.3	0.7	0.1
10	Australia	0.4	0.8	0.2
11	Italy	0.4	1.2	0.2
12	Kenya	0.4	1.3	0.5
13	Belgium	0.6	1.1	0.4
14	Indonesia	0.6	2.0	0.5
15	Peru	0.6	1.7	0.6
16	Brazil	0.7	1.2	0.2
17	Malta	0.7	1.0	0.5
18	Senegal	0.8	1.0	0.6
19	Greece	0.8	1.3	0.7
20	Thailand	0.8	0.8	0.5
21	Singapore	0.9	2.2	0.4
22	England	1.0	1.4	0.5
23	Greece	1.1	1.0	0.3
24	Singapore	1.2	2.3	0.4
25	Saudi Arabia	1.4	1.4	1.9*
26	Netherlands	18.0*	12.4*	2.8*
Pass/Fail		4.0	4.0	1.5

*Values indicate a fuel fails this particular test as indicated by the pass/fail criterion at the bottom of each column.

TABLE III
NAVY DISTILLATE (NATO F-76) WORLD-WIDE FUEL SURVEY

Code No.	Sample Location	Results of Three Storage Stability Tests in mg/100 ml		
		Bottle 43°C/18 wk	LPR 90°C/16 hr	D2274
1	Scotland	0.2	0.2	0.1
2	Panama	0.2	1.1	0.4
3	Japan	0.2	1.8	0.8
4	Philippines	0.3	3.0	1.8*
5	Iceland	0.5	0.7	0.5
6	Scotland	0.4	1.8	0.4
7	England	0.5	1.2	0.8
8	Turkey	0.6	1.1	1.1
9	Scotland	0.7	0.5	0.7
10	Japan	0.7	1.3	1.1
11	Guam	0.8	2.0	1.2
12	Diego Garcia	0.8	1.0	0.9
13	Japan	0.9	3.0	1.5*
14	Cuba	1.1	0.7	0.4
15	Spain	1.1	1.7	1.0
16	Japan	1.1	2.1	1.7*
17	Bermuda	1.2	1.4	0.3
18	Azores	1.4	2.4	0.7
19	Spain	1.6	1.8	0.8
20	Crete	1.6	3.1	1.8*
21	Portugal	1.7	1.2	1.0
22	Puerto Rico	3.9*	3.9*	2.9*
	Pass/Fail	4.0	4.0	1.5

*Values indicate a fuel fails this particular test as indicated by the pass/fail criterion at the bottom of each column.

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2nd International Conference on Long Term
Storage Stabilities of Liquid Fuels
San Antonio, Texas, July 29 - August 1, 1986

LIQUID PHASE OXIDATION OF SULFUR COMPOUNDS [47]

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ABSTRACT

There is contradiction in the literature regarding the role of organosulfur compounds on the oxidative stability of middle distillate fuels. Comparison of published results is complicated by differences in a large number of variables between investigations. Variations in fuel composition, reaction surface, hydroperoxide concentration, dissolved oxygen and reaction temperature all contribute to the variation in observed results. In an effort to clarify this situation, we have examined both the oxygen and t-butyl hydroperoxide liquid phase oxidation of hexyl sulfide, dodecyl thiol, thiophenes, thiophenol in benzene and a model fuel, tetradecane. Additionally, the reaction between thiophenol and active olefins such as styrene has been studied.

INTRODUCTION

Jet fuels deteriorate in quality with time. One of the significant and undesirable changes is the formation of solid deposits which can plug nozzles, filters and coat heat exchanger surfaces. Deposit formation in fuels is triggered by autoxidation reactions and is closely associated with oxygen and/or hydroperoxide concentration. Although slight thermal degradation is known to occur in nonoxidizing atmospheres, the presence of oxygen or active oxygen species such as hydroperoxides will greatly accelerate oxidative degradation of fuels as well as significantly lower the temperature at which undesirable products are formed. Thus, the stability of middle distillate fuels is frequently dependent upon the nature of potential autoxidation pathways which can occur. Heteroatoms (oxygen, nitrogen and sulfur) and ash have been found to comprise 40 percent of such deposits (1). The sulfur content of these deposits has been found to vary from 1 to 9 percent (2). Sulfur (0.4%) is the most abundant heteroatom present in jet fuel. Deposits formed in jet fuel in the presence of oxygen contained a greater percentage of sulfur than that present in the fuel itself (3). The formation of these deposits has been attributed to the participation of thiols (mercaptans), sulfides and disulfides (4). In jet fuels that have been deoxygenated, sulfides and disulfides have been found to lead to increased solid formation (5). By contrast, it has been demonstrated that sulfur compounds in lubricating oils act as antioxidants by decomposing peroxides (6).

The rates of reactions in autoxidation schemes are dependent on hydrocarbon structure, heteroatom concentration, oxygen concentration and temperature (7-8). Catalysts and free radical inhibitors can materially alter both the rate of oxidation and the product mix (8). If sufficient oxygen is present, the hydroperoxide concentration will reach a high level. If the available oxygen concentration is low, but the temperature raised, the hydroperoxide concentration will be limited by free radical decomposition. Under these conditions, fuel degradation can be associated both with hydroperoxide formation and decomposition. The detailed mechanism of hydroperoxide decomposition is complicated since free radicals are sensitive to solvent,

structural and stereoelectronic effects.

This paper is concerned with the reaction between a primary autoxidation product, a hydroperoxide, and organosulfur compounds of the type known to be present in middle distillate fuels. Specifically, we examine the tert-butyl hydroperoxide oxidation of hexyl sulfide, dodecyl thiol, thiophene and benzothiophene in both deaerated benzene and a model fuel, tetradecane, at 120 degrees C. In addition, we examine the co-oxidation of thiophenol with olefins such as styrene under the same reaction conditions.

EXPERIMENTAL

Reagents. tert-Butyl hydroperoxide, tBHP, (90%), hexyl sulfide, dodecyl thiol, thiophene, benzothiophene, thiophenol and styrene were obtained from Aldrich Chemical Co. They were distilled in vacuo to 99.9% purity. The solvents benzene (Aldrich Gold Label) and tetradecane (Fisher certified) were refluxed and distilled from calcium hydride.

Method. The reactions were carried out in sealed borosilicate glass tubes. The reagents (typically $3-9 \times 10^{-4}$ mol of tBHP and 6×10^{-4} mol of sulfur compound in 0.6ml of solvent) were weighed into 6 in. long, 1/4-in. o.d. Pyrex tubes closed at one end and fitted at the other with a stainless steel valve via a Swagelok (Teflon ferrules) fitting. The tube was attached to a vacuum system, cooled to 77K and subjected to several freeze-pump-thaw cycles. The tube was then subsequently flame-sealed below the valve. The ullage volume (0.30 ml) was kept constant for all runs. The deaerated samples were warmed to room temperature and immersed in a Cole-Parmer fluidized sand bath. The temperature was controlled by a Leeds and Northrup Electromax III temperature controller. The total pressure during each run was estimated to be less than 1 atm for the tetradecane solvent and 5.1 atm for the runs in benzene solvent. After the reaction period the sealed tube was quenched to 77K and opened.

Samples were heated for time periods of 15, 30, 60, 120 and 180 min except for those runs with the more reactive thiols (60 min). A search of the literature gives a few examples of catalytic behavior with glass systems (9-11). However, when a glass tube was partially filled with crushed Pyrex,

thus increasing the surface area, the results at 120C for the reaction time periods were not substantially altered.

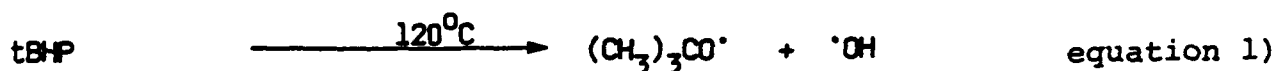
The samples were analyzed by combined GC/MS (EI mode). The GC/MS unit consisted of a Hewlett-Packard Model 5710 GC, a H-P Model 5982A mass spectrometer, and a Ribermag SADR GC/MS data system. An all glass GC inlet system was used in conjunction with a 0.31 mm x 50 m SP-2100 fused silica capillary column.

A material balance was assessed for each compound. The major peaks of the chromatogram account for approximately 81 to 99% of the original compounds. The 81% was observed only for tBHP in runs with hexyl sulfide at long reaction times. These runs also formed many partially oxidized products. The very small peaks account for another 5 to 10%. The product distribution was repeatable to 2 to 3% for each component.

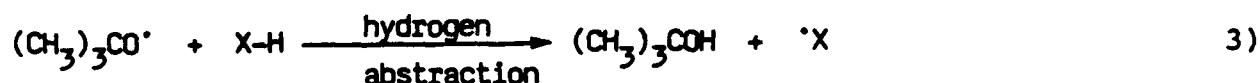
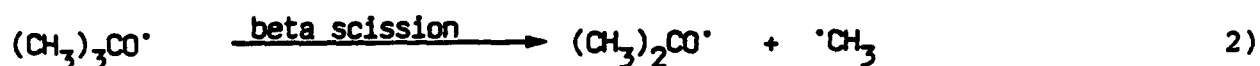
RESULTS AND DISCUSSION

The mechanism of autoinitiated tBHP decomposition can be depicted by the following equations:

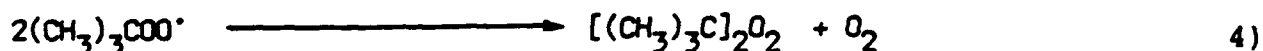
Self Initiation



Propagation



Termination



For all of the sulfur compounds, as shown in Tables 1, 2, and 3, small amounts of acetone were observed. The greater yield of t-butanol compared to acetone definitely shows that hydrogen abstraction was favored over cleavage in both benzene and tetradecane solvent under the conditions of this study. The increasing yield of acetone as reaction time increased, however, indicated that at long reaction times beta-scission was a viable competing process.

Hexyl Sulfide Products. The major product observed from the oxidation of hexyl sulfide by tBHP was hexyl sulfoxide. Its yield varied from 74.8% at 15 min to 85.3% at 30 min, gradually decreasing to 80.7% at 180 min of reaction. As shown in Table 1, other products included: Hexyl sulfone 1.2% at 15 min gradually increasing to 4.0% at 180 min; hexyl disulfide, 0.3% to 0.6%. Minor products included dihexyl thiosulfinate, 0.1%; hexanal, 0.2% at 15 min increasing to 0.3% at 60 min, decreasing to 0.2% at 120 min and disappearing at 180 min; hexene, 0.1% at 15 min, increasing to 0.3% at 120 min and decreasing to 0.2% at 180 min; and hexane, 0.1% at 15 min increasing to 0.4% at 120 min and decreasing to 0.2% at 180 min. Many trace products, yields less than 0.1%, were formed. Most of these products were partially oxidized substances that could not be readily identified by MS. An extensive discussion of the mechanism of formation for the entire product distribution can be found elsewhere (12).

The hexyl sulfoxide could result from several mechanisms. The most likely mechanism however, would be the reaction of the tBHP itself with the hexyl sulfide followed by a rapid proton transfer and O-O bond rupture, equation 6), (13).



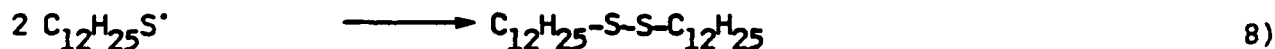
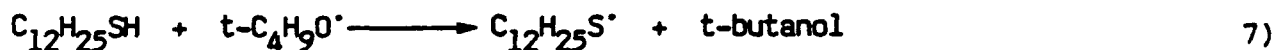
Expansion of the sulfur valence shell is probable in the processes involved in this step. Another mechanism could involve the attack of an oxygen centered radical, i.e., peroxy on sulfur followed by a beta scission (14).

The resulting sulfoxide once formed is quite stable, as can be seen from

the modest decrease in yield at extended reaction times, Table 1. The sulfoxide oxidation product, hexyl sulfone, varied in the present work from an initial 1.2% at 15 min to 4.0% at 180 min of reaction. This slight increase compared to the yield of hexyl sulfoxide at 180 min (80.7%) illustrates the resistance of the alkyl sulfoxide to oxidation by tBHP. The oxidation of a sulfoxide to a sulfone is believed to proceed by a mechanism similar to that for the sulfoxide formation.

Dodecyl thiol products. The major product from the oxidation of dodecyl thiol by tBHP was dodecyl disulfide, 74.4% at 15 min increasing to 78.8% at 30 min and then decreasing to 74.1% at 60 min. Other oxidation products included: dodecyl sulfoxide, 2.3% at 15 min decreasing to 2.1% at 60 min; dodecyl sulfone, 0.9% at 15 min increasing to 1.7% at 60 min. Minor reaction products observed were: Dodecyl sulfide, 1.9% at 15 min decreasing to 1.4% at 60 min; dodecanal, 0.6% at 15 min increasing to 1.1% at 60 min; dodecane, 0.1% at 15 min increasing to 0.4% at 60 min; and trace (less than 0.1%) amounts of dodecyl thiosulfinate.

When thiols are oxidized by air or peroxides, disulfides are the major product regardless of the presence or absence of a catalyst (15). The mechanism of thiol oxidation has been the subject of discussion for many years. Some reports support ionic mechanisms while others support a radical mechanism. We propose that a t-butoxy or peroxy radical generated from tBHP abstracts the thiol hydrogen, equation 7). Rapid dimerization, equation 8), then follows generating the major product dodecyl disulfide.



Dodecyl thiol in tetradecane. The reaction was similar both in benzene and tetradecane, but minor differences were found. The product mix, other than solvent products, was identical. Differences included slightly lowered yield

of t-butanol in tetradecane, 72.1% vs 76.7% in benzene, while the yield of acetone 8.6% was almost double that observed in benzene, 4.7%. This serves as an indication that equation 2) in the tBHP decomposition scheme was more favored in aliphatic solvent. The dodecyl thiol was slightly more reactive in the tetradecane. The dodecyl disulfide was formed in greater yield, 80.6% compared to 74.1% in benzene. Products observed from tetradecane solvent participation were tetradecanones and tetradecanols. These were minor products and are reported as totals of all isomers, because the isomers elute in an overlapping pattern. Tetradecanones for a 60 min stress were 0.3% and the tetradecanols were found to be 0.6%. As a contrast, no oxygenated products of the benzene solvent were observed.

Thiophene products. Thiophene compounds investigated were thiophene, 2,5-dimethyl thiophene and benzothiophene with tBHP in benzene solvent. Thiophene and its methylated analog do not yield simple, easy to identify products. In fact, no GC identifiable products were formed in any of the runs. Rather, an intractable water soluble solid results at all reaction times. Detailing the reaction mechanism for the thiophenes is further complicated in that the solid product itself is not thermally stable (16). Products identified in the solid from both thiophene and 2,5-dimethyl thiophene included the sulfoxide, the sulfone, and the condensation product, thionaphthene 1:1 dioxide, along with the 2,5-dimethyl analogs. The 2,5-dimethyl thiophene was considerably more reactive than the thiophene as measured by thiophene disappearance. The increased reactivity of the substituted thiophenes can be explained by the availability of the "lone-pair" sulfur electrons (17). The observed increase in ease of oxidation can likewise be attributed to this increased availability of the sulfur electrons.

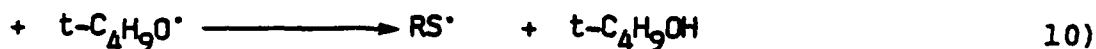
The thiophene ring system can survive moderate oxidizing conditions. However, if the ring is attacked, it generally breaks down to oxalic or other substituted carboxylic acids with the sulfur being converted to sulfuric acid (18). With tBHP, no evidence of ring opening was observed.

Benzothiophene was the least reactive sulfur compound studied. In the presence of tBHP, benzothiophene yields the sulfone as the major product and a trace of the sulfoxide product.

Thiophenol and styrene with excess oxygen or tBHP in benzene. The reaction

of thiophenol with an active olefin, such as styrene, in excess oxygen provides a useful variant of thiol chemistry termed "co-oxidation" (19). The major product, Table 3, observed was the addition product, 1-phenyl-(2-phenylthiyl) ethane; at 15 min its yield was 41.3% increasing to 71.2% at 30 min and decreasing to 68.3% at 60 min. Other products included: the 1-phenyl-(1-phenylthiyl) ethane isomer, 0.5% at 15 min increasing to 3.5% at 60 min; the dimer of styrene, 1,4-diphenyl butane, 0.2% at 60 min; 1-phenyl-(2-phenylethyl) sulfoxide, 1.7% at 15 min increasing to 5.8% at 60 min; 1,4-diphenyl-(2-phenylthiyl) butane; 1.1% at 15 min decreasing to 0.9% at 60 min; phenyl thiosulfonate, 0.3% at 60 min. Trace products (< 0.1%) included: 1-phenyl-(2-phenylethyl) sulfone, styrene oxide, phenyl methyl sulfide and 2-ethyl toluene. Table 3 also gives the results for a 15 min stress with tBHP. The product slate was about the same for both oxygen and tBHP, but the yields of individual components varied significantly. The major product, 1-phenyl-(2-phenylthiyl) ethane increased to 62.4% and the sulfoxide product was more than doubled at 3.9%.

In the presence of oxygen or tBHP, the following reactions can occur with a thiol.



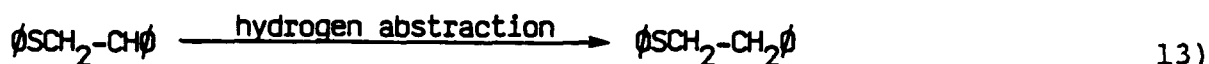
Where R = alkyl or aryl

The thiyl radical once formed can then react with an active olefin such as styrene. Specifically for thiophenol and styrene the reaction could be described by the following equations.



or





Equation 12) was the preferred pathway since it resulted in the more thermodynamically stable radical. The major product, 1-phenyl-(2-phenylthiyl) ethane, then resulted by hydrogen abstraction, equation 13). The other radical generated, equation 11), leads to one of the observed minor products, 1-phenyl-(1-phenylthiyl) ethane,

By a mechanism similar to equation 6), the sulfoxide forms from the 1-phenyl-(2-phenylthiyl) ethane.

SUMMARY

The observed deterioration of fuels can manifest itself in many ways, including the formation of insoluble deposits both in storage and in an engine fuel system or nozzle. Reactive species in petroleum fuels which may be involved in the deterioration are alkyl sulfides, thiols, aromatic thiols, thiophenes and hydroperoxides. Trace quantities of compounds such as sulfonic acids have also been implicated in deposit formation. This paper specifically examined the hydroperoxide or oxygen induced oxidation of hexyl sulfide, dodecyl thiol, thiophenol, thiophenes and the "co-oxidation" of thiophenol with styrene in both deaerated benzene and tetradecane solvents at 120C. The product mix was studied over various reaction times of 15 min to 180 min. For each compound, a common slate of products was observed for all reaction time periods. The yield of individual components, however, varied significantly with reaction time.

The major product derived from the tBHP was t-butanol. Other observed tBHP products included methane, acetone and isobutylene.

The major product from the hexyl sulfide oxidation was hexyl sulfoxide. Other sulfur containing products were hexyl sulfone, hexyl disulfide and hexyl

thiosulfinate. The major product from dodecyl thiol was dodecyl disulfide. Oxidized products included dodecyl sulfoxide, dodecyl sulfide and dodecyl sulfone. The thiophenes gave the sulfoxide, sulfones and the Diels-Alder product from these reactive species. The products formed from the thiophenes were observed to be water soluble. From the co-oxidation of thiophenol with styrene, the major product was 1-phenyl-(2-phenylthiyl) ethane. Other products included: 1-phenyl-(1-phenylthiyl) ethane and the oxidized products phenyl-(2-phenylethyl) sulfoxide and phenyl thiosulfonate.

Solvent participation was noted by the formation of toluene from benzene and tetradecanones and tetradecanols from tetradecane. No oxygenated products of benzene were observed.

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Table 1

Mole % Conversion for the Reaction of Hexyl Sulfide with
tert-Butyl Hydroperoxide in Benzene Solvent at 120°C.

	<u>CONVERSION (MOLE %)</u>				
	<u>Reaction Time (Min.)</u>				
	15	30	60	120	180
<u>TBHP Products^a</u>					
Acetone	1.0	1.5	1.5	1.5	2.5
t-Butanol	55.5	59.5	65.9	69.8	75.4
di-t-butyl peroxide	0.5	0.7	0.7	0.7	1.0
<u>Hexyl sulfide Products^b</u>					
Hexyl sulfoxide	74.8	85.9	81.6	81.9	80.7
Hexyl sulfone	1.2	1.4	3.0	3.4	4.0
Hexyl disulfide	0.3	0.5	0.5	0.5	0.6
Hexanal	0.2	0.2	0.3	0.2	—
Hexane	0.1	0.1	0.3	0.4	0.3
Hexene	0.1	0.1	0.1	0.3	0.2
Hexyl thiosulfinate	0.1	0.1	0.1	0.1	—
<u>Gaseous Products</u>					
Methane	0.8	0.8	1.0	1.4	1.6
Isobutylene	4.2	3.9	3.6	3.1	2.7
<u>Unreacted</u>					
TBHP	28.9	23.9	8.7	3.9	1.8
Hexyl Sulfide	22.5	13.9	8.2	3.9	2.9
<u>Trace Products</u>					
	6.7	7.8	9.7	10.1	8.1

a. based on the starting moles of TBHP

b. based on the starting moles of hexyl sulfide

c. summation of small peaks

Table 2

Mole % Conversion for the Reaction of Dodecyl Thiol with
tert-Butyl Hydroperoxide in Benzene and Tetradecane at 60 Min
at 120°C.

	<u>CONVERSION (MOLE %)</u>			
	Reaction Time (Min.)			
	15	30 <u>Benzene</u>	60	60 <u>Tetradecane</u>
<u>TBHP Products^a</u>				
Acetone	4.7	4.4	4.7	8.6
t-Butanol	59.2	65.4	76.7	72.1
di-t-Butyl peroxide	1.6	1.6	1.9	1.6
<u>Dodecyl thiol Products^b</u>				
Dodecyl disulfide	74.4	78.8	74.1	80.6
Dodecyl sulfide	1.9	1.8	1.4	2.9
Dodecyl sulfoxide	2.3	2.1	2.1	3.8
Dodecyl sulfone	0.9	1.5	1.7	2.2
Dodecanal	0.6	0.7	1.1	0.9
Dodecane	0.1	0.3	0.4	0.6
<u>Gaseous Products</u>				
Methane	0.9	1.3	1.4	0.9
Isobutylene	3.6	3.3	3.0	4.3
<u>Unreacted</u>				
TBHP	19.7	12.6	1.3	0.9
Dodecyl thiol	15.6	7.3	3.4	0.2
<u>Trace Products^c</u>				
	4.6	6.7	9.4	10.6

a. based on the starting moles of TBHP

b. based on the starting moles of dodecyl thiol

c. summation of small peaks

Table 3

Mole % Conversion for the Reaction of Styrene with Thiophenol
and Oxygen in Benzene Solvent at 120°C.

	<u>CONVERSION (MOLE %)</u>			
	<u>Reaction Time (Min)</u>			<u>tBHP</u>
	<u>Oxygen</u>			
	15	30	60	15
<u>Addition products^a</u>				
1-phenyl-(2-phenylthiyl) ethane	41.3	71.2	68.3	62.4
1-phenyl-(1-phenylthiyl) ethane	0.5	1.5	3.5	1.4
phenyl-(2-phenylethyl) sulfoxide	1.7	4.9	5.8	3.9
phenyl disulfide	1.1	1.7	2.3	1.7
1,4-diphenyl-(2-phenylthiyl) butane	1.1	0.9	0.9	1.9
phenyl thiosulfonate	---	0.2	0.3	1.1
1,4-diphenyl butane	---	---	0.2	0.2
<u>Unreacted</u>				
Styrene	24.7	2.0	1.6	13.2
Thiophenol	33.2	7.1	5.8	25.2
<u>Trace products^b</u>	2.2	4.3	6.6	3.2

a. based on the starting moles of styrene

b. summation of small peaks

Liquid-Phase Oxidation of Hexyl Sulfide and Dodecanethiol by *tert*-Butyl Hydroperoxide in Benzene and Tetradecane

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The *tert*-butyl hydroperoxide (tBHP) initiated oxidation of hexyl sulfide and dodecanethiol was examined in deaerated benzene and a model fuel, tetradecane, at 120 °C. Although kinetically complex, it was possible to relate the product distribution to a few competing reactions. The product mix was determined for several reaction time periods. The product slate was about the same for all time periods, but yields of individual components varied significantly with reaction time. The major lower molecular weight product was *tert*-butyl alcohol. Gaseous products included methane and isobutylene. The major product from dodecanethiol was dodecyl disulfide. Oxygenated products included dodecyl sulfoxide and dodecyl sulfone. From hexyl sulfide, the major product was hexyl sulfoxide. Other products included hexyl sulfone, hexyl thiosulfinate, and hexyl disulfide. Solvent participation was noted by the formation of toluene in benzene solvent and tetradecanones and tetradecanols in tetradecane solvent.

There is contradiction in the literature as to the role of organosulfur compounds on the oxidative stability of middle distillate fuels. Comparison of published results is complicated by differences in a large number of variables between investigations. Variation in fuel composition, reaction surface, hydroperoxide concentration, dissolved oxygen, and reaction temperature all contribute to the variation in observed results.

Fuel degradation is observed to occur under long-term low-temperature storage conditions (storage stability) as well as short-term, high-temperature stress (thermal oxidative stability) (Hazlett, 1980; Taylor, 1974; Scott, 1965; Taylor and Wallace, 1967). The latter situation is encountered under flight conditions where fuel serves as a coolant on its path to the combustion chamber. Although slight thermal degradation is known to occur in nonoxi-

dizing atmospheres, the presence of oxygen or active oxygen species such as hydroperoxides will greatly accelerate oxidative degradation of fuel as well as significantly lower the temperature at which undesirable products are formed. Thus, the stability of middle distillate fuels is frequently dependent upon the nature of potential autoxidation pathways which can occur.

Thompson et al. (1949) found that sulfur and disulfides were active promoters of instability in stored fuels, while aliphatic mercaptans and sulfides had little effect on the same fuels. Schwartz et al. (1964) reported that alkyl mercaptans, sulfides, and disulfides accelerated the formation of deposits in cracked gasolines.

Taylor and Wallace (1967) found that deposits formed in jet fuel in the presence of oxygen contained a greater percentage of sulfur than that present in fuel itself. The formation of these deposits has been attributed to the participation of mercaptans, sulfides, and disulfides (Taylor and Wallace, 1968a). In jet fuels that have been deoxygenated, sulfides and disulfides have been found to lead to increased solid formation (Taylor and Wallace, 1968b; Wallace, 1964).

By contrast, it has been demonstrated that sulfur compounds in lubricating oils act as antioxidants by decomposing peroxides (Denison, 1944). The autoxidation of compounds such as squalene has been found to be inhibited by the presence of alkyl sulfides or disulfides (Bernard et al., 1958).

The rates of reactions in autoxidation schemes are dependent on hydrocarbon structure, heteroatom concentration, oxygen concentration, and temperature (Morse, 1957; Hiatt and Irwin, 1968; Howard et al., 1968; Denisov, 1974). Catalyst and free-radical inhibitors can materially alter both the rate of oxidation and the product mix (Benson, 1964; Richardson, 1965; Mushrush et al., 1985).

If sufficient oxygen is present, the hydroperoxide concentration will reach a high level. If the available oxygen concentration is low but the temperature is raised, the hydroperoxide concentration will be limited by free-radical decomposition. This regimen (low oxygen and increasing temperature) is similar to the environment found in an aircraft fuel system. Under these conditions, fuel degradation can be associated both with hydroperoxide formation and/or decomposition.

The thermal decomposition of alkyl hydroperoxides, unlike that of dialkyl peroxides, is complex (Walling, 1957; Hiatt and Irwin, 1968; Gray and Williams, 1959). At temperatures greater than 120 °C, *tert*-butyl hydroperoxide, tBHP, decomposes rapidly by an autoinitiated pathway (Hiatt, 1980; Mosher and Durham, 1960). The major reaction pathway in the 120 °C (or higher) decomposition of tBHP involves attack by free radicals present in the solution. The detailed mechanism of hydroperoxide decomposition is complicated since free radicals are sensitive to structural, solvent, and stereoelectronic effects.

This paper is concerned with the reaction between a primary autoxidation product, a hydroperoxide, and organo sulfides and mercaptans. Specifically, we examine the *tert*-butyl hydroperoxide oxidation of hexyl sulfide and dodecyl mercaptan in both deaerated benzene and a model fuel, tetradecane, at 120 °C. The reactions were studied for time periods from 15 to 180 min. Additionally, we have developed reaction conditions and an analytical method of high reproducibility which may be applicable to the study of other hydroperoxide oxidative processes.

Experimental Section

Reagents. *tert*-Butyl hydroperoxide, tBHP, (90%), hexyl sulfide and dodecyl mercaptan were obtained from

Aldrich Chemical Co. They were distilled in vacuo to 99.9% purity. The solvents benzene (Aldrich Gold Label) and tetradecane (Fisher certified) were refluxed and distilled from CaH₂.

Method. The reactions were carried out in sealed borosilicate glass tubes. The reagents (typically 3–9 × 10⁻⁴ mol of tBHP and 6 × 10⁻⁴ mol of hexyl sulfide or 6 × 10⁻⁴ mol of dodecyl mercaptan in 0.6 mL of solvent) were weighed into 6-in.-long, 1/4-in.-o.d. borosilicate tubes closed at one end and fitted at the other with a stainless steel valve via a Swagelok (Teflon ferrules) fitting. The tube was attached to a vacuum system, cooled to 77 K, and subjected to several freeze-pump-thaw cycles. The tube was then subsequently flame-sealed below the valve. The ullage volume (0.30 mL) was kept constant for all runs. The deaerated samples were warmed to room temperature and immersed in a Cole-Parmer fluidized sand bath. The temperature (120 °C) was controlled by a Leeds and Northrop Electromax III temperature controller. The total pressure during each run was estimated to be less than 1 atm for the tetradecane solvent (all boil above 120 °C) and 5.1 atm for the runs in benzene solvent. After the reaction period, the sealed tube was quenched to 77 K and opened. The tube was capped and warmed to room temperature, and the internal standards were added. The solution was transferred to a screw cap vial (Teflon cap liner) and stored at 0 °C until analysis. Since a typical chromatogram required 90 min, two internal standards were added. One, *p*-xylene, afforded quantitation for peaks with short retention times and a second, 1-phenyltridecane, for the peaks with longer retention times.

Samples were heated for time periods of 15, 30, 60, 120, and 180 min except for those runs with the more reactive mercaptan (60 min maximum). All tubes were subjected to the same cleaning procedure. They were filled with toluene, cleaned with a nylon brush, rinsed with toluene twice and then with methylene chloride, and dried in air at 150 °C for 8 h. A search of the literature gives a few examples of catalytic behavior with glass systems (Benson, 1964; Kirk and Knox, 1960; Hiatt et al., 1968); however, when a glass tube was filled with crushed borosilicate glass, thus increasing the surface area, the results at 120 °C for the above time periods were not substantially altered.

The samples were analyzed by two techniques, both based on gas chromatography. Peak identification for both techniques was based on retention time matching with standards and mass spectrometry. In the first, a Varian gas chromatograph Model 3700 with flame ionization detector (FID) and equipped with a 50-m × 0.20-mm-i.d. wall-coated open tubular (OV-101) fused silica capillary column gave the necessary resolution to distinctly separate the individual components. A carrier gas flow of 1 mL/min was combined with an inlet split ratio of 60:1, a temperature program with an initial hold at 50 °C for 8 min, and a ramp for 4 deg/min to a final temperature of 260 °C.

In the second technique, gases formed during the reaction were analyzed by using a Perkin-Elmer Model Sigma 2 gas chromatograph equipped with a 6-ft 5A molecular sieve column or a 4-ft Porapak/S column. For the gas analysis, the column was operated at 55 °C. The chromatogram was recorded and integrated on a Hewlett-Packard Model 3390A reporting integrator. For this procedure, the valve was left on the tube during the reaction at 120 °C, and after the appropriate period, the tube valve was connected directly to a GC gas sampling valve via a Swagelok connection. An external standard was used for calibration. A pressure gauge measured the pressure in the sample loop at the time of analysis.

Table I. Mole Percent Conversion for the Reaction of Hexyl Sulfide with *tert*-Butyl Hydroperoxide in Benzene Solvent at 120 °C

	conversion, mol %, at reaction time, min				
	15	30	60	120	180
TBHP products^a					
acetone	1.0	1.5	1.5	1.5	2.5
<i>tert</i> -butyl alcohol	55.5	59.5	65.9	69.8	75.4
di- <i>tert</i> -butyl peroxide	0.5	0.7	0.7	0.7	1.0
hexyl sulfide products^b					
hexyl sulfoxide	74.8	85.9	81.6	81.9	80.7
hexyl sulfone	1.2	1.4	3.0	3.4	4.0
hexyl disulfide	0.3	0.5	0.5	0.5	0.6
hexanal	0.2	0.2	0.3	0.2	
hexane	0.1	0.1	0.3	0.4	0.3
hexene	0.1	0.1	0.1	0.3	0.2
hexyl thiosulfinate	0.1	0.1	0.1	0.1	
gaseous products					
methane	0.8	0.8	1.0	1.4	1.6
isobutylene	4.2	3.9	3.6	3.1	2.7
unreacted					
TBHP	28.9	23.9	8.7	3.9	1.8
hexyl sulfide	22.5	13.9	8.2	3.9	2.9
trace products ^c	6.7	7.8	9.7	10.1	8.1

^aBased on the starting moles of TBHP. ^bBased on the starting moles of hexyl sulfide. ^cSummation of small peaks.

A material balance was assessed for each compound. The major peaks of the chromatogram account for approximately 81–99% of the original compounds. The 81% was observed only for tBHP in runs with hexyl sulfide at long reaction times. These runs also formed many partially oxidized products. The very small peaks account for another 5–10%. The product distribution was repeatable to 2–3% for each component.

Results and Discussion

The thermal decomposition of an alkyl peroxide is complex. At temperatures of 120 °C or greater, tBHP decomposes by an autoinitiated pathway (Howard, 1983). The major reaction pathway in the 120 °C decomposition of tBHP, however, involves its attack by free radicals in the solution. The detailed mechanism of tBHP decomposition is highly dependent upon the specific reaction conditions employed since radical reaction behavior is sensitive to structural, solvent, and stereoelectronic effects.

The results in Table I illustrate that the product distribution from the reaction of tBHP with hexyl sulfide in deaerated benzene solvent can be conveniently divided into tBHP- and sulfide-derived products. The quantities in Table I are based on percent conversion from the moles of reactants originally present. Products derived solely from hexyl sulfide are calculated on the basis of the starting amount of hexyl sulfide. The tBHP-derived products (for example, *tert*-butyl alcohol) are similarly calculated based on the starting amount of tBHP. Oxidation products (i.e., tBHP + hexyl sulfide) are calculated on the basis of moles of hexyl sulfide. The values in Table II were likewise calculated using dodecanethiol.

From tBHP, the major product was *tert*-butyl alcohol. Small amounts of acetone, methane, isobutylene, and the tBHP radical termination product di-*tert*-butyl peroxide were also observed. Hexyl sulfide derived products included hexane, hexene, and hexenal; oxidized products included the major product hexyl sulfoxide along with hexyl sulfone and hexyl disulfide. From dodecanethiol, Table II, products included the major product dodecyl disulfide along with dodecyl sulfoxide, dodecyl sulfide, dodecyl sulfone, dodecane, and dodecanal.

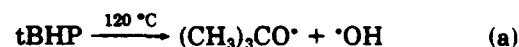
Solvent participation was noted by the formation of trace quantities of toluene and other substituted benzenes from benzene and tetradecanols and tetradecanones from tetradecane.

Table II. Mole Percent Conversion for the Reaction of Dodecanethiol with *tert*-Butyl Hydroperoxide in Benzene Solvent at 120 °C

	conversion, mol %, at reaction time, min		
	15	30	60
TBHP products^a			
acetone	4.7	4.4	4.7
<i>tert</i> -butyl alcohol	59.2	65.4	76.7
di- <i>tert</i> -butyl peroxide	1.6	1.6	1.9
dodecanethiol products^b			
dodecyl disulfide	74.4	78.8	74.1
dodecyl sulfide	1.9	1.8	1.4
dodecyl sulfoxide	2.3	2.1	2.1
dodecyl sulfone	0.9	1.5	1.7
dodecanal	0.6	0.7	1.1
dodecane	0.1	0.3	0.4
gaseous products			
methane	0.9	1.3	1.4
isobutylene	3.6	3.3	3.0
unreacted			
TBHP	19.7	12.6	1.3
dodecanethiol	15.6	7.3	3.4
trace products ^c	4.6	6.7	9.4

^aBased on the starting moles of TBHP. ^bBased on the starting moles of dodecanethiol. ^cSummation of small peaks.

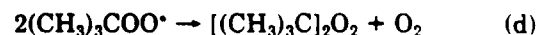
tBHP Products. The mechanism of autoinitiated tBHP decomposition can be depicted as self-initiation



propagation



termination



Small amounts of acetone were formed ranging from 1.5% in the presence of hexyl sulfide to 4.7% with dodecanethiol at 60 min. The greater yield of *tert*-butyl alcohol compared to acetone definitely shows that hydrogen abstraction was favored over cleavage in benzene solvent under the con-

ditions of this study. The increasing yield of acetone indicated, however, that at long reaction times β scission was a viable competing process.

Gaseous Products. The gaseous products formed included isobutylene, methane, and a trace amount (0.1%) of ethane. No free oxygen was observed in any of the runs. As indicated in Table I, isobutylene was 4.2% initially and decreased to 2.7% at 180 min. Methane increased from 0.8% at 15 min to 1.6% at 180 min. For dodecanethiol, Table II, isobutylene was 3.6% initially and decreased to 3.0% at 60 min. Methane increased from 0.9% at 15 min to 1.4% at 60 min.

Isobutylene probably resulted from the acid-catalyzed dehydration of *tert*-butyl alcohol. Acids can be generated by several pathways as will be shown later. The decreasing yield of isobutylene was not surprising in light of the many pathways open to a reactive olefin in a radical environment.

The yield of methane was similar to that of acetone for the oxidation of hexyl sulfide. This was an expected result since they both form via β scission of the alkoxy radical (reaction b). The reactive methyl radical easily abstracts hydrogen to yield methane rather than reacting with other radicals present in the system. This accounted for the low yield of methyl-radical-derived products.

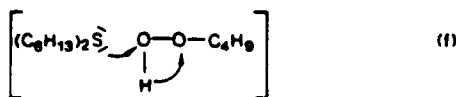
The lack of measured oxygen does not mean that it was not formed. It could form from a terminating reaction of two *tert*-butyl peroxy radicals and then be consumed immediately by any of several pathways.

Hexyl Sulfide Products. The major product observed from the oxidation of hexyl sulfide by tBHP was hexyl sulfoxide. Its yield varied from 74.8% at 15 min to 85.9% at 30 min, gradually decreasing to 80.7% at 180 min of reaction. Other products included hexyl sulfone, 1.2% at 15 min, gradually increasing to 4.0% at 180 min; hexyl disulfide, 0.3% to 0.6%; and a trace amount of dihexyl thiosulfinate (0.1%).

Minor products formed were hexanal, 0.2% at 15 min, increasing to 0.3% at 60 min, decreasing to 0.2% at 120 min, and disappearing at 180 min; hexene, 0.1% at 15 min, increasing to 0.3% at 120 min and decreasing to 0.2% at 180 min; and hexane, 0.1% at 15 min, increasing to 0.4% at 120 min, and decreasing to 0.2% at 180 min.

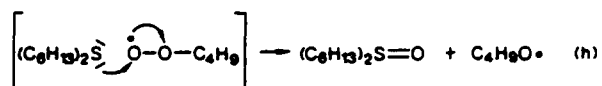
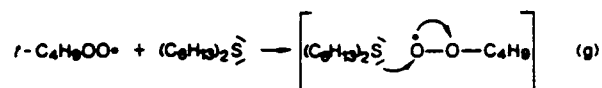
Many trace products, yields less than 0.1%, were formed. Most of these products were partially oxidized substances that could not be readily identified by MS. Trace products that were identified included hexanoic acid, *tert*-butyl hexyl sulfide, ethyl hexyl sulfide, and hexyl thiosulfonate.

The hexyl sulfoxide could result from several mechanisms. The most likely pathway to the sulfoxide would be from the reaction of the *tert*-butyl hydroperoxide itself (step f) with the hexyl sulfide followed by a rapid proton transfer and O-O bond rupture (Curci et al., 1966). Expansion of the sulfur valence shell is probable in the processes involved in step f. A second mechanism involves attack of an oxygen-centered radical, i.e., peroxy, on sulfur followed by a β scission (Rahman and Williams, 1970).



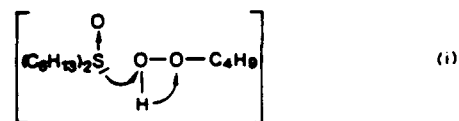
On the basis of bond dissociation energy consideration alone, the *tert*-butyl peroxy radical is probably the least reactive and most plentiful radical present in the system (Muahrush et al., 1985). This would favor an oxidation reaction, steps g and h, involving this radical over a termination involving the very reactive alkoxy radical which would be expected, rather, to propagate the chain by re-

acting with tBHP to renew the peroxy radical concentration.



The resulting sulfoxide once formed is quite stable, as can be seen from the modest decrease in yield at extended reaction times. The sulfoxide oxidation product, hexyl sulfone, varied in the present work from an initial 1.2% at 15 min to 4.0% at 180 min of reaction. This slight increase compared to the yield of hexyl sulfoxide at 180 min (80.7%) definitively illustrates the resistance of the alkyl sulfoxide to oxidation by tBHP.

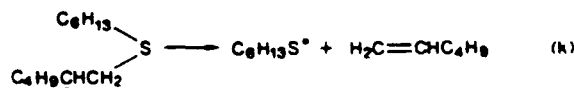
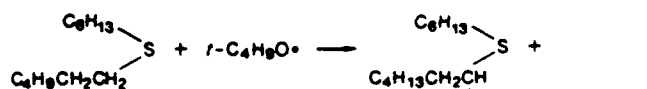
The further oxidation of a sulfoxide to a sulfone, step i, is believed to proceed by a mechanism similar to that for sulfoxide formation from an alkyl sulfide (Curci et al., 1966).



The formation of an alkyl sulfone is a facile reaction only in the presence of a strong oxidant or when the reaction is catalyzed by transition-metal ions (Henbest and Khan, 1968).

The cleavage of a C-S bond in sulfides is known to occur in thermal and photochemical reactions (Calvert and Pitts, 1966). The most direct means of generating a sulfur-centered radical is the homolysis of a bond to sulfur. However, most simple alkyl sulfides are thermally quite stable (C-S bond dissociation energies are ca. 74 kcal/mol) and quite unreactive toward oxygen (Correa and Riley, 1985).

In the presence of *tert*-butyl hydroperoxide, the *tert*-butyl peroxy or *tert*-butoxy radicals generated could abstract the hydrogen α or β , step j, to the sulfur of the hexyl sulfide. Attack by an alkoxy radical is the more probable pathway, since it is a more energetic species than the *tert*-butyl peroxy radical. An $\text{S}_{\text{H}}2$ mechanism and a subsequent β scission (step k) yields both a thiyl radical and hexene (Migita et al., 1973; Ohno and Ohnishi, 1971) from the β radical. Trace products, observed from this step were a shorter chain sulfide and a C_4 hydrocarbon, can be assigned to the α -radical sequence. An $\text{S}_{\text{H}}2$ mechanism and a subsequent β scission (step k) yields both a thiyl radical and hexene (Migita et al., 1973; Ohno and Ohnishi, 1971). Product distribution, Table I, indicates that the β -radical formation is the preferred over the α radical as a reaction pathway.



The observed hexanal can be formed by several reaction pathways. Among these are the thermal rearrangement

of the hexyl sulfoxide (Barnard-Smith and Ford, 1965) or, more likely, the coupling of a *tert*-butyl peroxy radical with the α radical formed in step j. Scission would then result in an aldehyde and an alkoxy radical.

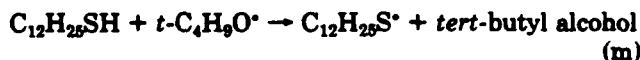
The hexyl disulfide product was formed by dimerization of the thiyl radical. Thiyl radical products were in low concentration at all reaction time periods (Table I). Consequently, the thiyl termination product, hexyl disulfide (step l), was a minor product at all reaction times (1% at 180 min).



The other minor observed product, hexyl thiosulfinate, probably was the result of oxidation of the disulfide. Only trace amounts, 0.1% at all reaction times, of this oxy-sulfur compound were detected.

Dodecanethiol Products. The major product observed from the oxidation of dodecanethiol by tBHP was dodecyl disulfide, 74.4% at 15 min, increasing to 78.8% at 30 min, and then decreasing to 74.1% at 60 min. Other oxidation products included dodecyl sulfoxide, 2.3% at 15 min, decreasing to 2.1% at 60 min; dodecyl sulfone, 0.9% at 15 min, increasing to 1.7% at 60 min; and trace (less than 0.1%) amounts of dodecyl thiosulfinate. Other minor reaction products found were dodecyl sulfide, 1.9% at 15 min, decreasing to 1.4% at 60 min; dodecanal, 0.6% at 15 min, increasing to 1.1% at 60 min; and dodecane 0.1% at 15 min, increasing to 0.4% at 60 min.

When thiols are oxidized by air or peroxides, disulfides are the major product regardless of the presence or absence of a catalyst (Wallace, 1966; Schrauzer and Sibert, 1970). The mechanism of thiol oxidation has been the subject of discussion for many years. Some reports support ionic mechanisms, while others support radical processes (Cohen and Aktpis, 1966; Wagner and Zepp, 1974). The results in the present work, Table II, support a radical mechanism. We propose that a *tert*-butoxy or peroxy radical generated from tBHP abstracts the thiol hydrogen (step m). The rapid dimerization, step n, then follows generating the major product dodecyl disulfide.



By contrast, hydrogen abstraction by a thiyl radical to yield a thiol is only observed in cases involving very stable thiyl radicals with active hydrogen donors (Kice, 1973). The thiyl radical once formed has not been observed to undergo β scission to yield a thione and an alkyl radical (Van Swet and Kooyman, 1968). In the present work, thiones were not detected, even in trace amounts, in the product mix.

The dodecyl sulfoxide probably resulted from the same pathways mentioned for hexyl sulfoxide, steps f-h. The dodecyl sulfoxide yield was not observed to decrease significantly due to further oxidation to the sulfone, similar to step i, or, for example, its subsequent reaction with the starting thiol.

The minor products observed from the oxidation of dodecanethiol were dodecyl sulfide, dodecanal, and dodecane. In a mixture as complicated as this, it is difficult to write a detailed mechanism for the formation of these minor products. For example, at a 30-min reaction period, 6.7 mol % represents the partially oxidized products. Do the minor products form from these products or is another mechanism operating? The results do not permit a definitive answer.

Table III. Mole Percent Conversion for the Reaction of Dodecanethiol with *tert*-Butyl Hydroperoxide in Benzene and Tetradecane Solvents at 120 °C

	conversion, mol %, at 60 min	
	benzene	tetradecane
TBHP products ^a		
acetone	4.7	8.6
<i>tert</i> -butyl alcohol	76.7	72.1
di- <i>tert</i> -butyl peroxide	1.9	1.6
dodecanethiol products ^b		
dodecyl disulfide	74.1	80.6
dodecyl sulfoxide	2.1	3.8
dodecyl sulfone	1.7	2.2
dodecyl sulfide	1.4	2.9
dodecanal	1.1	0.9
dodecane	0.4	0.6
gaseous products		
methane	1.4	0.9
isobutylene	3.0	4.3
solvent product		
toluene	0.1	
tetradecanones		0.3
tetradecanols		0.6
unreacted		
TBHP	1.3	0.9
dodecanethiol	3.4	0.2
trace products ^c	9.4	10.6

^a Based on the starting moles of TBHP. ^b Based on the starting moles of dodecanethiol. ^c Summation of small peaks.

Dodecanethiol in Tetradecane. Table III depicts the results for a 60-min reaction in both deaerated benzene and tetradecane solvent. The reaction was similar in both solvents, but minor differences were found. The product mix other than solvent products was identical. Differences included a slightly lowered yield of *tert*-butyl alcohol in tetradecane, 72.1% vs. 76.7% in benzene, while the yield of acetone, 8.6%, was almost double that observed in benzene, 4.7%. This was an indication that step b in the tBHP decomposition scheme was more favored in aliphatic solvent and that this step proceeded at a greater rate. The dodecanethiol was slightly more reactive in tetradecane solvent. The major product, dodecyl disulfide, was formed in greater yield, 80.6% compared to 74.1% in benzene. Oxidation products of dodecanethiol were consequently observed in higher yields in tetradecane solvent.

Products observed from tetradecane solvent participation were tetradecanones and tetradecanols. These were minor reaction products. The tetradecanones and tetradecanols are reported as totals of all isomers, because the isomers elute in an overlapping pattern. Further complicating the analysis is the coelution of the tetradecanones and tetradecanols. To analyze for these substances, the alcohols were silylated with Tri-Sil (Sweely et al., 1963). Alcohols react to form silyl ethers which have a higher volatility and thus a different retention time, permitting a separation of tetradecanones and tetradecanols. No oxygenated products of the benzene solvent were observed.

Summary

Alkyl sulfides, alkanethiols, and hydroperoxides are reactive species which are known to be present in turbine fuels. Sulfur (0.4%) is the most abundant heteroatom present in middle distillate fuels. The observed deterioration of fuels can manifest itself in many ways, including the formation of insoluble deposits both in storage and in an engine fuel system or nozzle. Trace quantities of compounds such as sulfonic acids have also been implicated in deposit formation. This paper specifically examined the *tert*-butyl hydroperoxide oxidation of hexyl sulfide and

dodecanethiol in both deaerated benzene and tetradecane solvents at 120 °C. The variation in product mix was studied over reaction times of 15–180 min. A common variety of products was observed for all reaction time periods. The yield of individual components, however, varied significantly with reaction time.

The major product derived from tBHP was *tert*-butyl alcohol. Other observed tBHP products included methane, acetone, and isobutylene.

The major product from the hexyl sulfide oxidation was hexyl sulfoxide. Other sulfur-containing products were hexyl sulfone, hexyl disulfide, and hexyl thiosulfinate. The major product from dodecanethiol was dodecyl disulfide. Oxidized products included dodecyl sulfoxide, dodecyl sulfide, and dodecyl sulfone. Trace products included hexene, hexane, and hexanal from hexyl sulfide and dodecane and dodecanal from dodecanethiol.

Solvent participation was noted by the formation of toluene from benzene and tetradecanones and tetradecanols from tetradecane. No oxygenated products of the benzene were observed.

Registry No. tBHP, 75-91-2; $(C_6H_{13})_2S$, 6294-31-1; $(C_6H_{13})_2S=O$, 2180-20-3; C_6H_6 , 71-43-2; $C_{12}H_{26}SH$, 112-55-0; $(C_{12}H_{25})_2S_2$, 2757-37-1; tetradecane, 629-59-4.

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Received for review March 31, 1986

Accepted December 8, 1986



NRL Memorandum Report 5985

Results of the Third CRC Cooperative Test Program on Hydroperoxide Potential of Jet Fuels

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May 21, 1987

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited.		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
4. PERFORMING ORGANIZATION REPORT NUMBER(S) NRL Memorandum Report 5985			7a. NAME OF MONITORING ORGANIZATION		
6a. NAME OF PERFORMING ORGANIZATION Naval Research Laboratory	6b. OFFICE SYMBOL (if applicable) Code 6180	7b. ADDRESS (City, State, and ZIP Code)			
6c. ADDRESS (City, State, and ZIP Code) Washington, DC 20375-5000		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER			
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Naval Air Propulsion Center	8b. OFFICE SYMBOL (if applicable)	10. SOURCE OF FUNDING NUMBERS			
8c. ADDRESS (City, State, and ZIP Code) P.O. Box 7176 Trenton, NJ 08628		PROGRAM ELEMENT NO. 63724N	PROJECT NO. 20838	TASK NO. 251950	WORK UNIT ACCESSION NO. DN580-087
11. TITLE (Include Security Classification) Results of the Third CRC Cooperative Test Program on Hydroperoxide Potential of Jet Fuels					
12. PERSONAL AUTHOR(S) Hall,* J. M. and Hazlett, R. N.					
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 2/86 TO 1/87	14. DATE OF REPORT (Year, Month, Day) 1987 May 21		15. PAGE COUNT 47	
16. SUPPLEMENTARY NOTATION *Geo-Centers, Inc., Newton Centre, MA 02159					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Jet fuels Cooperative experiments		
			Peroxidation		
			CRC tests		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
Eight laboratories conducted tests on nine fuels to evaluate an accelerated storage stability test procedure for measuring the hydroperoxide forming potential of jet fuels. Based on the cooperative work reported herein the 65°C accelerated test readily distinguishes between stable and unstable fuels in approximately 3 weeks stress time. Consequently it appears useful for screening jet fuels for their long-time oxidation stability. Thus this test is recommended as a Go-No-Go test and this is what was sought in these studies. On the other hand, the variability of results within and between laboratories would seem to preclude its use as a precise quantitative tool.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL R. N. Hazlett			22b. TELEPHONE (Include Area Code) (202) 767-3559	22c. OFFICE SYMBOL Code 6180	

AMERICAN CHEMICAL SOCIETY
Division of Fuel Chemistry

Volume 32, No. 1
Preprints of Papers Presented at
Denver, Colorado
April 5-10, 1987

REACTIONS INVOLVING HYDROPEROXIDE FORMATION IN JET FUELS

By

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INTRODUCTION

Hydroperoxides in jet fuels attack elastomers in aircraft fuel systems with consequent leaks or inoperation of fuel controls. Problems have been associated with Jet A, JP-4, and JP-5 jet fuels. The first reported incidents occurred with Jet A in Japan in 1962 when fuel hoses of neoprene or nitrile rubber cracked and leaked (1). In 1976 the U.S. Navy experienced attack on neoprene fuel pump diaphragms on jets operating in the Philippines (2). More recent problems have been encountered in Thailand with JP-4 when Buna-N O-rings cracked and leaks from fuel pumps occurred. All incidents involved fuels which had been hydrotreated and had peroxide levels from 1 to 8 milliequivalents of active oxygen per kilogram of fuel (peroxide number, P.N.).

Examination of fuels refined by different processes has indicated that significantly higher peroxide concentrations exist in fuels which have been severely hydrotreated. The U.S. Navy has continuing concerns with this topic due to increasing hydrogenation for jet fuel processing. In addition, shale-derived fuel production will involve more extensive and higher pressure hydrotreatment. It has been demonstrated that sulfur compounds in lubricating oils act as antioxidants by decomposing peroxides (3). It is believed that hydrogenation is responsible for removing natural inhibitors, including sulfur compounds, to peroxide formation.

Hydroperoxide concentration has been found to be a factor in fuel instability. Fuel degradation is observed to occur under long-term low-temperature storage conditions (storage stability) as well as short-term high-temperature stress (thermal oxidative stability) (4-7). The latter situation is found during flight conditions, where fuel serves as a coolant on its path to the combustion chamber. Although slight thermal degradation is found to occur in nonoxidizing atmospheres, the presence of oxygen or active species such as hydroperoxides will greatly accelerate oxidative degradation

as well as significantly lower the temperature at which undesirable changes in fuel take place. The rates of reactions in autoxidation schemes are dependent on hydrocarbon structure, heteroatom concentration, oxygen concentration, and temperature (8-10). If sufficient oxygen is present, the hydroperoxides will reach a high level. If the available oxygen is low, but the temperature raised, the hydroperoxide concentration will be limited by free radical decomposition. Under these conditions, fuel degradation can be associated with both hydroperoxide formation and decomposition.

Several solutions to the problem of fuel peroxidation have been suggested. Antioxidants have been mandated by some authorities, particularly for hydrocracked fuels. Viton elastomers and other materials have been proposed as replacement materials but their low temperature properties make them marginal for aircraft use. Clay filtration has been suggested as a means for field removal of hydroperoxides but this treatment has been found to be too expensive (2). Although hindered phenols have given satisfactory peroxide control, those phenols which are permitted in the jet fuel specifications were developed for gum control in gasoline. Their effectiveness for peroxide control was found to be marginal, depending on structure (11). It is necessary to investigate the relationship of temperature on peroxide concentration in fuel as it relates to peroxide formation as well as fuel stability.

Sulfur is the most abundant heteroatom present in jet fuels (up to 0.4% allowed by specifications). Deposits formed in jet fuel in the presence of oxygen contain a higher percentage of sulfur than that present in the fuel itself (12). The formation of these deposits has been attributed to the participation of sulfides, disulfides, and thiols (mercaptans) (13). In jet fuels that have been deoxygenated, sulfides and disulfides have been found to lead to increased solid formation (14). Examination of the reactions between both alkyl and aromatic thiols with tert-butylperoxide have indicated that aromatic thiols are more reactive than other classes of sulfur compounds with hydroperoxides. The reaction of thiophenol with tBP was found to produce trace amounts of sulfonic acid while depleting the amount of both reactants in solution (15). It is desirable to test the relationship between sulfur compound reactivity and peroxide formation using an aryl thiol as a model dopant under accelerated storage conditions.

This paper reports on the hydroperoxide formation in hydrocracked JP-5 jet fuels at various temperatures, in both the presence and absence of antioxidants. The results of using thiophenol as a model dopant for four stable, hydrocracked jet fuels under 65C accelerated storage conditions and the effect on peroxide formation versus added sulfur concentration are also reported.

EXPERIMENTAL

Fuels and Reagents. The fuels examined for the temperature effects study included a shale JP-5 with antioxidant, a hydrocracked petroleum JP-5 with and without antioxidant, and a petroleum JP-4 without antioxidant. The four fuels investigated for the sulfur versus peroxide concentration study were the same shale-II JP-5 used in the temperature study (J-22), a Jet-A, a hydrocracked JP-5 and a hydrofined JP-5 from Esso Petroleum Corporation, Ontario, Canada. Thiophenol was obtained from Aldrich Chemical Co. and was

distilled in vacuo to 99.9% purity.

Method. Tests were carried out in brown borosilicate glass bottles, 500 ml total capacity, capped with teflon liners, containing 300 ml of fuel per bottle. Test for temperature effects on peroxidation were carried out at 43, 65, 80 and 100C. To test the relationship of added sulfur to peroxide concentration, duplicate samples of the four other fuels were prepared, with 0.10 and 0.05% sulfur in the form of thiophenol weighed into one sample of each fuel. Stress tests were conducted at 65C for five weeks. Samples were analyzed weekly for peroxide concentration by ASTM method D3703-95. Sulfur concentration was monitored weekly with a Tracor 565 gas chromatograph equipped with a sulfur specific 700A Hall electrolytic conductivity detector.

RESULTS AND DISCUSSION

Rolls-Royce defined the peroxidation potential of a fuel with an accelerated 100C test for 24 hours (1). The relevance of this test to ambient storage conditions was of interest, so stress tests were conducted at 43, 65, 80 and 100C.

The peroxide numbers for the different temperatures are listed in Table I. The stress times were selected according to the Arrhenius relation, namely doubling (or halving) of reaction rate for every 10°C change in temperature, and then modified based on previous results from our laboratory. Thus time factors of 30:1 and 10:1 were used for 43C and 65C test instead of the calculated values of 52:1 and 11.3:1. Columns in the Table are labeled "equivalent hours at 100C." The actual storage times at the several temperatures are shown at the end of the data table.

Data for the two JP-5 samples, with and without oxidant are plotted in the Figures 1 and 2. Time factors for multiplying the abscissa are listed on the graphs for the various temperatures.

The data reveal appreciable variation in peroxide number as a function of time, temperature and fuel. Two fuels, petroleum JP-5 and JP-4 both without antioxidant, show fair agreement between the temperatures based on equivalent time periods. In at least two cases (Fuels 3 and 4), peroxide levels at all times were lower at the lower temperatures. With the two fuels containing antioxidants (Fuels 1 and 3), results at the lower temperatures were quite different from results at the higher temperatures, and therefore not predictable from the higher temperature test.

Important difference in fuel response to temperature is illustrated by comparing Figures 1 and 2. The hydrocracked JP-5 without antioxidant (Fuel 2), Figure 1, produces peroxide at a linear rate with respect to time for the initial portion of the tests. The time factors are also reliable in the 1-3 day equivalent time frame.

Shale-II JP-5 (Fuel 1) containing an antioxidant behaves quite differently. Peroxidation follows an exponential rate. The most probable explanation for this observation is the depletion with time of the antioxidant. The rate of peroxidation was not predictable from the time factors. Specifically, the rate was much faster at 80 and 100C than the low temperature data would indicate.

Based on these observations, the 65C stress test was chosen for the sulfur concentration study. Added sulfur concentrations of 0.10 and 0.05% sulfur (weight/volume) were used. The data for these tests are represented in

Tables II and III respectively.

For both sulfur concentrations, the control samples, fuel only, exhibited similar behavior. Differences in actual peroxide numbers between the two tests could be attributed to thermodynamic differences in the ovens that were used. It was interesting that in Jet A peroxide formation occurred in a cyclic pattern. The petroleum derived JP-5 samples formed peroxides at a greater rate than the shale JP-5 or Jet A.

The most important aspect of both sets of data was that the samples doped with sulfur in the form of thiophenol did not undergo peroxidation as rapidly as the fuel by itself. In fact, thiophenol addition eliminated ROOH present in starting samples in most tests, and after the first week in the other tests. In the samples doped with 0.10% sulfur, peroxide formation was not observed until the fourth week of the stress test. When the concentration of added sulfur was reduced (halved) peroxide formation began one week earlier with three of the fuels, indicating a relationship between added sulfur concentration and peroxide formation (or peroxide inhibition). Neither of the doped samples of the hydrocracked JP-5 showed evidence of peroxide formation throughout the duration of the tests.

The sulfur concentration of the samples was found to decrease throughout the tests as measured by the sulfur specific detector on the gas chromatograph. The emergence of new peaks on the chromatogram indicated the formation of new sulfur-containing compounds, however concentrations were too low to permit identification. Since aromatic thiols are quite reactive in the presence of peroxides, the thiophenol most likely undergoes oxidation by the peroxide species. These reactions could be similar to other observed liquid phase oxidation reactions that take place between thiophenol and t-butyl hydroperoxide (15).

CONCLUSIONS

The effect of adding sulfur in the form of an aromatic thiol, thiophenol, was significant to peroxide formation. Thiophenol has been found to act as an inhibitor or controller of peroxide formation in Jet A, Shale-II derived JP-5, and petroleum derived JP-5. Hydro-treated jet fuels exhibited higher peroxide formation and concentration than other fuels. Hydro-treatment reduces the sulfur content of the fuel, which removes those naturally occurring sulfur compounds which act as inhibitors to peroxide formation. There appeared to be a "critical concentration" of sulfur at which peroxide formation was inhibited. If this concentration of sulfur was decreased or consumed, peroxidation took place in an uncontrolled manner.

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Fuel	Temp. °C	Time Factor		Equivalent Hours at 100°C		Peroxidation at Various Temperatures		Actual Storage Times		All Fuels	
		30:1	4:1	1:1	30:1	4:1	1:1	30:1	4:1	30:1	4:1
1. Shale JP-5 w/A.O.	43	-	-	-	1.03	1.45	2.53	1.05	1.10	1.03	1.45
	65	-	-	-	1.80	2.44	4.33	1.80	2.44	1.80	2.44
	80	-	-	-	1.10	1.45	2.53	1.10	1.45	1.10	1.45
	100	-	-	-	1.03	1.45	2.53	1.03	1.45	1.03	1.45
2. Petroleum JP-5	43	-	-	-	1.03	1.45	2.53	1.03	1.45	1.03	1.45
	65	-	-	-	1.80	2.44	4.33	1.80	2.44	1.80	2.44
	80	-	-	-	1.10	1.45	2.53	1.10	1.45	1.10	1.45
	100	-	-	-	1.03	1.45	2.53	1.03	1.45	1.03	1.45
3. Petroleum JP-5 w/A.O.	43	-	-	-	1.03	1.45	2.53	1.03	1.45	1.03	1.45
	65	-	-	-	1.80	2.44	4.33	1.80	2.44	1.80	2.44
	80	-	-	-	1.10	1.45	2.53	1.10	1.45	1.10	1.45
	100	-	-	-	1.03	1.45	2.53	1.03	1.45	1.03	1.45
4. Petroleum JP-4 No A.O.	43	-	-	-	1.03	1.45	2.53	1.03	1.45	1.03	1.45
	65	-	-	-	1.80	2.44	4.33	1.80	2.44	1.80	2.44
	80	-	-	-	1.10	1.45	2.53	1.10	1.45	1.10	1.45
	100	-	-	-	1.03	1.45	2.53	1.03	1.45	1.03	1.45

TABLE II
Jet Fuel Peroxidation at 65°C with Added Thiophenol
0.10% Sulfur Dopant

Week	Shale-II JP-5		Jet A		Hydrocracked JP-5		Hydrofined JP-5	
	Control	Doped	Control	Doped	Control	Doped	Control	Doped
0	0.25	0.25	0.00	0.00	0.00	0.00	0.16	0.16
1	0.24	0.00	0.19	0.00	0.18	0.00	0.57	0.00
2	0.31	0.00	0.44	0.00	0.49	0.00	1.16	0.00
3	0.37	0.00	0.19	0.00	1.10	0.00	1.73	0.00
4	0.51	1.29	0.40	0.51	4.08	0.00	5.38	0.26
5	0.48	0.97	0.26	0.40	10.82	0.00	8.47	0.25

TABLE III
Jet Fuel Peroxidation at 65°C with Added Thiophenol
0.05% Sulfur Dopant

Week	Shale-II JP-5		Jet A		Hydrocracked JP-5		Hydrofined JP-5	
	Control	Doped	Control	Doped	Control	Doped	Control	Doped
0	0.69	0.00	0.12	0.00	0.10	0.00	0.24	0.00
1	0.70	0.00	0.18	0.00	0.60	0.00	1.58	0.00
2	0.73	0.00	0.16	0.00	2.09	0.00	6.01	0.00
3	0.94	0.45	0.28	0.54	12.41	0.00	37.66	0.61
4	1.11	0.68	0.26	0.22	25.27	0.00	62.05	0.51
5	1.56	0.88	0.29	0.81	56.67	0.00	59.92	0.25

FIGURE 1

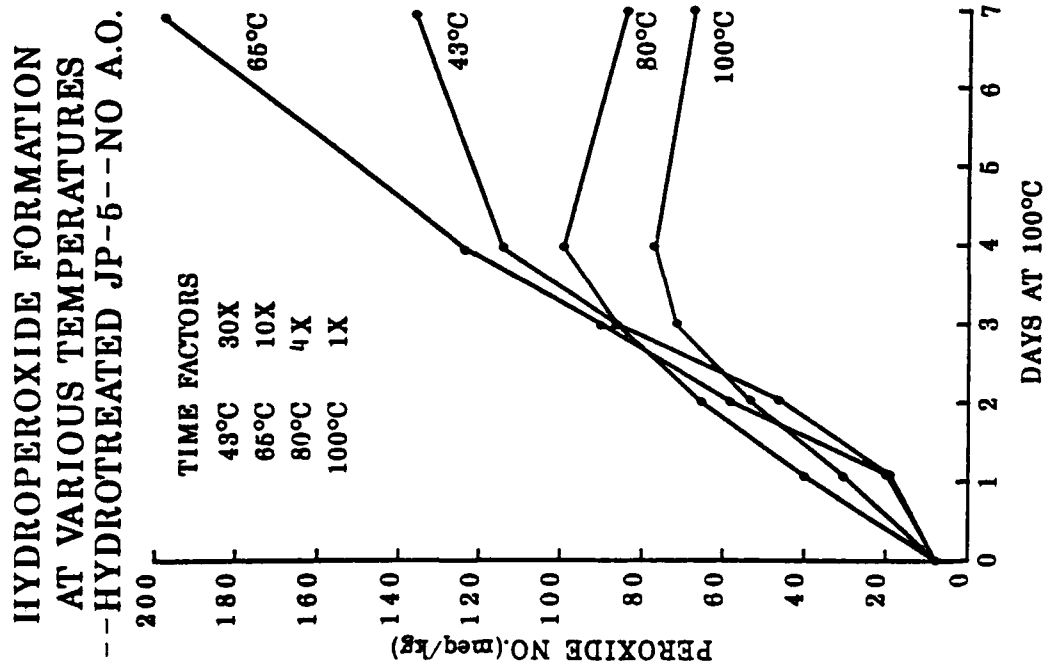
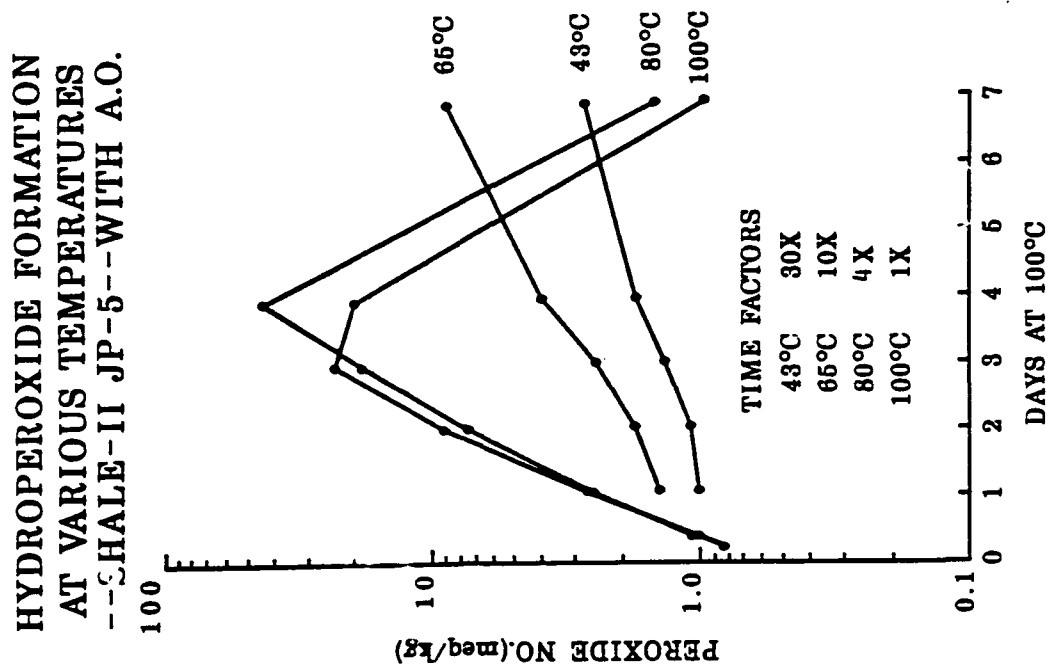


FIGURE 2



AMERICAN CHEMICAL SOCIETY
Division of Fuel Chemistry

Volume 32, No. 1

Preprints of Papers Presented at
Denver, Colorado
April 5-10, 1987

LIQUID PHASE OXIDATION OF THIOPHENOL AND OLEFINS
BY OXYGEN AND t-BUTYL HYDROPEROXIDE

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INTRODUCTION

In supersonic Navy aircraft, aerodynamic heating can cause metal skin temperature to rise to high levels. At Mach 2.7, it has been estimated that the fuel in an uninsulated wing tank could reach 430F (1). Hydrocarbon fuels subjected to such temperatures have been shown to undergo considerable degradation. This observed degradation can be manifested by the formation of deposits on fillers, in nozzles and on combustor surfaces (2-5). These deposits are the consequence of free radical autooxidation reactions. Trace levels of sulfur compounds have been found to influence the deposit formation process. It has been shown that jet fuels low in sulfur content are relatively stable and that fuels of high sulfur content are fairly unstable (6,7). Presently, it is not possible to relate the observed instability to specific sulfur species. Heteroatoms (oxygen, nitrogen and sulfur) and ash have been found to comprise 40 percent of such deposits (8). The sulfur content of these deposits has been found to vary from 1 to 9% (9). Sulfur (0.4%) is the most abundant heteroatom present in the fuel itself.

Deposits formed in jet fuel in the presence of oxygen contained a greater percentage of sulfur than that present in the fuel itself (10). In previous work in our laboratory, it was observed that thiols, sulfides and aldehydes could be readily oxidized by hydroperoxides (11-13).

The rates of the reactions in autooxidation schemes are dependent on structure, oxygen concentration and temperature (14-16). Catalysts, free radical initiators and inhibitors can materially alter both the rate and the oxidation pathways (17,18).

Although slight thermal deterioration of fuel is known to occur in non-oxidizing atmospheres, the presence of elemental oxygen will greatly

accelerate the deterioration of fuel properties as well as significantly lower the temperature at which undesirable products are formed. Thus the stability of jet fuels is frequently dependent upon the nature of potential autooxidation pathways which can take place under aircraft operating conditions.

If sufficient oxygen is present, the hydroperoxide concentration will reach a high level. If the available oxygen is low, but the temperature is raised, the hydroperoxide level will be limited by free radical decomposition. This regimen, low oxygen and increasing temperature, is similar to the environment in an aircraft fuel system. In this situation fuel degradation can be associated with the reaction of hydroperoxides with the other moieties in the fuel.

This paper is concerned with the reaction between a primary autooxidation product, a hydroperoxide, with thiophenol in the presence of the active olefins, indene and styrene. The reactions were carried out in deaerated benzene with t-butyl hydroperoxide or in benzene with an oxygen overpressure.

EXPERIMENTAL

Reagents. tert-Butyl hydroperoxide, tBHP, (90%), thiophenol, indene and styrene were obtained from Aldrich Chemical Co. They were distilled in vacuo to 99.9% purity. Benzene (Aldrich Gold Label) was refluxed and distilled from calcium hydride.

Method. The reactions were carried out in sealed borosilicate glass tubes. The reagents (typically 3-9x10⁻⁴ mol of tBHP and 6x10⁻⁴ mol of both thiophenol and olefin in 0.6ml of solvent) were weighed into 6 in. long, 1/4-in. o.d. borosilicate glass tubes closed at one end and fitted at the other with a stainless steel valve via a Swagelok (teflon ferrules) fitting. The tube was attached to a vacuum system, cooled to 77K and subjected to several freeze-pump-thaw cycles. For those runs in oxygen, the solution was bubbled extensively with oxygen, a 40 - 45 psi over pressure of oxygen was then added. The tube was then subsequently flame-sealed below the valve. The ullage volume (0.30 ml) was kept constant for all runs. The deaerated samples were warmed to room temperature and immersed in a Cole-Parmer fluidized sand bath. The temperature was controlled by a Leeds and Northrup Electromax III temperature controller. The total pressure during each run was estimated to be 5.1 atm for the runs in benzene solvent. After the reaction period (15, 30, 60 min) the sealed tube was quenched to 77K and opened.

The samples were analyzed by combined GC/MS (EI mode). The GC/MS unit consisted of a Hewlett-Packard Model 5710 GC, a H-P Model 5982A mass spectrometer, and a Albermag SADR GC/MS data system. An all glass GC inlet system was used in conjunction with a 0.31 mm x 50 m SP-2100 fused silica capillary column.

Gases formed during the reaction were analyzed using a Perkin-Elmer Model Sigma 2 gas chromatograph equipped with a 6 ft. 5A Molecular Sieve column. In this mode, the column was operated at 55C. The chromatogram was recorded and integrated on a Hewlett-Packard Model 3390A reporting integrator. An external standard was used for calibration. A gauge measured the pressure in the sample loop at the time of analysis.

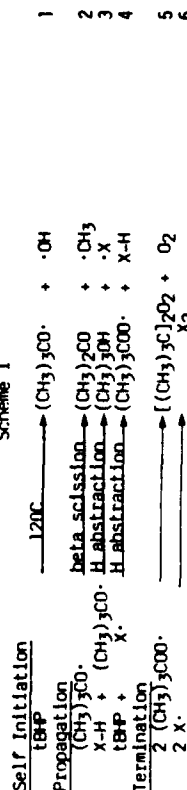
RESULTS AND DISCUSSION

At temperatures of 120C or greater, tBHP decomposes rapidly by an autoinitiated pathway (19,20). The major reaction pathway in the 120C decomposition of tBHP involves attack by free radicals present in the solution. The detailed mechanism is complicated since free radicals are sensitive to structural, solvent and stereoelectronic effects.

The results in Tables 1 and 2 illustrate the product distribution for the tBHP, styrene, indene and thiophenol derived products. The quantities in the tables are expressed in terms of mole percent conversion from the moles of reactant originally present. Products derived solely from tBHP (for example acetone) are calculated based on the starting amount of tBHP. The same is true for products from the thiophenol (i.e., phenyl disulfide). Oxidation products are calculated based on the moles of olefin originally present.

From tBHP, the major product was t-butanol. Small amounts of acetone, methane, isobutylene and the tBHP radical termination product, di-t-butyl peroxide, were also observed. The mechanism of autoinitiated tBHP decomposition can be depicted in Scheme I.

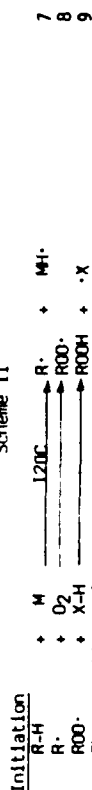
Scheme I



The greater yield of t-butanol compared to acetone, Tables 1 and 2, definitively show that hydrogen abstraction was favored over scission under the conditions of this study. Solvent participation was noted by the formation of trace quantities of toluene and other substituted benzenes from benzene.

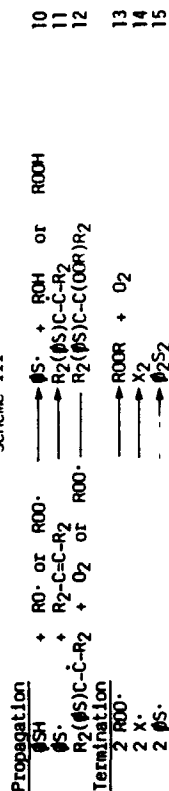
The reaction mechanism, initiation step, in the presence of molecular oxygen can be depicted by Scheme II.

Scheme II



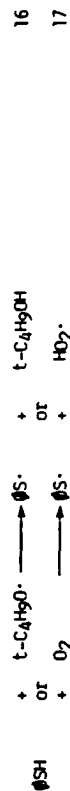
The reaction of the hydroperoxide, step 9, would then follow the same pathways as indicated for steps 1-6 in Scheme I. The reaction of thiophenol and active olefins with oxygen provides a useful co-variant of thiol chemistry termed "co-oxidation" (21). The radicals that result from either Schemes I or II could subsequently react with either the thiophenol and/or olefins that are present in the reaction mixture. This process can be described by Scheme III.

Scheme III

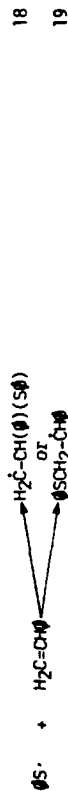


Styrene - thiophenol reaction products The major product, Table 1, observed was the addition product 1-phenyl-2-phenylthiyl ethane. Its yield at 15 min was 41.3% increasing to 71.2% at 30 min and decreasing to 68.3% at 60 min. Other products included: the 1-phenyl-1-phenylthiyl ethane isomer, 0.5% at 15 min increasing to 3.5% at 60 min; the dimer of styrene, 1,4-diphenyl butane, 0.2% at 60 min; 1-phenyl-2-phenylethyl sulfide, 1.7% at 15 min increasing to 5.8% at 60 min; 1-phenyl-2-phenylethyl sulfoxide, 1.1% at 15 min decreasing to 0.9% at 60 min and phenyl thiosulfonate, 0.3% at 60 min. Trace products (0.1% yield) included: phenyl disulfide, 1-phenyl-2-phenylethyl sulfone, styrene oxide, phenyl methyl sulfide and 2-ethyl toluene. The product slate was the same for both oxygen and tBHP, but the yields of individual components varied significantly. In general, the tBHP reaction was faster as would be expected, than the reaction starting with elemental oxygen. In the presence of tBHP, the major product, 1-phenyl-2-phenylthiyl ethane, increased to 62.4% at 15 min and the sulfoxide product was more than doubled at 3.9% for the same time period.

The reaction of molecular oxygen or tBHP with thiophenol can proceed by the following chain mechanism (steps 16-17). The t-butoxy radical is more reactive than the t-butyl peroxy radical and consequently is a more probable reactant in such a mechanism (11).



The thiyl radical once formed can then react by several different pathways. In a solution with a high molar concentration of an active olefin, the reaction would proceed as shown in steps 18-19.



Equation 19 was the preferred pathway since it resulted in the more thermodynamically stable radical. The major product, 1-phenyl-2-phenylthiyl ethane, then results by hydrogen abstraction. The other radical generated, equation 18, leads to one of the observed minor products, 1-phenyl-1-phenylthiyl ethane. Other pathways could involve the reaction of radicals generated in steps 11 or 12 with additional olefin to give products of high molecular weight.

The sulfoxide product, phenyl-2-phenylethyl sulfoxide, could result from

several mechanisms. The most likely mechanism however, would be the reaction of the hydroperoxide with the sulfide formed in step 19. Expansion of the sulfur valence shell is probable in the processes involved in this step. The resulting sulfoxide once formed is quite stable, as can be seen from the gradual increase in yield, Table 1, at extended reaction time.

Table 1
Mole % Conversion for the Reaction of Styrene with Thiophenol
and Oxygen or t-Butyl Hydroperoxide at 120°C

Addition Products ^a	CONVERSION (MOLE%)			
	Reaction Time (Min)			
	Oxygen	15	60	tBHP
1-phenyl-2-phenylthiyl ethane	71.2	41.3	68.3	62.4
1-phenyl-1-phenylthiyl ethane	1.5	0.5	3.5	1.4
phenyl-2-phenylethyl sulfoxide	4.9	1.7	5.8	3.9
phenyl disulfide	1.7	1.1	2.3	1.7
1,4-diphenyl-2-phenylthiyl butane	0.9	1.1	0.9	1.9
phenyl thiosulfonate	0.2	---	0.3	1.1
1,4-diphenyl butane	---	---	0.2	0.2
Unreacted				
styrene	2.0	34.7	1.6	13.2
thiophenol	7.1	33.2	5.8	25.2
tBHP Products				
acetone	---	---	---	0.9
t-butanol	---	---	---	57.1
di-t-butyl peroxide	---	---	---	0.1
isobutylene	---	---	---	2.3
Trace Products ^b	4.3	2.2	6.6	3.2

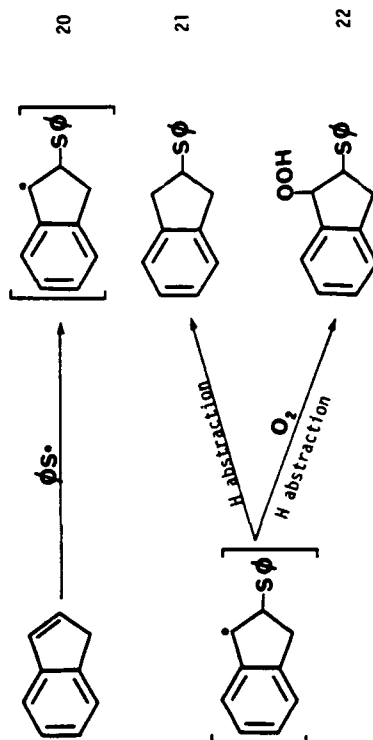
a. based on the starting moles of styrene

b. summation of small peaks

Indene - thiophenol reaction products. The products from this co-oxidation reaction can be conveniently divided into primary and secondary reaction products. As shown in Table 2, the major primary reaction product was 2-phenylthiyl indan, 39.4 mole % at 15 min increasing to 58.2% at 30 min and then decreasing to 55.8% at 60 min. The secondary products were formed

by the spontaneous rearrangement of either 2-phenyl thyl-1-indanyl or 1-phenylthiyl-2-indanyl hydroperoxide. Neither hydroperoxide isomer was detected by GC/MS. The observed products from this rearrangement were: 2-phenylthiyl-1-indanone, 0.8% at 15 min increasing to 2.1% at 60 min; 2-phenylthiyl-1-indanone, 0.4% at 15 min increasing to 0.8% at 60 min; and 1-phenylthiyl-2-indanone, 0.2% at 15 min increasing to 0.4% at 60 min. Other products included: from the thiophenol, phenyl disulfide, 2.1% at 15 min increasing to 6.1% at 60 min and phenyl thiosulfonate, 0.1% at 15 min increasing to 0.5% at 60 min. From the 15 min run employing tBHP, products formed were: acetone, 0.7%; t-butanol, 54.3%; di-t-butyl peroxide, 0.5% and isobutylene, 3.2%. As shown in Table 2, many trace products (<0.1% yield) were formed. They were the result of oxidation of the indene, scission of the indene double bond or the more extensive oxidation of other products.

The processes for the reaction of oxygen or tBHP with thiophenol and indene proceeds as shown in Schemes I - III. The most probable step for the formation of the indanyl radical and its subsequent reactions are shown in steps 20-22. The thyl radical can also undergo a dimerization reaction to produce the disulfide, step 15, and subsequently more extensive oxidation to yield the thiosulfonate product.



The 2-phenylthiyl indanyl radical, step 20, can react by several pathways. Hydrogen abstraction, step 21, would lead to the major observed product 2-phenylthiyl indan. Step 22, the reaction with oxygen would lead to the secondary product, 2-phenylthiyl-1-indanyl hydroperoxide. This secondary product was not detected by GC/MS, but the alcohols and ketones from its decomposition were found. Based on other hydroperoxide studies, it was not surprising that this hydroperoxide compound was not observed (11,12).

A comparison of the amounts of olefin and thiophenol remaining at different reaction times, Tables 1 and 2 indicates that the indene system is less reactive than styrene. The results at 15 min with tBHP also show that the indene system is less reactive. In the indene system, sulfoxides and

sulfones were only observed as minor products.

Table 2

Mole % Conversion for the Reaction of Indene with Thiophenol and Oxygen or t-Butyl Hydroperoxide at 120°C

CONVERSION (MOLE %)

Addition Products ^a	Reaction Time (Min)			tBP
	15	Oxygen 30	60	15
2-phenylthiyl Indan	39.4	58.2	55.8	48.3
2-phenylthiyl-1-Indanol	0.8	1.7	2.1	1.6
1-phenylthiyl-2-Indanol	0.2	0.4	0.4	0.4
2-phenylthiyl-1-Indanone	0.4	0.8	0.8	0.6
phenyl disulfide	2.1	3.8	6.1	2.7
phenyl thiosulfonate	0.1	0.2	0.5	0.3
Unreacted				
Indene	49.2	34.9	26.2	43.4
thiophenol	44.3	31.1	20.7	39.7
tBP Products				
acetone	---	---	---	0.7
t-butanol	---	---	---	54.3
isobutylene	---	---	---	3.2
di-t-butyl peroxide	---	---	---	0.5
Minor Products (0.1% or less)				
1-Indanone	~	2-Indanone		
1-Indanol	2-Indanol			
toluene	1-methyl, 2-ethyl benzene			
2-phenylsulphinyll-1-Indanol				
1-phenylsulphinyll-2-Indanol				
2-phenylsulphinyll-1-Indanol				
1-phenylsulphinyll-2-Indanol				
Trace Products ^b	3.2	3.1	4.6	2.9

a. based on the starting moles of Indene.
b. summation of small peaks

CONCLUSION

There are similarities and differences in the styrene and indene systems. The major product in both systems was an addition product; Styrene and thiophenol in the presence of oxygen or tBP at 120°C formed 1-phenyl-2-phenylthiyl ethane while indene under the same conditions formed 2-phenylthiyl indan. The styrene system formed sulfoxides in appreciable yield while these compounds were not observed with the indene system. Indene formed alcohol and ketone products that were not observed with the styrene indicating a different mechanism for these products. Styrene was more reactive than the indene under the conditions of this study.

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LIQUID PHASE OXIDATION OF THIOPHENOL AND INDENE
BY t-BUTYL HYDROPEROXIDE AND OXYGEN

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ABSTRACT

The tert-butyl hydroperoxide (tBHP) or oxygen initiated oxidation of thiophenol in the presence of the active olefin indene was examined in benzene at 120°C. The reaction is kinetically complex, but it was possible to relate the product distribution to a few competing reactions. The product mix was determined for several reaction time periods. The product slate was similar for all time periods, but yields of the individual components varied significantly with increasing reaction time. Gaseous products included isobutylene and a trace of methane. The major product from tBHP was t-butanol. The major product observed from thiophenol was phenyl disulfide. Addition products included the major product 2-phenylthiyl indan. Oxidation products included: indanols, indanones, and the sulfoxide and sulfone of the major product 2-phenylthiyl indan. Solvent participation was noted by trace amounts of toluene.

INTRODUCTION

In supersonic Navy aircraft, aerodynamic heating can cause metal skin temperature to rise to high levels. At mach 2.7, it

Catalysts, free radical initiators and inhibitors can materially alter both the rate of oxidation and the product mix (Richardson, 1965; Howard and Ingold, 1969; Benson and Shaw, 1970).

Although slight thermal deterioration of fuel is known to occur in non-oxidizing atmospheres, the presence of elemental oxygen will greatly accelerate the deterioration of fuel properties as well as significantly lower the temperature at which undesirable products are formed. Thus the stability of jet fuels is frequently dependent upon the nature of potential autoxidation pathways which can take place under aircraft operating conditions.

Thompson et al., 1949, found that sulfur and disulfides were active promoters of instability in stored fuels while aliphatic thiols and sulfides had little effect on the same fuels. Schwartz et al., 1964, reported that alkyl mercaptans, sulfides and disulfides accelerated the formation of deposits in cracked gasolines.

Taylor + Wallace, 1967, found that deposits formed in jet fuel in the presence of oxygen contained a greater percentage of sulfur than that present in the fuel itself. The formation of these deposits has been attributed to the participation of mercaptans, sulfides and disulfides (Taylor and Wallace, 1968). In jet fuels that have been deoxygenated, sulfides and disulfides have been found to lead to increased solid formation

The previous work on thiophenol with olefins such as indene was performed at temperatures in the range of 20-40°C with an excess of oxygen (Ford et al., 1958, 1962; Kharasch, et al., 1951). The major product under these conditions, 2-phenylthiyl-1-indanyl hydroperoxide, was only observed to be a minor product in the present study. The thrust of the earlier work was a study of the stereochemistry for the formation of the major product. The present work is concerned with the complete slate of products and the reaction mechanism both for the oxygen and t-butyl hydroperoxide induced autoxidation of thiophenol in the presence of the active olefin indene in benzene solvent at 120°C.

EXPERIMENTAL

Reagents. tert-Butyl hydroperoxide, tBHP, (90%), thiophenol, indene were obtained from Aldrich Chemical Co. They were distilled in vacuo to 99.9% purity. Benzene (Aldrich Gold Label) was refluxed and distilled from calcium hydride. The distillation of any peroxide requires caution. For t-butyl hydroperoxide we employ the following conditions: a small volume, 15-20ml, under sufficient vacuum such that the temperature does not rise above 30°C.

Method. The reactions were carried out in sealed borosilicate glass tubes. The reagents (typically $3-9 \times 10^{-4}$ mol of tBHP and 6×10^{-4} mol of both thiophenol and indene in 0.6ml of benzene)

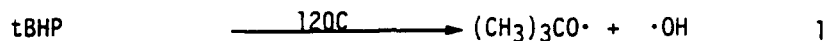
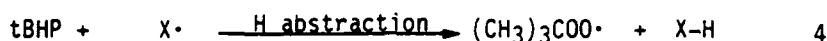
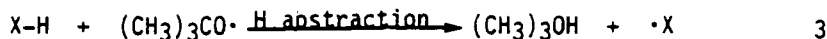
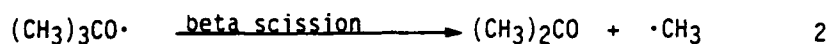
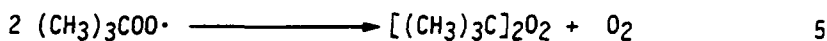
1 mL/min was combined with an inlet split ratio of 60:1 and a temperature program with an initial hold at 50°C for 8 min, a ramp of 4°C/min, and a final temperature of 260°C.

Gases formed during the reaction were analyzed using a Perkin-Elmer Model Sigma 2 gas chromatograph equipped with a 6 ft. 5A Molecular Sieve column. In this mode, the column was operated at 55°C. The chromatogram was recorded and integrated on a Hewlett-Packard Model 3390A reporting integrator. An external standard was used for calibration. A gauge measured the pressure in the sample loop at the time of analysis.

RESULTS AND DISCUSSION

At temperatures of 120°C or greater, tBHP decomposes rapidly by an autoinitiated pathway (Mosher and Durham, 1960; Hiatt, 1980). The major reaction pathway in the 120°C decomposition of tBHP involves attack by free radicals present in the solution. The detailed mechanism is complicated since free radicals are sensitive to structural, solvent and stereoelectronic effects.

The results in Table I illustrate the product distribution for the tBHP, indene and thiophenol derived products. The quantities are expressed in terms of mole percent conversion from the moles of reactant originally present. Products derived solely from tBHP (for example acetone) are calculated based on

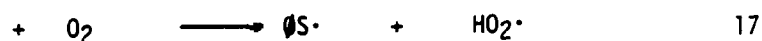
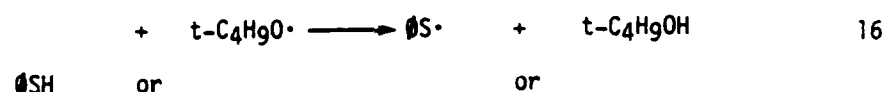
Self InitiationPropagationTermination

Scheme I

Additionally, the hydrogen abstraction from thiophenol by the t-butoxy radical, step 3, occurs at a much more rapid rate than from other functional groups studied previously. Under the same reaction conditions, Mushrush and Hazlett 1985a, reported for the reaction of alkyl aldehydes with tBHP a yield of 30.0% t-butanol for a 15 min stress period. This is to be contrasted with the 54.3% of t-butanol in the present study at the same time period. This difference in reactivity was not surprising. Hydrogen abstraction is more difficult from a hydrocarbon than a thiol (Denisov, 1974). From the beta-scission step, the yield of acetone in the present work was observed to be less than from the reaction of tBHP with alkyl aldehydes. Mushrush and Hazlett, 1985a, reported that for a 15 min time period the yield of acetone from the reaction of tBHP with alkyl aldehydes was

result from either Scheme I or II could subsequently react primarily with thiophenol. The thiyl radical formed reacts overwhelmingly with olefins that are present in the reaction mixture. This process can be described by Scheme III.

The reaction of molecular oxygen or tBHP with thiophenol can proceed by the following chain mechanism (steps 16-17). The t-butoxy radical is more reactive than the t-butyl peroxy radical and consequently is a more probable reactant in such a mechanism (Walling, 1957).



The thiyl radical once formed can then react by several different pathways. In a solution with a high molar concentration of an active olefin, the reaction could proceed as shown in steps 18-19 (Ford et al., 1958; Kharasch et al., 1957).

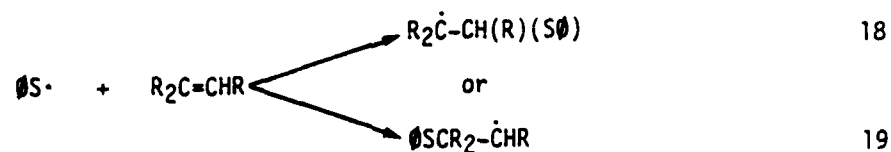


Table I

Mole % Conversion for the Reaction of Indene with Thiophenol
and Oxygen or t-Butyl Hydroperoxide at 120C

	CONVERSION (MOLE %)			
	Reaction Time (Min)			tBHP
	Oxygen			
	15	30	60	15
<u>Addition Products^a</u>				
2-phenylthiyl indan	39.4	58.2	55.8	48.3
2-phenylthiyl-1-indanol	0.8	1.7	2.1	1.6
1-phenylthiyl-2-indanol	0.2	0.4	0.4	0.4
2-phenylthiyl-1-indanone	0.4	0.8	0.8	0.6
phenyl disulfide	2.1	3.8	6.1	2.7
phenyl thiosulfonate	0.1	0.2	0.5	0.3
<u>Unreacted</u>				
indene	49.2	34.9	26.2	43.4
thiophenol	44.3	31.1	20.7	39.7
<u>tBHP Products</u>				
acetone	----	----	----	0.7
t-butanol	----	----	----	54.3
isobutylene	----	----	----	3.2
di-t-butyl peroxide	----	----	----	0.5
<u>Minor Products (0.1% or less)</u>				
1-indanone	2-indanone			
1-indanol	2-indanol			
toluene	methane			
2-phenylsulphinyl-1-indanol				
1-phenylsulphinyl-2-indanol				
2-phenylsulphonyl-1-indanol				
1-phenylsulphonyl-2-indanol				
Trace Products ^b	3.2	3.1	4.6	2.9

Reactant concentrations for all runs were identical

a. based on the starting moles of indene.

b. summation of small peaks

The thiyl radical can also undergo a dimerization reaction to produce the disulfide, step 15, and subsequently more extensive oxidation to yield the thiosulfonate product, step 23. These are minor products compared to 2-phenylthiyl indan.

The 2-phenylthiyl indanyl radical, step 20, can react by several pathways. Hydrogen abstraction, step 21, would lead to the major observed product 2-phenylthiyl indan. Step 22, the reaction with oxygen would lead to the secondary product, 2-phenylthiyl-1-indanyl hydroperoxide. This secondary product was not detected by GC/MS, but the alcohols and ketones from its decomposition were found. Based on other hydroperoxide studies, it was not surprising that this hydroperoxide compound was not observed (Mushrush and Hazlett, 1985a, 1987).

SUMMARY AND CONCLUSIONS

Deterioration of fuels can manifest itself in many ways, including the formation of insoluble deposits both in storage and in vehicle fuel systems. Alkyl hydroperoxides and sulfur compounds such as thiols and olefins are reactive species which are known to be present in turbine fuels. Sulfur (up to 0.4%) is the most abundant heteroatom present in military jet fuels. At present, it is not possible to correlate instability with specific sulfur compounds. This paper specifically examined the

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RECEIVED: August 10, 1987

ACCEPTED: September 11, 1987

3rd International Conference on Long Term

Storage Stabilities of Liquid Fuels

London, England September 13 - 16, 1988

JET FUEL INSTABILITY: ORGANO-SULFUR HYDROPEROXIDE INTERACTIONS

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ABSTRACT

The role of organosulfur compounds and hydroperoxides on the oxidative stability of middle distillate fuels is not well understood. Differences in fuel composition, reaction surface, hydroperoxide concentration, dissolved oxygen and reaction temperature all contribute to the variation in observed results. In an effort to clarify this situation, we have examined the t-butyl hydroperoxide liquid phase oxidation of hexyl sulfide, dodecyl thiol, hexyl disulfide, substituted thiophenes, and thiophenol in benzene and a model fuel, tetradecane. The relationship between organo-sulfur compounds and the peroxidation of JP-5 have been studied under conditions of accelerated storage.

INTRODUCTION

The formation of solid deposits in middle distillate fuels has been a continuing problem in the utilization of these fuels. Deposits can plug nozzles, filters and coat heat exchanger surfaces. Deposit formation in fuels is triggered by autoxidation reactions. Although slight thermal degradation is known to occur in nonoxidizing atmospheres, the presence of

oxygen or active oxygen species such as hydroperoxides will greatly accelerate oxidative degradation of fuels as well as significantly lower the temperature at which undesirable products are formed. The stability of middle-distillate fuels is consequently dependent upon the nature of potential autoxidation pathways which can occur. Heteroatoms and ash have been found to comprise up to 40 percent of such deposits [1]. The sulfur content of these deposits has been found to vary from 0.3 to 9 percent [2-5]. Sulfur (0.4%, maximum allowable) is the most abundant heteroatom present in jet fuel. The source of sulfur in these deposits has been attributed to the participation of thiols (mercaptans), sulfides and disulfides [6]. In jet fuels that have been deoxygenated, sulfides and disulfides have been found to lead to increased solid formation [7]. By contrast, it has been demonstrated that sulfur compounds in lubricating oils act as antioxidants by decomposing peroxides [8].

The rates of reactions in autoxidation schemes are dependent on hydrocarbon structure, heteroatom concentration and speciation, oxygen concentration, and temperature [9-10]. Catalysts and free radical inhibitors can materially alter both the rate of oxidation and the product mix [10]. If sufficient oxygen is present, the hydroperoxide concentration will reach a high concentration. If the available oxygen is low, but the temperature raised, the hydroperoxide concentration will be limited by free radical decomposition. Under these conditions, fuel degradation can be associated both with hydroperoxide formation and decomposition. The detailed mechanism of hydroperoxide decomposition is complicated since free radicals are sensitive to the slight changes in their chemical environment.

This paper is concerned with the reaction between a primary autoxidation product, a hydroperoxide, and organosulfur compounds of the type known to be present in middle distillate fuels. Specifically, we examine the tert-butyl hydroperoxide oxidation of hexyl sulfide, dodecyl thiol, substituted thiophenes, and hexyl disulfide in both deaerated benzene and a model fuel, tetradecane, at 120°C. In addition, the relationship between organo-sulfur compounds and peroxidation of JP-5 was examined using model dopants added to JP-5 jet fuel and stressed under 65°C accelerated storage conditions. Samples were analyzed on a weekly basis for peroxides and sulfur compound concentration.

EXPERIMENTAL

Reagents. tert-Butyl hydroperoxide, tBHP, (90%), hexyl sulfide, dodecyl thiol, thiophene, benzothiophene, thiophenol and hexyl disulfide were obtained from Aldrich Chemical Co. They were distilled in vacuo to 99.9% purity. The solvents benzene (Aldrich Gold Label) and tetradecane (Fisher certified) were refluxed and distilled from calcium hydride. JP-5 fuel was a stable jet fuel supplied by a U.S. west coast refiner without antioxidant. It was filtered before use, but otherwise used as received.

Method. The reactions were carried out in sealed borosilicate glass tubes. The reagents (typically $3-9 \times 10^{-4}$ mol of tBHP and 6×10^{-4} mol of sulfur

compound in 0.6 ml of solvent) were weighed into 6 in. long, 1/4-in. o.d. Pyrex tubes closed at one end and fitted at the other with a stainless steel valve via a Swagelok (Teflon ferrules) fitting. The tube was attached to a vacuum system, cooled to 77K and subjected to several freeze-pump-thaw cycles. The tube was then subsequently flame-sealed below the valve. The ullage volume (0.30 ml) was kept constant for all runs. The deaerated samples were warmed to room temperature and immersed in a Cole-Parmer fluidized sand bath. The temperature was controlled by a Leeds and Northrup Electromax III temperature controller. The total pressure during each run was estimated to be less than 1 atm for the tetradecane solvent and 5.1 atm for the runs in benzene solvent. After the reaction period the sealed tube was quenched to 77K and opened.

Samples were heated for time periods of 15, 30, 60, 120 and 180 min except for those runs with the more reactive thiols (60 min maximum). A search of the literature gives a few examples of catalytic behavior with glass systems [11-12]. However, when a glass tube was partially filled with crushed Pyrex, thus increasing the surface area, the results at 120°C for the reaction time periods were not substantially altered.

The samples were analyzed by combined GC/MS (EI mode). The GC/MS unit consisted of a Hewlett-Packard Model 5710 GC, a H-P Model 5982A mass spectrometer, and a Ribermag SADR GC/MS data system. Also, a Finnigan Model 700 ITD coupled to a 5890A Hewlett-Packard GC and the Finnigan Data Reduction Program was employed. An all glass GC inlet system was used in conjunction with a 0.31 mm x 50 m SP-2100 fused silica capillary column for both MS systems.

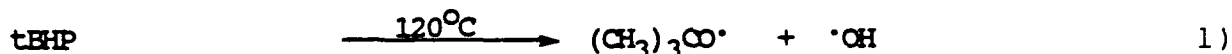
A material balance was assessed for each compound. The major peaks of the chromatogram account for approximately 81 to 99% of the original compounds. The 81% was observed only for tBHP in runs with hexyl sulfide at long reaction times. These runs also formed many partially oxidized products. The very small peaks account for another 5 to 10%. The product distribution was repeatable to 2 to 3% for each component.

Accelerated Storage. The method has been described in detail elsewhere [13], but in brief tests were carried out in brown borosilicate glass bottles, 500 ml total capacity, capped with teflon liners, containing 300 ml of fuel per bottle. Stress tests were conducted at 65°C for eight weeks. Samples were analyzed weekly for peroxide concentration by a modified ASTM D3702-85. A Mettler DL20 automatic titrator was employed thus eliminating the need for a starch indicator. Sulfur concentration was monitored weekly with a Tracor 565 gas chromatograph equipped with a 0.31 mm x 50 m SP-2100 fused silica capillary column and a sulfur specific 700A Hall electrolytic conductivity detector. Samples were analysed in triplicate with an external standard.

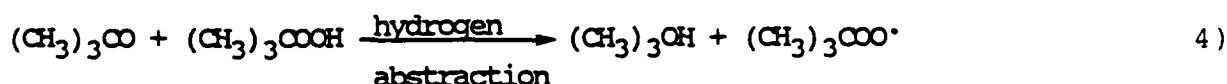
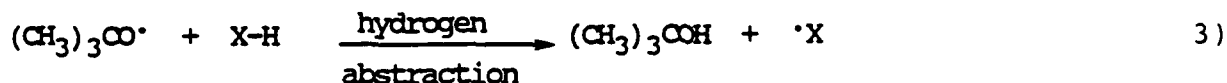
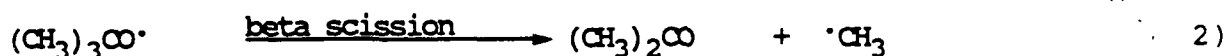
RESULTS AND DISCUSSION

tBHP products. The mechanism of autoinitiated tBHP decomposition can be depicted by the following equations:

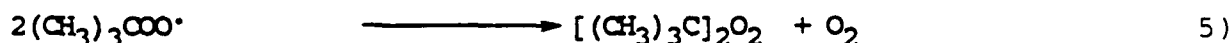
Self Initiation



Propagation



Termination



The major product from tBHP when reacted with various classes of organo-sulfur compounds was t-butanol, equations 3) and 4), with yields up to 75%. Small amounts of acetone, equation 2) up to 3.5%, were also observed. The greater yield of t-butanol compared to acetone definitely shows that hydrogen abstraction was favored over cleavage under the conditions of this study. The increasing yield of acetone as reaction time increased, however, indicated that at long reaction times beta-scission was a viable competing process to hydrogen abstraction. Other products noted, 1 - 2%, from tBHP included: isobutylene, methane, and di-t-butyl peroxide. Methane resulted from a hydrogen abstraction by the methyl radical, equation 2), di-t-butyl peroxide from equation 5), and isobutylene from an acid catalyzed dehydration of t-butanol.

Sulfide products. The major product observed from the oxidation of hexyl sulfide by tBHP was hexyl sulfoxide. Its yield varied from 74.8% at 15 min to 85.3% at 30 min, gradually decreasing to 80.7% at 180 min of reaction. Other products included: hexyl sulfone, 1.2% at 15 min gradually increasing to 4.0% at 180 min; hexyl disulfide, 0.3% to 0.6%. Minor products included dihexyl thiosulfinate, 0.1%; hexanal, 0.2% at 15 min increasing to 0.3% at 60 min, decreasing to 0.2% at 120 min and disappearing at 180 min; hexene, 0.1% at 15 min, increasing to 0.3% at 120 min and decreasing to 0.2% at 180 min; and hexane, 0.1% at 15 min increasing to 0.4% at 120 min and decreasing to 0.2% at 180 min. Many trace products, yields less than 0.1%, were formed. Most of these products were partially oxidized substances that could not be readily identified by MS. An extensive discussion of the mechanism of formation for the entire product distribution can be found

elsewhere [14].

The hexyl sulfoxide could result from several mechanisms. The most likely mechanism however, would be the reaction of the tBHP itself with the hexyl sulfide followed by a rapid proton transfer and O-O bond rupture, equation 7), [15].

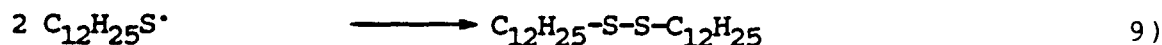


Expansion of the sulfur valence shell is probable in the processes involved in this step. Another mechanism could involve the attack of an oxygen centered radical, i.e., peroxy on sulfur followed by a beta scission [16].

The resulting sulfoxide once formed is quite stable. The sulfoxide oxidation product, hexyl sulfone, varied in the present work from an initial 1.2% at 15 min to 4.0% at 180 min of reaction. This slight increase compared to the yield of hexyl sulfoxide at 180 min (80.7%) illustrates the resistance of an alkyl sulfoxide to oxidation by a hydroperoxide. The oxidation of a sulfoxide to a sulfone is believed to proceed by a mechanism similar to that for the sulfoxide formation.

Thiol products. The major product from the oxidation of dodecyl thiol by tBHP was dodecyl disulfide, 74.4% at 15 min increasing to 78.8% at 30 min and then decreasing to 74.1% at 60 min. Other oxidation products included: dodecyl sulfoxide, 2.3% at 15 min decreasing to 2.1% at 60 min; dodecyl sulfone, 0.9% at 15 min increasing to 1.7% at 60 min. Minor reaction products observed were: Dodecyl sulfide, 1.9% at 15 min decreasing to 1.4% at 60 min; dodecanal, 0.6% at 15 min increasing to 1.1% at 60 min; dodecane, 0.1% at 15 min increasing to 0.4% at 60 min; and trace (less than 0.1%) amounts of dodecyl thiosulfinate. In addition, small amounts of dodecyl sulfonic acid were observed. To determine this product, the solution was derivatized to the methyl ester and determined by solid probe MS.

The mechanism of thiol oxidation has been the subject of discussion for many years [17]. We support the thesis that the t-butoxy or peroxy radical generated from tBHP abstracts the thiol hydrogen, equation 8). Rapid dimerization, equation 9), then follows generating the major product dodecyl disulfide.



Thiol in tetradecane. The reaction was similar both in benzene and tetradecane, but minor differences were found. The product slate, other than solvent products, was identical. Differences included slightly lowered yield of t-butanol in tetradecane, 72.1% vs 76.7% in benzene, while the yield of acetone 8.6% was increased from that observed in benzene. The major product dodecyl disulfide was formed in greater yield, 80.6% compared to 74.1% in benzene. Dodecyl sulfonic acid was also noted in this solvent. Products observed from tetradecane solvent participation were tetradecanones and tetradecanols. These were minor products and are reported as totals of all isomers, because the isomers elute in an overlapping pattern. Tetradecanones for a 60 min stress were 0.3% and the tetradecanols were found to be 0.6%. By contrast, no oxygenated products of the benzene solvent were observed.

Thiophene products. Thiophene compounds investigated were thiophene, tetrahydrothiophene, 2,5-dimethyl thiophene and benzothiophene. Reactions with tBHP were conducted in benzene solvent. The reaction for thiophene with tBHP is illustrated in equations 10) - 12).

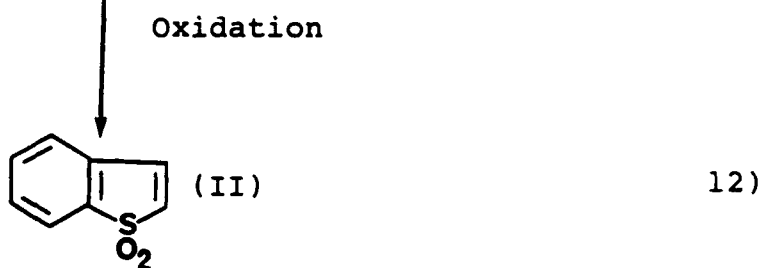
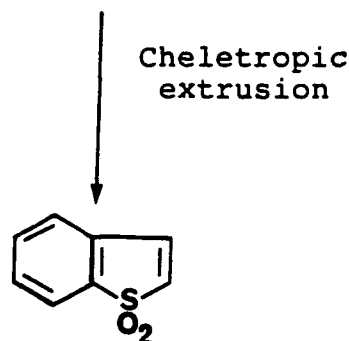
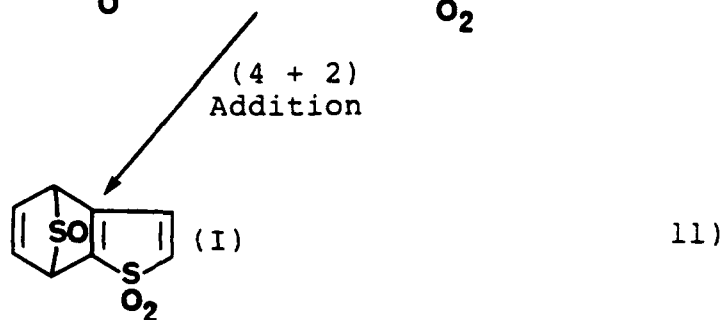
The oxidation of tetrahydrothiophene by tBHP gave the sulfoxide as the major product; at 15 min the yield was 13.8% increasing to 26.8% at 180 min. A mechanism similar to equation 7) would be predicted for the sulfoxide formation. From tBHP, t-butanol increased from 34.1% at 15 min to 68.6% at 180 min, acetone increased from 1.3% to 2.3% at 180 min. Other products included: tetrahydrothiophene sulfone, methane, isobutylene, and di-t-butyl peroxide. Thus this cyclic sulfide gave a product slate similar to an aliphatic sulfide although the yields were much lower.

Thiophene and its methylated analog do not yield simple, easy to identify products. In fact, no GC identifiable products were formed in any of the runs. Rather, an intractable water soluble solid results at all reaction times. Detailing the reaction mechanism for the thiophenes is further complicated in that the solid product itself is not thermally stable [16]. Products identified in the solid from both thiophene and 2,5-dimethyl thiophene included traces of the sulfoxide, the sulfone, and the water soluble Diels-Alder condensation products, 4:7:8:9-tetrahydro-4:7-sulphinyl thionaphthene 1:1-dioxide (I), and thionaphthene 1:1 dioxide (II), along with the 2,5-dimethyl analogs. Both products were identified by solid probe MS. Confirmation of both structures was by synthesis of the compounds and a comparison of their MS spectra [18]. The 2,5-dimethyl thiophene was more reactive than the thiophene as measured by thiophene disappearance.

The literature contains little information on thiophene oxidation especially in a radical environment [19-21]. The thiophene ring system can survive moderate oxidizing conditions. However, if the ring is attacked, it generally breaks down to oxalic or other substituted carboxylic acids with the sulfur being converted to sulfuric acid [22]. With tBHP, no evidence of ring opening was observed.

Benzothiophene was the least reactive, as measured by reactant

disappearance, sulfur compound studied. At the end of a 180 min stress period >97% of the benzothiophene remained unreacted. In the presence of tBHP, benzothiophene yields minor amounts of the sulfone product and a trace of the sulfoxide product.

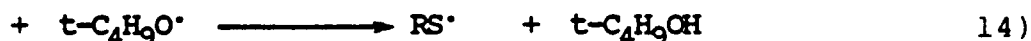


Thiol, olefin products. The reaction of thiols with active olefins, such as styrene and indene was investigated with both oxygen and tBHP. For the styrene reaction with molecular oxygen and thiophenol the major product observed was the addition product, 1-phenyl-(2-phenylthiyl) ethane; at 15 min its yield was 41.3% increasing to 71.2% at 30 min and decreasing to 68.3% at 60 min. Other products included: the 1-phenyl-(1-phenylthiyl) ethane isomer, 1,4-diphenyl butane, 1-phenyl-(2-phenylethyl) sulfoxide, 1,4-diphenyl-(2-phenylthiyl) butane, and phenyl thiosulfonate. Trace products (< 0.1%) included: 1-phenyl-(2-phenylethyl) sulfone, styrene

oxide, phenyl methyl sulfide and 2-ethyl toluene. For a 15 min stress with tBHP, the product slate was the same for both oxygen and tBHP, but the yields of individual components varied significantly. The major product, 1-phenyl-(2-phenylthiyl) ethane increased to 62.4% and the sulfoxide product was more than doubled at 3.9% in the presence of the stronger oxidant, tBHP.

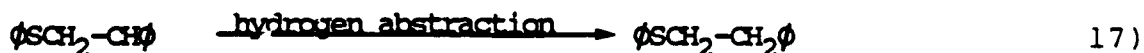
The product slate for the indene reaction with oxygen included both addition and oxidation products. The major addition product observed was 2-phenylthiyl indan; at 15 min its yield was 39.4% increasing to 58.2% at 30 min and decreasing to 55.8% at 60 min. Another addition product was phenyl disulfide. Oxidation products included: 2-phenylthiyl-1-indanol and indanone, 1-phenylthiyl-2-indanol and indanone, and phenyl thiosulfonate. Minor products included: 1- and 2-indanols and indanones, 2-phenylsulphinyl-1-indanols, 1-phenylsulphinyl-2-indanols, 2-phenylsulphonyl-1-indanol, and 1-phenyl sulphonyl-2-indanol. The major product showed a significant increase in yield when the reaction was carried out with tBHP, 48.3% at 15 min. In these tBHP runs, t-butanol was the major product from the hydroperoxide.

The reactions with either molecular oxygen or tBHP and a thiol can be described by the following mechanism steps. The thiyl radical once formed



Where R = alkyl or aryl

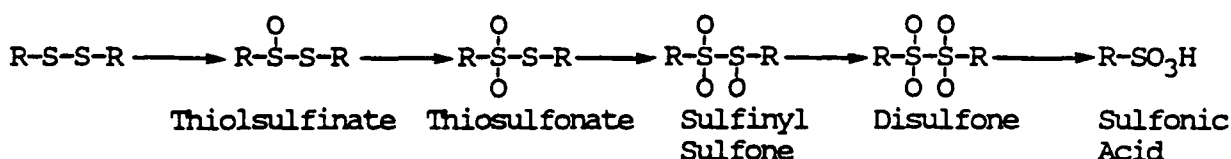
can then react with an active olefin. For styrene, the reaction sequence with thiophenol can be described by the following equations.



Equation 16) was the preferred pathway since it resulted in the more thermodynamically stable radical. For styrene the major product, 1-phenyl-

(2-phenylthiyl) ethane, then resulted from hydrogen abstraction, equation 17). The other radical generated, equation 15), leads to one of the observed minor products, 1-phenyl-(1-phenylthiyl) ethane. For the reaction with indene, only the 2-phenylthiyl indan reaction product was observed from steps 15) and 16).

Disulfide products. Oxidation of disulfides leads ultimately to sulfonic acids, but several of the oxidation intermediates can be obtained. In the present work in the presence of the mild tBHP oxidant at 120°C the major products observed are the intermediate oxidation products with only a minor amount of sulfonic acid produced. For hexyl disulfide, two major oxidized products were observed, the hexyl thiolsulfonate and the hexyl disulfone. Minors amounts of the hexyl thiol, hexyl sulfoxide and hexyl sulfone were observed. tBHP products included the major product t-butanol, along with acetone, and isobutylene. The observed disulfide oxidation products can be interpreted by the following mechanism.



Accelerated Storage. The above results indicated that some sulfur compounds might be inhibitors for controlling hydroperoxide formation in jet fuels. Therefore, samples of an aviation turbine fuel that undergoes extensive peroxidation were doped with different classes of organo-sulfur compounds at 0.03% added sulfur and analyzed for hydroperoxide formation during a 65°C/eight week stress period. The organo-sulfur compounds employed as dopants included: n-nonyl thiol, n-butyl sulfoxide, n-butyl sulfone, 2-butyl thiophene, and benzothiophene. Figure 1 shows the results for both the undoped control and the n-nonyl thiol doped JP-5 fuel. This dopant was dramatic in its control of hydroperoxide formation. It eliminated measurable hydroperoxides. Figure 2 shows the effect of added sulfur in the form of n-butyl sulfoxide. This dopant also exhibited control over peroxidation. The results for n-butyl sulfone, Figure 3, are different. A slight enhancing action on peroxidation was noted. n-Butyl thiophene, Figure 4, and benzothiophene, exhibited no controlling action. In fact, a negative synerism was operating to increase peroxidation above control levels.

The results of the accelerated storage tests can be interpreted based on model studies. Thiols as reported in this paper are readily oxidized, forming small amounts of sulfonic acids. Sulfoxides are somewhat resistant to oxidation at 120°C, while sulfones are stable at temperatures well above 120°C. These observations could account for the behavior noted with these dopants under accelerated storage conditions. Model studies have indicated that the thiophenes are the most oxidation resistant organo-sulfur compounds under the relatively mild conditions of this investigation. Alkyl substituted thiophenes and benzothiophene were the most unreactive sulfur

compounds studied. At stress times of 180 min at 120°C, >97% of benzothiophene remained unreacted. Results for the thiophene dopant studies show that they do not control the formation of hydroperoxides. Since they are so oxidation resistant, the hydroperoxide concentration increases are uncontrolled.

SUMMARY

The observed deterioration of fuels can manifest itself in many ways, including the formation of insoluble deposits both in storage and in an engine fuel system or nozzle. Reactive species in petroleum fuels which may be involved in the deterioration are alkyl sulfides, thiols, aromatic thiols, disulfides, thiophenes and hydroperoxides. Trace quantities of compounds such as sulfonic acids have also been implicated in deposit formation. This paper specifically examined the hydroperoxide or oxygen induced oxidation of hexyl sulfide, dodecyl thiol, thiophenol, hexyl disulfide, substituted thiophenes, and the co-oxidation of thiophenol with the active olefins, styrene and indene, in both deaerated benzene and tetradecane solvents at 120°C. The product mix was studied over various reaction times of 15 min to 180 min. For each organo-sulfur compound, a common slate of products was observed for all reaction time periods. The yield of individual components, however, varied significantly with reaction time. The major product derived from the tBHP was t-butanol. Other observed tBHP products included methane, acetone and isobutylene. The major product from the hexyl sulfide oxidation was hexyl sulfoxide. Other sulfur containing products were hexyl sulfone, hexyl disulfide and hexyl thiosulfinate. The major product from dodecyl thiol was dodecyl disulfide. Oxidized products included dodecyl sulfoxide, dodecyl sulfide and dodecyl sulfone. Hexyl disulfide gave primarily oxidation products, hexyl thiosulfonate, and hexyl disulfone. The substituted thiophenes gave sulfoxides, sulfones and the Diels-Alder product from these reactive species. The Diels-Alder products formed from the thiophenes were observed to be water soluble. From the co-oxidation of thiophenol with styrene, the major product was 1-phenyl-(2-phenylthiyl) ethane. Other products included: 1-phenyl-(1-phenylthiyl) ethane and the oxidized products phenyl-(2-phenylethyl) sulfoxide and phenyl thiosulfonate. For indene, the major addition product observed was 2-phenylthiyl indan. Oxidation products included the 2-phenylthiyl-1-indanol and indanone. These products were derived from the breakdown of hydroperoxide of indane. Minor amounts of the oxidized addition products were also observed.

The results of the accelerated storage studies with sulfur dopants in jet fuel can be interpreted based on the results and mechanisms observed with model compounds.

Solvent participation was noted by the formation of toluene from benzene and tetradecanones and tetradecanols from tetradecane. No oxygenated products of benzene were observed.

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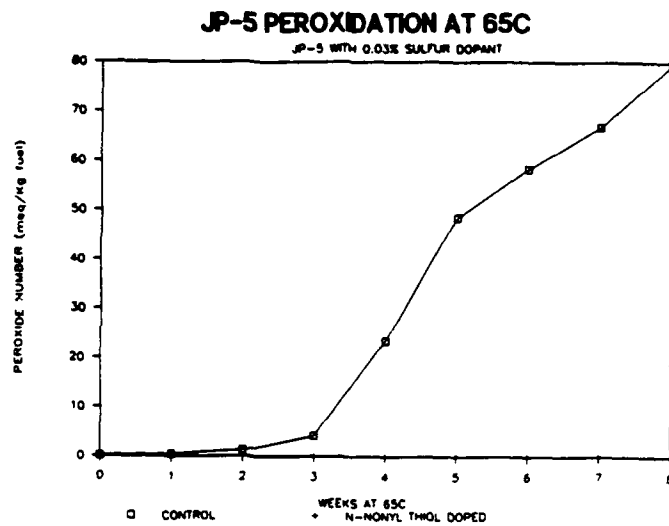


Figure 1

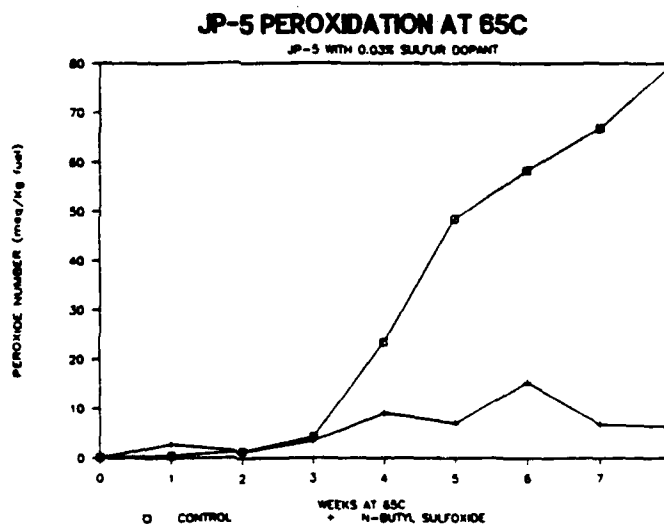


Figure 2

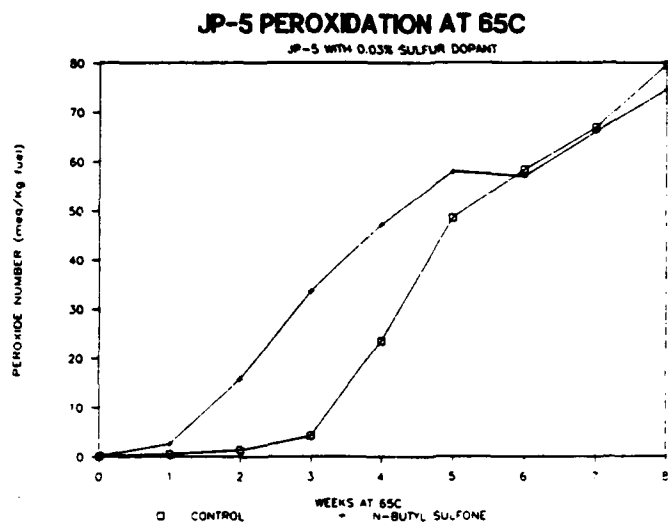


Figure 3

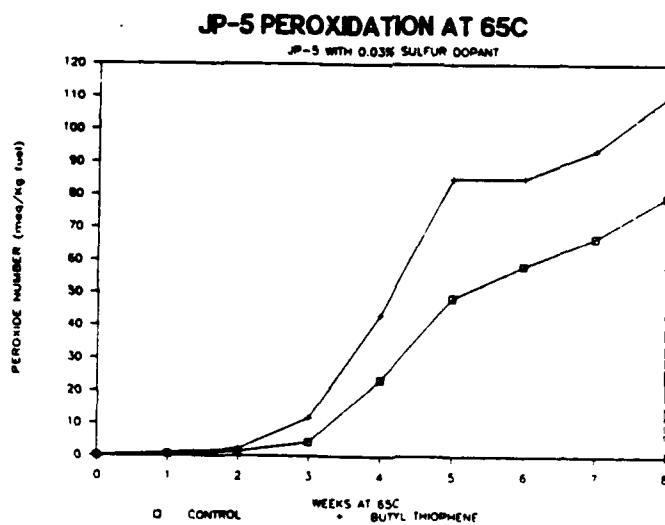


Figure 4

3rd International Conference on Long Term
Storage Stabilities of Liquid Fuels
London, England September 13 - 16, 1988

HYDROPEROXIDE FORMATION AND REACTIVITY IN JET FUELS

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ABSTRACT

Hydroperoxides in jet fuels attack elastomers in aircraft fuel systems resulting in leaks or inoperation of fuel controls. Examination of fuels refined by different processes has indicated that significantly higher peroxide concentrations exist in fuels which have been severely hydrotreated. It is believed that hydrogenation is responsible for removing natural inhibitors, including sulfur compounds, to peroxide formation. To test this thesis, the relationship between aryl thiols and peroxidation of jet fuels was examined using model dopant studies under 65°C accelerated storage conditions. Samples were analysed on a weekly basis for peroxides and sulfur compound concentration. Thiophenol demonstrated effectiveness in reducing and/or controlling peroxide concentration for an equivalent ambient storage time of approximately two years.

INTRODUCTION

Hydroperoxides in jet fuels attack elastomers in aircraft fuel systems with consequent leaks or inoperation of fuel controls. Problems have been associated with Jet A, JP-4, and JP-5 jet fuels. The first reported incidents occurred with Jet A in Japan in 1962 when fuel hoses of neoprene or nitrile rubber cracked and leaked (1). In 1976 the U.S. Navy experienced attack on neoprene fuel pump diaphragms on jets operating in

the Phillipines (2). More recent problems have been encountered in Thailand with JP-4 when Buna-N O-rings cracked and leaks from fuel pumps occurred (3). All incidents involved fuels which had been hydrotreated and had peroxide levels from 1 to 8 milliequivalents of active oxygen per kilogram of fuel (peroxide number or P.N.).

Examination of fuels refined by different processes has indicated that significantly higher peroxide concentrations develop in fuels which have been severely hydrotreated. The U.S. Navy has continuing concerns with this topic due to increasing hydrogenation for jet fuel processing. In addition, lower grade crudes and future shale-derived fuel production will involve more extensive and higher pressure hydrotreatment. It has been demonstrated that sulfur compounds in lubricating oils act as antioxidants by decomposing peroxides (4). It is believed that hydrogenation is responsible for removing natural inhibitors, including sulfur compounds, to peroxide formation.

Hydroperoxide concentration has been found to be a factor in fuel instability. Fuel degradation is observed to occur under long-term low-temperature storage conditions (storage stability) as well as short-term high-temperature stress (thermal oxidative stability) (5,6,7,8). The latter situation is found during flight conditions, where fuel serves as a coolant on its path to the combustion chamber. Although slight thermal degradation is found to occur in non-oxidizing atmospheres, the presence of oxygen or active species such as hydroperoxides will greatly accelerate oxidative degradation as well as significantly lower the temperature at which undesirable changes in fuel take place. The rates of reactions in autoxidation schemes are dependant on hydrocarbon structure, heteroatom concentration, oxygen concentration, and temperature (9,10,11). If sufficient oxygen is present, the hydroperoxides will reach a high level. If the available oxygen is low, but the temperature raised, the hydroperoxide concentration will be limited by free radical decomposition. Under these conditions, fuel degradation can be associated with both hydroperoxide formation and decomposition.

Several solutions to the problem of fuel peroxidation have been suggested. Antioxidants have been mandated by some authorities, particularly for hydrotreated fuels. Viton elastomers and other materials have been proposed as replacement materials but their low temperature properties make them marginal for aircraft use. Clay filtration has been suggested as a means for field removal of hydroperoxides but this treatment has been found to be too expensive (2). Although hindered phenols have given satisfactory peroxide control, those phenols which are permitted in the jet fuel specifications were developed for gum control in gasoline. Their effectiveness for peroxide control was found to be marginal, depending on structure (12). Rolls-Royce defined the peroxidation potential of a fuel with an accelerated 100°C test for 24 hours (1). Investigations into the relationship of temperature to peroxide concentration in fuel, along with determining the relevance of the 100°C test to ambient storage conditions, indicated that fuels containing antioxidants behaved differently at different temperatures, and

in fuels without antioxidants, peroxide levels were lower than expected at the lower temperatures (12). A comparison of peroxidation rates in two fuels, one with and one without antioxidant, showed that a fuel without antioxidant produced peroxides at a linear rate while a fuel containing antioxidant produced peroxides in an exponential fashion, indicating a depletion with time of the antioxidant and its ability to control peroxidation (12).

Sulfur is the most abundant heteroatom present in jet fuels (up to 0.4% allowed by specifications). Deposits formed in jet fuel in the presence of oxygen contain a higher percentage of sulfur than that present in the fuel itself (13). The formation of these deposits has been attributed to the participation of sulfides, disulfides, and thiols (mercaptans) (14). In jet fuels that have been deoxygenated, sulfides and disulfides have been found to lead to increased solid formation (15). Examination of the reactions between both alkyl and aromatic thiols with tert-butylhydroperoxide have indicated that aromatic thiols are more reactive than other classes of sulfur compounds with hydroperoxides. The reaction of thiophenol with tBHP was found to produce trace amounts of sulfonic acid while depleting the amount of both reactants in solution (16). It was thus desirable to test the relationship between sulfur compound reactivity and peroxide formation using an aryl thiol as a model dopant under accelerated storage conditions.

This paper discusses the effect on hydroperoxide formation of using an aryl thiol, thiophenol, as a dopant in a Jet A, a shale-derived jet fuel, and two jet fuel blending stocks under 65°C accelerated storage conditions. A 65°C stress test was chosen for the sulfur compound study based on previous time-temperature peroxidation studies completed at NRL (12). The effect on peroxide formation versus added sulfur concentrations is also reported.

EXPERIMENTAL

Fuels and Reagents. The four fuels used in the investigation were a Shale-II JP-5, a Jet-A, a Hydrocracked and a Hydrofined Jet A blending stock. Thiophenol was obtained from Aldrich Chemical Co. and was distilled in vacuo to 99.9% purity.

Method. The stress test was patterned after that used by the laboratories which participated in the recent Coordinating Research Council cooperative studies on peroxidation (17). Tests were carried out in brown borosilicate glass bottles, 500 ml total capacity, capped with teflon liners, containing 300 ml of fuel per bottle. Duplicate samples of the four fuels were prepared, with sulfur in the form of thiophenol weighed into one sample of each fuel. The first series of samples were prepared by adding 0.10% sulfur (weight/volume) from thiophenol, followed by sets with 0.05, 0.03 and 0.01% added sulfur concentrations. Stress tests were conducted for five weeks for the samples containing 0.10 and 0.05% added sulfur. The samples containing 0.03 and 0.01% added sulfur were stressed at 65°C for eight weeks. Samples were analyzed weekly for peroxide concentration by ASTM method D3703-85 from the control and test bottles for each fuel.

A Mettler DL20 automatic titrator was employed for the 0.03 and 0.01% added sulfur tests, eliminating the use of starch solution from the ASTM method. Thiophenol concentrations were monitored weekly with a Tracor 565 gas chromatograph equipped with a sulfur specific 700A Hall electrolytic conductivity detector. Samples were analysed in triplicate against an external standard for thiophenol, which was also analysed in triplicate.

RESULTS AND DISCUSSION

An original added sulfur concentration of 0.10% sulfur (weight/volume) from thiophenol was used. To examine the effect of added sulfur concentration on peroxidation, a second test was run using 0.05% added sulfur from thiophenol. Based on the results of the 0.05% added sulfur test, additional series were run using 0.03 and 0.01% added sulfur from thiophenol. The data for these tests are presented in Tables I, II, III, and IV respectively.

For all of the sulfur concentration tests, the control samples, fuel only, exhibited similar behavior. Differences in actual peroxide numbers between tests can be attributed to slight temperature differences in the ovens that were used, and to the fact that the fuel samples had been in storage for varying times before these tests were started. It was interesting that in the Jet A control samples peroxide formation occurred in a cyclic pattern. This has been observed in other peroxidation studies with Jet A. The two Jet A blending stocks formed peroxides at a greater rate than the Shale JP-5 or the Jet A samples.

The most important aspect of all the tests was that the samples doped with sulfur in the form of thiophenol did not undergo peroxidation as rapidly as the fuel only samples. In fact, thiophenol addition eliminated any ROOH present in starting samples of all four fuels in the 0.05% added sulfur series, and after the first week in the Shale II and Hydrocracked Jet A blending stock samples in the 0.10% test. In the samples doped with 0.10% sulfur, peroxide formation was not observed until the fourth week of the stress test. When the concentration of added sulfur was reduced (halved) peroxide formation began one week earlier in the three fuels which did exhibit peroxidation, indicating a relationship between added sulfur concentration and peroxide formation (or peroxide inhibition). None of the doped samples of the Hydrofined Jet A blending stock showed evidence of peroxide formation throughout the duration of the tests.

In the series doped with 0.03% added sulfur from thiophenol, peroxides were eliminated after one week of 65°C stress in all of the samples except for the Shale II JP-5, which contained a larger starting concentration of peroxides that required two weeks to be reduced to zero as measured by the ASTM method. The Jet A sample began to exhibit peroxidation in the third week of the test, while the Shale II and Hydrocracked Jet A blending stock samples did not show any trace of peroxidation until the fourth week, before disappearing again to re-emerge in the seventh week of the test. Even though peroxidation was not observed until later in this test than in the 0.10 and 0.05% added sulfur samples, the 0.03% added sulfur controlled peroxidation, most noticeably

in the Hydrocracked and Hydrofined Jet A blending stock samples, which did not exhibit any peroxidation during the test, in spite of the fact that both of these samples peroxidized extensively when the thiophenol was absent.

The samples doped with 0.01% added sulfur from thiophenol also demonstrated the ability of added sulfur to control peroxidation. In the Shale II and Hydrocracked Jet A blending stock samples, the starting peroxide concentrations were gradually decreased to zero after three weeks of stress. Peroxidation wasn't evident in the Shale II sample until the sixth week of the test, but began again in the Hydrocracked Jet A blending stock sample in the fifth week of stress. This can be explained by comparing the relative peroxide levels present in the control samples, 0.991 meq active O_2 /Kg fuel versus 29.200 meq active O_2 /Kg fuel for the Shale II and Hydrocracked blending stock samples, respectively. The 0.01% added sulfur was not enough to control the large amount of peroxide formation after five weeks in the Hydrocracked Jet A blending stock sample. The Jet A samples, both control and doped, exhibited interesting cyclic behavior similar to that in the 0.03% added sulfur study, while the doped Hydrofined Jet A blending stock sample did not undergo peroxidation during the test after the starting peroxide concentration was depleted.

The thiophenol concentrations in the doped samples decreased throughout the tests as measured by the sulfur specific electrolytic conductivity detector on the gas chromatograph. Tables V and VI contain the data for the 0.10 and 0.05% sulfur from thiophenol doped samples, respectively. Samples were analysed in triplicate and compared to an external standard for thiophenol which was also analysed in triplicate. Average values are reported and were used for all calculations. It is interesting to note that the sulfur concentrations decreased more rapidly and to a greater extent in the doped Shale II, Jet A and Hydrocracked blending stock samples, those fuels which did exhibit some peroxidation, than in the Hydrofined blending stock sample which did not exhibit peroxidation during the test. This was true for both concentrations of added sulfur with the exception of the Hydrocracked sample which depleted slower in the 0.05% doped test. The presence of new peaks on the chromatogram indicated the formation of new sulfur-containing compounds, however concentrations were too low to permit identification. It should be noted that in the 0.10% doped samples there were still measurable sulfur concentrations for the duration of the stress test, but for the 0.05% doped samples, the added thiophenol disappeared much faster and was completely depleted between the fourth and fifth weeks of the test for the Shale II and Jet A samples. A direct comparison of the sulfur concentration to peroxidation in the Shale samples can be seen in Figures 1 and 2 for the 0.10 and 0.05% doped samples, respectively. The place on the graphs where the lines intersect indicates the approximate concentration of added sulfur at which peroxidation is no longer controlled. It should be noted that this concentration was approximately 0.4 mg of sulfur for the 0.10% doped sample and 0.2 mg sulfur for the 0.05% doped sample.

The results for the 0.03 and 0.01% added sulfur from thiophenol

studies are reported in Tables VII and VIII, respectively. The doped samples in these series exhibited behavior similar to the first two tests. The sulfur concentrations in the two Hydrofined Jet A blending stock samples did not decrease as rapidly or to the same extent as the concentrations in the other fuels. The sulfur concentration in the 0.03% sulfur doped Shale JP-5 sample was depleted by the eighth week of the test while the concentration in the 0.01% doped sample was zero by the third week of the test. In the Hydrocracked Jet A blending stock samples there were low sulfur concentrations throughout the duration of the tests, with the 0.01% doped sample dropping to zero by week five. The 0.03% doped Jet A sample exhibited cyclic peroxide formation and a rapid decrease in sulfur concentration, while the 0.01% doped sample showed an immediate decrease in sulfur concentration during the first week of stress. Figures 3 and 4 provide a direct comparison of the sulfur concentration to the peroxidation of the samples doped with 0.03 and 0.01% added sulfur. According to this data, the concentration at which peroxidation was no longer controlled was about 0.03 mg added sulfur for the 0.03% doped sample. This concentration was reached at the end of six weeks of stress and peroxidation began between the sixth and seventh week of the test. In the sulfur concentration versus peroxidation graph for the shale sample with 0.01% added sulfur, peroxide inhibition stops in the fifth week of stress when the added thiophenol concentration was reduced to zero as measured by the sulfur detector. The comparison of sulfur concentration to peroxidation indicated that control or inhibition of peroxidation was lost at approximately 0.2 ± 0.1 mg of added sulfur in all fuel samples.

CONCLUSIONS

The effect of adding sulfur in the form of an aromatic thiol, thiophenol, was significant to peroxide formation. Thiophenol has been found to act as an inhibitor or controller of peroxide formation in Jet A, Shale-II derived JP-5, and petroleum derived Jet A blending stocks. Hydrotreated jet fuels exhibited higher peroxide formation and concentration than other fuels. Hydrotreatment reduces the sulfur content of the fuel, which removes the naturally occurring sulfur compounds which possibly act as inhibitors to peroxide formation. There appeared to be a minimum concentration of sulfur as thiophenol above which peroxide formation was inhibited. If this concentration was decreased or consumed, peroxidation began.

Since aromatic thiols are quite reactive in the presence of peroxides, the thiophenol most likely undergoes oxidation by the peroxide species. These reactions could be similar to other observed liquid phase oxidation reactions that take place between thiophenol and t-butyl hydroperoxide.

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Table I

JET FUEL PEROXIDATION AT 65°C WITH ADDED THIOPHENOL 0.10% SULFUR DOPANT

WEEK	<u>SHALE-II JP-5</u>		<u>JET A</u>		<u>HYDROCRACKED JET A BLENDING STOCK</u>		<u>HYDROFINED JET A BLENDING STOCK</u>	
	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED
0	0.25	0.25	0.00	0.00	0.16	0.16	0.00	0.00
1	0.24	0.00	0.19	0.00	0.57	0.00	0.18	0.00
2	0.31	0.00	0.44	0.00	1.16	0.00	0.49	0.00
3	0.37	0.00	0.19	0.00	1.73	0.00	1.10	0.00
4	0.51	1.29	0.40	0.51	5.38	0.26	4.08	0.00
5	0.48	0.97	0.26	0.40	8.47	0.25	10.82	0.00

Table II

JET FUEL PEROXIDATION AT 65°C WITH ADDED THIOPHENOL 0.05% SULFUR DOPANT

WEEK	<u>SHALE-II JP-5</u>		<u>JET A</u>		<u>HYDROCRACKED JET A BLENDING STOCK</u>		<u>HYDROFINED JET A BLENDING STOCK</u>	
	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED
0	0.69	0.00	0.12	0.00	0.24	0.00	0.10	0.00
1	0.70	0.00	0.18	0.00	1.58	0.00	0.60	0.00
2	0.73	0.00	0.16	0.00	6.01	0.00	2.09	0.00
3	0.94	0.45	0.28	0.54	37.66	0.61	12.41	0.00
4	1.11	0.68	0.26	0.22	62.05	0.51	25.27	0.00
5	1.56	0.88	0.29	0.81	59.92	0.25	56.67	0.00

Table III

JET FUEL PEROXIDATION AT 65°C WITH ADDED THIOPHENOL 0.03% SULFUR DOPANT

WEEK	<u>SHALE-II JP-5</u>		<u>JET A</u>		<u>HYDROCRACKED JET A BLENDING STOCK</u>		<u>HYDROFINED JET A BLENDING STOCK</u>	
	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED
0	0.60	0.60	0.01	0.01	0.27	0.27	0.06	0.06
1	0.62	0.14	0.04	0.00	0.96	0.00	0.32	0.00
2	0.72	0.00	0.05	0.00	1.88	0.00	0.78	0.00
3	0.84	0.00	0.00	3.98	4.20	0.00	2.46	0.00
4	0.90	0.01	0.09	0.01	10.04	0.01	5.89	0.00
5	0.93	0.00	0.05	0.50	22.43	0.00	13.26	0.00
6	0.99	0.00	0.00	0.70	49.03	0.00	28.54	0.00
7	1.14	0.03	0.13	1.38	77.88	0.62	60.62	0.00
8	1.29	0.15	0.07	0.88	97.40	0.36	77.44	0.00

Table IV

JET FUEL PEROXIDATION AT 65°C WITH ADDED THIOPHENOL 0.01% SULFUR DOPANT

WEEK	<u>SHALE-II JP-5</u>		<u>JET A</u>		<u>HYDROCRACKED JET A BLENDING STOCK</u>		<u>HYDROFINED JET A BLENDING STOCK</u>	
	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED
0	0.51	0.51	0.00	0.00	0.25	0.25	0.06	0.06
1	0.60	0.20	0.10	1.04	1.02	0.73	0.50	0.00
2	0.67	0.17	0.13	0.72	2.37	0.11	1.32	0.00
3	0.81	0.00	0.20	0.89	4.66	0.00	3.63	0.00
4	0.85	0.00	0.17	0.55	13.22	0.00	13.79	0.00
5	0.99	0.00	0.21	0.59	29.20	0.22	29.10	0.00
6	1.08	0.23	0.17	0.42	55.33	0.14	48.57	0.00
7	1.12	0.33	0.19	0.72	89.57	0.19	78.27	0.00
8	1.51	0.48	0.24	0.65	131.13	0.28	124.98	0.00

Table V

SULFUR CONCENTRATION vs. TIME
0.10% SULFUR DOPANT FROM THIOPHENOL

<u>SHALE-II JP-5</u>		<u>JET A</u>		<u>H-CRACKED JET A STOCK</u>		<u>H-FINED JET A STOCK</u>	
WEEK	mg. S/2mL	WEEK	mg. S/2mL	WEEK	mg. S/2mL	WEEK	mg. S/2mL
0	2.20	0	2.08	0	2.12	0	2.10
1	1.16	1	0.98	1	0.92	1	1.78
2	0.51	2	0.81	2	0.74	2	1.47
3	0.43	3	0.63	3	0.67	3	1.58
4	0.26	4	0.47	4	0.48	4	1.43
5	0.24	5	0.41	5	0.47	5	1.38

Table VI

SULFUR CONCENTRATION vs. TIME
0.05% SULFUR DOPANT FROM THIOPHENOL

<u>SHALE-II JP-5</u>		<u>JET A</u>		<u>H-CRACKED JET A STOCK</u>		<u>H-FINED JET A STOCK</u>	
WEEK	mg. S/2mL	WEEK	mg. S/2mL	WEEK	mg. S/mL	WEEK	mg. S/2mL
0	1.00	0	1.00	0	1.00	0	1.00
1	0.76	1	0.25	1	0.86	1	0.37
2	0.23	2	0.33	2	0.63	2	0.76
3	0.15	3	0.16	3	0.78	3	0.33
4	0.02	4	0.15	4	0.38	4	0.21
5	0.00	5	0.00	5	0.49	5	0.16

Table VII

SULFUR CONCENTRATION vs. TIME
0.03% SULFUR DOPANT FROM THIOPHENOL

<u>SHALE-II JP-5</u>		<u>JET A</u>		<u>H-CRACKED JET A STOCK</u>		<u>H-FINED JET A STOCK</u>	
WEEK	mg. S	WEEK	mg. S	WEEK	mg. S	WEEK	mg. S
0	0.61	0	0.60	0	0.60	0	0.60
1	0.13	1	0.17	1	0.17	1	0.31
2	0.05	2	0.03	2	0.12	2	0.20
3	0.06	3	0.01	3	0.01	3	0.21
4	0.05	4	0.01	4	0.05	4	0.19
5	0.05	5	0.01	5	0.03	5	0.18
6	0.03	6	0.01	6	0.05	6	0.13
7	0.03	7	0.01	7	0.01	7	0.10
8	0.00	8	0.01	8	0.00	8	0.10

Table VIII

SULFUR CONCENTRATION vs. TIME
0.01% SULFUR DOPANT FROM THIOPHENOL

<u>SHALE-II JP-5</u>		<u>JET A</u>		<u>H-CRACKED JET A STOCK</u>		<u>H-FINED JET A STOCK</u>	
WEEK	mg. S	WEEK	mg. S	WEEK	mg. S	WEEK	mg. S
0	0.21	0	0.20	0	0.21	0	0.20
1	0.03	1	0.00	1	0.01	1	0.09
2	0.02	2	0.00	2	0.00	2	0.12
3	0.00	3	0.00	3	0.01	3	0.05
4	0.00	4	0.00	4	0.00	4	0.07
5	0.00	5	0.00	5	0.00	5	0.06
6	0.00	6	0.00	6	0.00	6	0.04
7	0.00	7	0.00	7	0.00	7	0.03
8	0.00	8	0.00	8	0.00	8	0.05

Figure 1

SULFUR CONCENTRATION vs. PEROXIDATION

SHALE II JP-5 WITH 0.10% THIOPHENOL

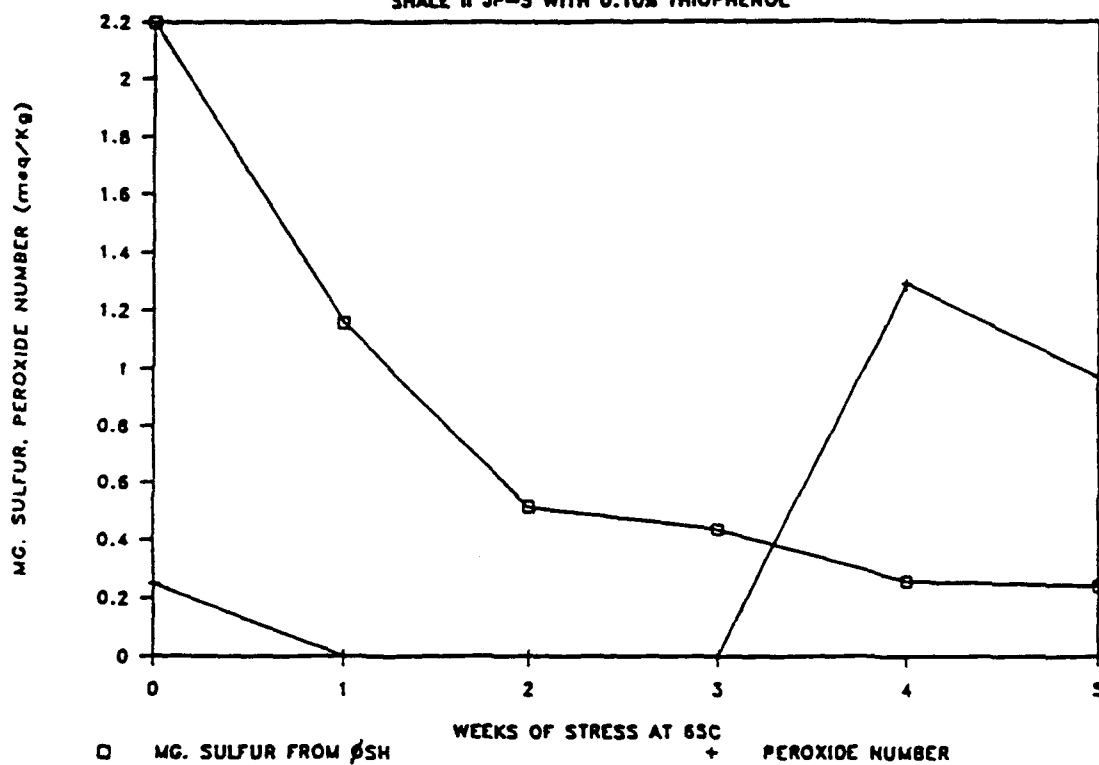


Figure 2

SULFUR CONCENTRATION vs. PEROXIDATION

SHALE II JP-5 WITH 0.05% THIOPHENOL

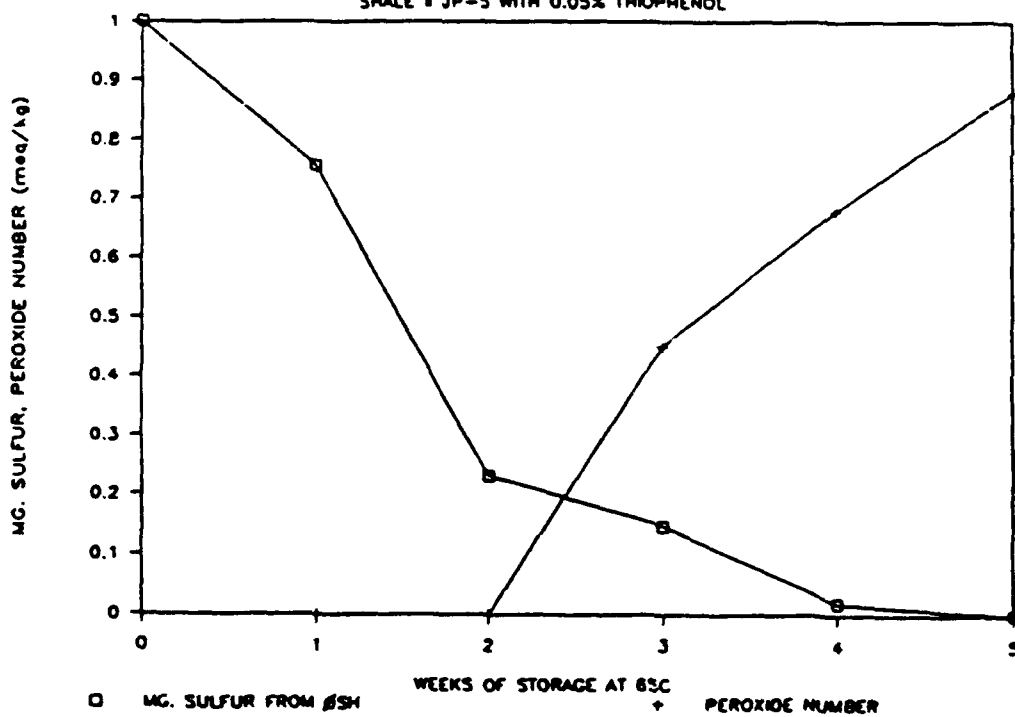


Figure 3

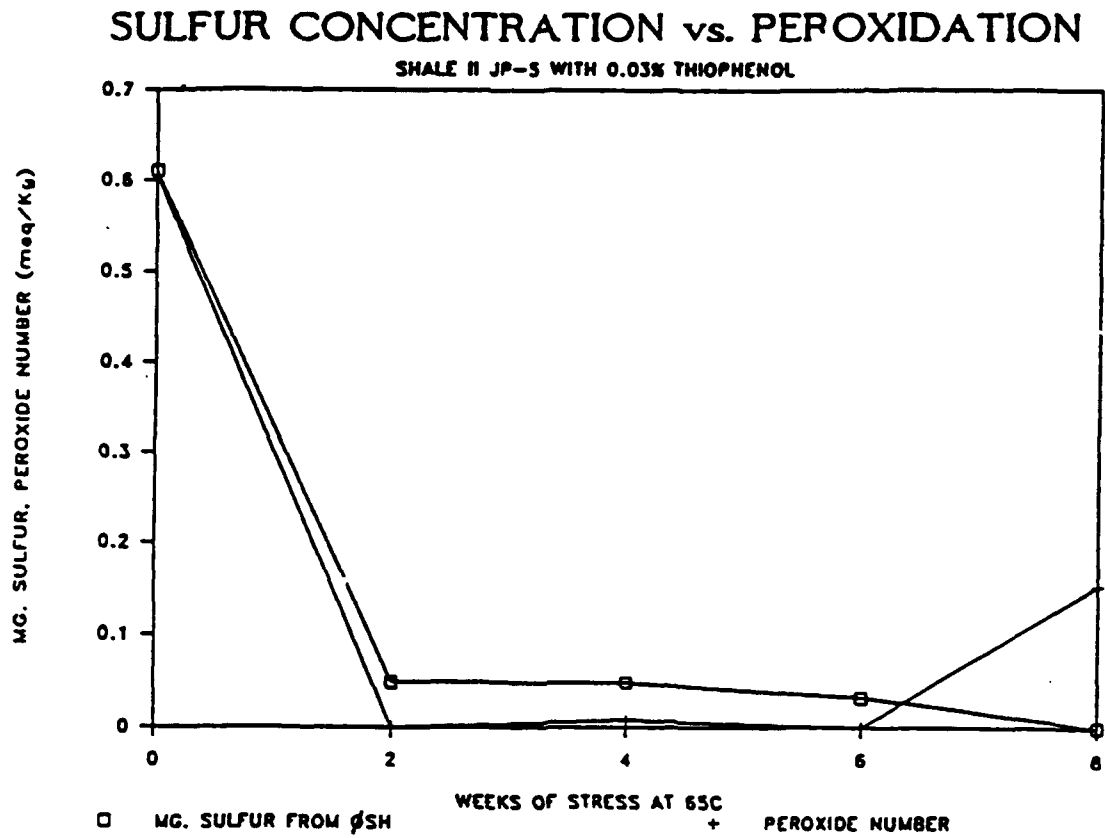
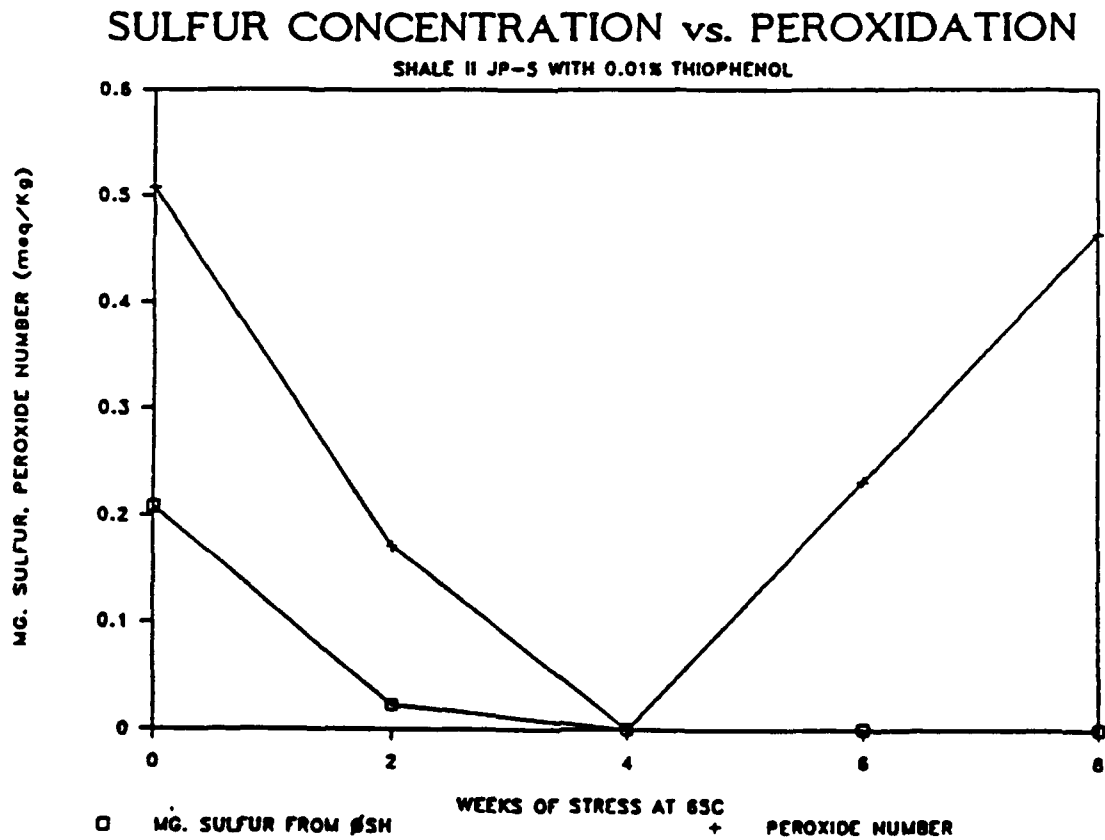


Figure 4



Hydroperoxide Formation and Reactivity in Jet Fuels

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Received September 19, 1988. Revised Manuscript Received November 4, 1988

Hydroperoxides in jet fuels attack elastomers in aircraft fuel systems, resulting in leaks or inoperation of fuel controls. Examination of fuels refined by different processes has indicated that significantly higher peroxide concentrations exist in fuels which have been severely hydrotreated. It is believed that hydrogenation is responsible for removing natural inhibitors, including sulfur compounds, to peroxide formation. To test this thesis, the relationship between arenethiols and peroxidation of jet fuels was examined by using model dopant studies under 65 °C accelerated storage conditions. Samples were analyzed on a weekly basis for peroxides and sulfur compound concentration. Thio-phenol demonstrated effectiveness in reducing and/or controlling peroxide concentration for an equivalent ambient storage time of approximately 2 years.

Introduction

Hydroperoxides in jet fuels attack elastomers in aircraft fuel systems with consequent leaks or inoperation of fuel controls. Problems have been associated with Jet A, JP-4, and JP-5 jet fuels. The first reported incidents occurred with Jet A in Japan in 1962 when fuel hoses of neoprene or nitrile rubber cracked and leaked.¹ In 1976 the U.S. Navy experienced attack on neoprene fuel pump diaphragms on jets operating in the Philippines.² More recent problems have been encountered in Thailand with JP-4 when Buna-N O-rings cracked and leaks from fuel pumps occurred.³ All incidents involved fuels that had been hydrotreated and had peroxide levels from 1 to 8 mequiv of active oxygen/kg of fuel (peroxide number or PN).

Examination of fuels refined by different processes has indicated that significantly higher peroxide concentrations develop in fuels that have been severely hydrotreated. The U.S. Navy has continuing concerns with this topic due to increasing hydrogenation for jet fuel processing. In addition, lower grade crudes and future shale-derived fuel production will involve more extensive and higher pressure hydrotreatment. It has been demonstrated that sulfur compounds in lubricating oils act as antioxidants by decomposing peroxides.⁴ It is believed that hydrogenation is responsible for removing natural inhibitors, including sulfur compounds, to peroxide formation.

Hydroperoxide concentration has been found to be a factor in fuel instability. Fuel degradation is observed to occur under long-term low-temperature storage conditions (storage stability) as well as short-term high-temperature stress (thermal oxidative stability).⁵⁻⁸ The latter situation is found during flight conditions, where fuel serves as a coolant on its path to the combustion chamber. Although slight thermal degradation is found to occur in nonoxidizing atmospheres, the presence of oxygen or active species such as hydroperoxides will greatly accelerate oxidative degradation as well as significantly lower the temperature at which undesirable changes in fuel take place. The rates of reactions in autoxidation schemes are dependent on hydrocarbon structure, heteroatom concentration, oxygen concentration, and temperature.⁹⁻¹¹ If sufficient oxygen is present, the hydroperoxides will reach a high level. If the available oxygen is low, but the temperature is raised, the hydroperoxide concentration will

be limited by free-radical decomposition. Under these conditions, fuel degradation can be associated with both hydroperoxide formation and decomposition.

Several solutions to the problem of fuel peroxidation have been suggested. Antioxidants have been mandated by some authorities, particularly for hydrotreated fuels. Viton elastomers and other materials have been proposed as replacement materials, but their low-temperature properties make them marginal for aircraft use. Clay filtration has been suggested as a means for field removal of hydroperoxides but this treatment has been found to be too expensive.² Although hindered phenols have given satisfactory peroxide control, those phenols that are permitted in the jet fuel specifications were developed for gum control in gasoline. Their effectiveness for peroxide control was found to be marginal, depending on structure.¹² Rolls-Royce defined the peroxidation potential of a fuel with an accelerated 100 °C test for 24 h.¹ Investigations into the relationship of temperature to peroxide concentration in fuel, along with determining the relevance of the 100 °C test to ambient storage conditions, indicated that fuels containing antioxidants behaved differently at different temperatures, and in fuels without antioxidants, peroxide levels were lower than expected at the lower temperatures.¹² A comparison of peroxidation rates in two fuels, one with and one without antioxidant, showed that a fuel without antioxidant produced peroxides at a linear rate while a fuel containing antioxidant produced peroxides

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Table I. Jet Fuel Peroxidation at 65 °C with Added Thiophenol 0.10% Sulfur Dopant

week	Shale-II JP-5		Jet A		Hydrocracked Jet A blending stock		Hydrofined Jet A blending stock	
	control	doped	control	doped	control	doped	control	doped
0	0.25	0.25	0.00	0.00	0.16	0.16	0.00	0.00
1	0.24	0.00	0.19	0.00	0.57	0.00	0.18	0.00
2	0.31	0.00	0.44	0.00	1.16	0.00	0.49	0.00
3	0.37	0.00	0.19	0.00	1.73	0.00	1.10	0.00
4	0.51	1.29	0.40	0.51	5.38	0.26	4.08	0.00
5	0.48	0.97	0.26	0.40	8.47	0.25	10.82	0.00

Table II. Jet Fuel Peroxidation at 65 °C with Added Thiophenol 0.05% Sulfur Dopant

week	Shale-II JP-5		Jet A		Hydrocracked Jet A blending stock		Hydrofined Jet A blending stock	
	control	doped	control	doped	control	doped	control	doped
0	0.69	0.00	0.12	0.00	0.24	0.00	0.10	0.00
1	0.70	0.00	0.18	0.00	1.58	0.00	0.60	0.00
2	0.73	0.00	0.16	0.00	6.01	0.00	2.09	0.00
3	0.94	0.45	0.28	0.54	37.66	0.61	12.41	0.00
4	1.11	0.68	0.26	0.22	62.05	0.51	25.27	0.00
5	1.56	0.88	0.29	0.81	59.92	0.25	56.67	0.00

Table III. Jet Fuel Peroxidation at 65 °C with Added Thiophenol 0.03% Sulfur Dopant

week	Shale-II JP-5		Jet A		Hydrocracked Jet A blending stock		Hydrofined Jet A blending stock	
	control	doped	control	doped	control	doped	control	doped
0	0.60	0.60	0.01	0.01	0.27	0.27	0.06	0.06
1	0.62	0.14	0.04	0.00	0.96	0.00	0.32	0.00
2	0.72	0.00	0.05	0.00	1.88	0.00	0.78	0.00
3	0.84	0.00	0.00	3.98	4.20	0.00	2.46	0.00
4	0.90	0.01	0.09	0.01	10.04	0.01	5.89	0.00
5	0.93	0.00	0.05	0.50	22.43	0.00	13.26	0.00
6	0.99	0.00	0.00	0.70	49.03	0.00	28.54	0.00
7	1.14	0.03	0.13	1.38	77.88	0.62	60.62	0.00
8	1.29	0.15	0.07	0.88	97.40	0.36	77.44	0.00

in an exponential fashion, indicating a depletion with time of the antioxidant and its ability to control peroxidation.¹²

Sulfur is the most abundant heteroatom present in jet fuels (up to 0.4% allowed by specifications). Deposits formed in jet fuel in the presence of oxygen contain a higher percentage of sulfur than that present in the fuel itself.¹³ The formation of these deposits has been attributed to the participation of sulfides, disulfides, and thiols (mercaptans).¹⁴ In jet fuels that have been deoxygenated, sulfides and disulfides have been found to lead to increased solid formation.¹⁵ Examination of the reactions between both alkyl and aromatic thiols with *tert*-butyl hydroperoxide (tBHP) have indicated that aromatic thiols are more reactive than other classes of sulfur compounds with hydroperoxides. The reaction of thiophenol with tBHP was found to produce trace amounts of sulfonic acid while depleting the amount of both reactants in solution.¹⁶ It was thus desirable to test the relationship between sulfur compound reactivity and peroxide formation by using an arenethiol as a model dopant under accelerated storage conditions.

This paper discusses the effect on hydroperoxide formation of using an arenethiol, thiophenol, as a dopant in a Jet A, a shale-derived jet fuel, and two jet fuel blending stocks under 65 °C accelerated storage conditions. A 65

°C stress test was chosen for the sulfur compound study based on previous time-temperature peroxidation studies completed at NRL.¹² The effect on peroxide formation versus added sulfur concentrations is also reported.

Experimental Section

Fuels and Reagents. The four fuels used in the investigation were Shale-II JP-5, Jet-A, a Hydrocracked Jet A blending stock, and a Hydrofined Jet A blending stock. Thiophenol was obtained from Aldrich Chemical Co. and was distilled in vacuo to 99.9% purity.

Method. The stress test was patterned after that used by the laboratories which participated in the recent Coordinating Research Council cooperative studies on peroxidation.¹⁷ Tests were carried out in brown borosilicate glass bottles, 500-mL total capacity, capped with Teflon liners, containing 300 mL of fuel per bottle. Duplicate samples of the four fuels were prepared, with sulfur in the form of thiophenol weighed into one sample of each fuel. The first series of samples were prepared by adding 0.10% sulfur (weight/volume) from thiophenol, followed by sets with 0.05, 0.03, and 0.01% added sulfur concentrations. Stress tests were conducted for 5 weeks for the samples containing 0.10 and 0.05% added sulfur. The samples containing 0.03 and 0.01% added sulfur were stressed at 65 °C for 8 weeks. Samples were analyzed weekly for peroxide concentration by ASTM Method D3703-85 from the control and test bottles for each fuel. A Mettler DL20 automatic titrator was employed for the 0.03 and 0.01% added sulfur tests, eliminating the use of starch solution from the ASTM method. Thiophenol concentrations were monitored weekly with a Tracor 565 gas chromatograph equipped with a sulfur-specific 700A Hall electrolytic conductivity detector. The chromatography program used started at 60 °C for 8 min, with a ramp of 10 °C/min to a final temperature of 260 °C. Samples

(13) Wallace, T. J. In *Advances in Petroleum Chemistry and Refining*; Wiley-Interscience: New York, 1964; pp 353-407.

(14) Taylor, W. F.; Wallace, T. J. *Ind. Eng. Chem. Prod. Res. Dev.* 1968, 7, 198.

(15) Taylor, W. F. *Ind. Eng. Chem. Prod. Res. Dev.* 1976, 15, 64.

(16) Mushrush, G. W.; Hazlett, R. N.; Hardy, D. R.; Watkins, J. M. Liquid Phase Oxidation of Sulfur Compounds. In *Conference Proceedings, 2nd International Conference on Long Term Storage Stabilities of Liquid Fuels*; Southwest Research Institute: San Antonio, TX, 1986; Vol. 2, pp 512-525.

(17) Determination of the Hydroperoxide Potential of Jet Fuels. Report No. 559; Coordinating Research Council: Atlanta, GA, Apr 1988.

Table IV. Jet Fuel Peroxidation at 65 °C with Added Thiophenol 0.01% Sulfur Dopant

week	Shale-II JP-5		Jet A		Hydrocracked Jet A blending stock		Hydrofined Jet A blending stock	
	control	doped	control	doped	control	doped	control	doped
0	0.51	0.51	0.00	0.00	0.25	0.25	0.06	0.06
1	0.60	0.20	0.10	1.04	1.02	0.73	0.50	0.00
2	0.67	0.17	0.13	0.72	2.37	0.11	1.32	0.00
3	0.81	0.00	0.20	0.89	4.66	0.00	3.63	0.00
4	0.85	0.00	0.17	0.55	13.22	0.00	13.79	0.00
5	0.99	0.00	0.21	0.59	29.20	0.22	29.10	0.00
6	1.08	0.23	0.17	0.42	55.33	0.14	48.57	0.00
7	1.12	0.33	0.19	0.72	89.57	0.19	78.27	0.00
8	1.51	0.46	0.24	0.65	131.13	0.28	124.98	0.00

were analyzed in triplicate against an external standard for thiophenol, which was also analyzed in triplicate.

Results and Discussion

Thiophenol was the sulfur compound used as a dopant in this study. The first reaction series in this study employed 0.01% total sulfur (weight/volume) weighed out as thiophenol. To examine the effect of added sulfur concentration on peroxidation, a second test was run by using 0.05% added sulfur from thiophenol. On the basis of the results of the 0.05% added sulfur test, additional series were run by using 0.03 and 0.01% added sulfur from thiophenol. The data for these tests are presented in Tables I-IV, respectively.

For all of the sulfur concentration tests, the control samples, fuel only, exhibited similar behavior. Differences in actual peroxide numbers between tests can be attributed to slight temperature differences in the ovens that were used and to the fact that the fuel samples had been in storage for varying times before these tests were started. It was interesting that in the Jet A control samples peroxide formation occurred in a cyclic pattern. This has been observed in other peroxidation studies with Jet A. The two Jet A blending stocks formed peroxides at a greater rate than the Shale JP-5 or the Jet A samples.

The most important aspect of all the tests was that the samples doped with sulfur in the form of thiophenol did not undergo peroxidation as rapidly as the fuel only samples. In fact, thiophenol addition eliminated any ROOH present in starting samples of all four fuels in the 0.05% added sulfur series, and after the first week in the Shale II and Hydrocracked Jet A blending stock samples in the 0.10% test. In the samples doped with 0.10% sulfur, peroxide formation was not observed until the fourth week of the stress test. When the concentration of added sulfur was reduced (halved) peroxide formation began 1 week earlier in the three fuels that did exhibit peroxidation, indicating a relationship between added sulfur concentration and peroxide formation (or peroxide inhibition). None of the doped samples of the Hydrofined Jet A blending stock showed evidence of peroxide formation throughout the duration of the tests.

In the series doped with 0.03% added sulfur from thiophenol, peroxides were eliminated after 1 week of 65 °C stress in all of the samples except for the Shale-II JP-5, which contained a larger starting concentration of peroxides that required 2 weeks to be reduced to zero as measured by the ASTM method. The Jet A samples began to exhibit peroxidation in the third week of the test, while the Shale-II and Hydrocracked Jet A blending stock samples did not show any trace of peroxidation until the fourth week, before disappearing again to reemerge in the seventh week of the test. Even though peroxidation was not observed until later in this test than in the 0.10 and 0.05% added sulfur samples, the 0.03% added sulfur controlled peroxidation, most noticeably in the Hydrocracked and

Table V. Sulfur Concentration vs Time for 0.10% Sulfur Dopant from Thiophenol

Shale-II JP-5		Jet A		Hydrocracked Jet A stock		Hydrofined jet A stock	
week	mg of S/2 mL	week	mg of S/2 mL	week	mg of S/2 mL	week	mg of S/2 mL
0	2.20	0	2.08	0	2.12	0	2.10
1	1.16	1	0.98	1	0.92	1	1.78
2	0.51	2	0.81	2	0.74	2	1.47
3	0.43	3	0.63	3	0.67	3	1.58
4	0.26	4	0.47	4	0.48	4	1.43
5	0.24	5	0.41	5	0.47	5	1.38

Table VI. Sulfur Concentration vs Time for 0.05% Sulfur Dopant from Thiophenol

Shale-II JP-5		Jet A		Hydrocracked Jet A stock		Hydrofined Jet A stock	
week	mg of S/2 mL	week	mg of S/2 mL	week	mg of S/2 mL	week	mg of S/2 mL
0	1.00	0	1.00	0	1.00	0	1.00
1	0.76	1	0.25	1	0.86	1	0.37
2	0.23	2	0.33	2	0.63	2	0.76
3	0.15	3	0.16	3	0.78	3	0.33
4	0.02	4	0.15	4	0.38	4	0.21
5	0.00	5	0.00	5	0.49	5	0.16

Hydrofined Jet A blending stock samples, which did not exhibit any peroxidation during the test, in spite of the fact that both of these samples peroxidized extensively when the thiophenol was absent.

The samples doped with 0.01% added sulfur from thiophenol also demonstrated the ability of added sulfur to control peroxidation. In the Shale-II and Hydrocracked Jet A blending stock samples, the starting peroxide concentrations were gradually decreased to zero after 3 weeks of stress. Peroxidation was not evident in the Shale-II sample until the sixth week of the test, but began again in the Hydrocracked Jet A blending stock sample in the fifth week of stress. This can be explained by comparing the relative peroxide levels present in the control samples, 0.991 mequiv of active O₂/kg of fuel versus 29.200 mequiv of active O₂/kg of fuel for the Shale-II and Hydrocracked blending stock samples, respectively. The 0.01% added sulfur was not enough to control the large amount of peroxide formation after 5 weeks in the Hydrocracked Jet A blending stock sample. The Jet A samples, both control and doped, exhibited interesting cyclic behavior similar to that in the 0.03% added sulfur study, while the doped Hydrofined Jet A blending stock sample did not undergo peroxidation during the test after the starting peroxide concentration was depleted.

The thiophenol concentrations in the doped samples decreased throughout the tests as measured by the sulfur-specific electrolytic conductivity detector on the gas chromatograph. Tables V and VI contain the data for the 0.10 and 0.05% sulfur from thiophenol-doped samples, respectively. Samples were analyzed in triplicate and

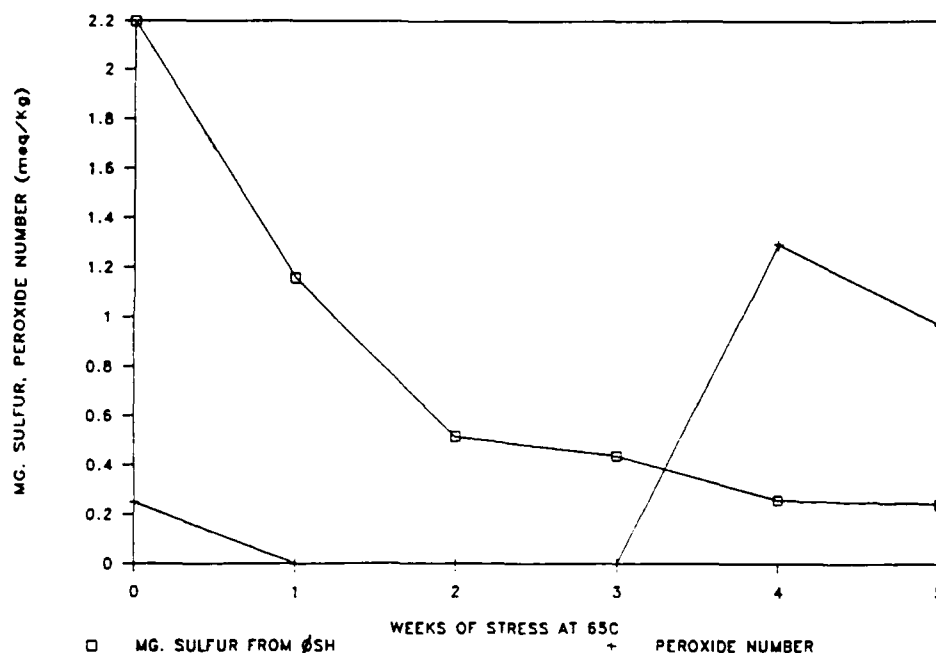


Figure 1. Sulfur concentration versus peroxidation for Shale-II JP-5 with 0.10% thiophenol.

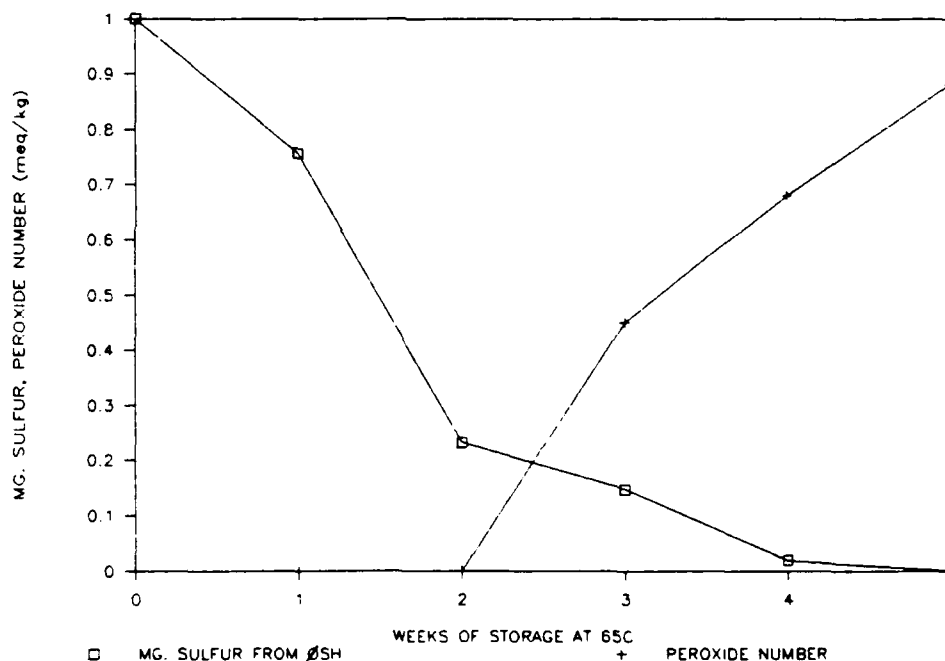


Figure 2. Sulfur concentration versus peroxidation for Shale-II JP-5 with 0.05% thiophenol.

compared to an external standard for thiophenol, which was also analyzed in triplicate. Average values are reported and were used for all calculations. It is interesting to note that the sulfur concentrations decreased more rapidly and to a greater extent in the doped Shale-II, Jet A, and Hydrocracked blending stock samples, those fuels that did exhibit some peroxidation, than in the Hydrofined blending stock sample, which did not exhibit peroxidation during the test. This was true for both concentrations of added sulfur with the exception of the Hydrocracked sample, which depleted slower in the 0.05% doped test. The presence of new peaks on the chromatogram indicated the formation of new sulfur-containing compounds; however, concentrations were too low to permit identification. It should be noted that in the 0.10% doped samples there were still measurable sulfur concentrations for the duration of the stress test, but for the 0.05% doped samples, the

added thiophenol disappeared much faster and was completely depleted between the fourth and fifth weeks of the test for the Shale-II and Jet A samples. A direct comparison of the sulfur concentration to peroxidation in the Shale-II samples can be seen in Figures 1 and 2 for the 0.10 and 0.05% doped samples, respectively. The place on the graphs where the lines intersect indicates the approximate concentration of added sulfur at which peroxidation is no longer controlled. It should be noted that this concentration was approximately 0.4 mg of sulfur for the 0.10% doped sample and 0.2 mg of sulfur for the 0.05% doped sample.

The results for the 0.03 and 0.01% added sulfur from thiophenol studies are reported in Tables VII and VIII, respectively. The doped samples in these series exhibited behavior similar to the first two tests. The sulfur concentrations in the two Hydrofined Jet A blending stock

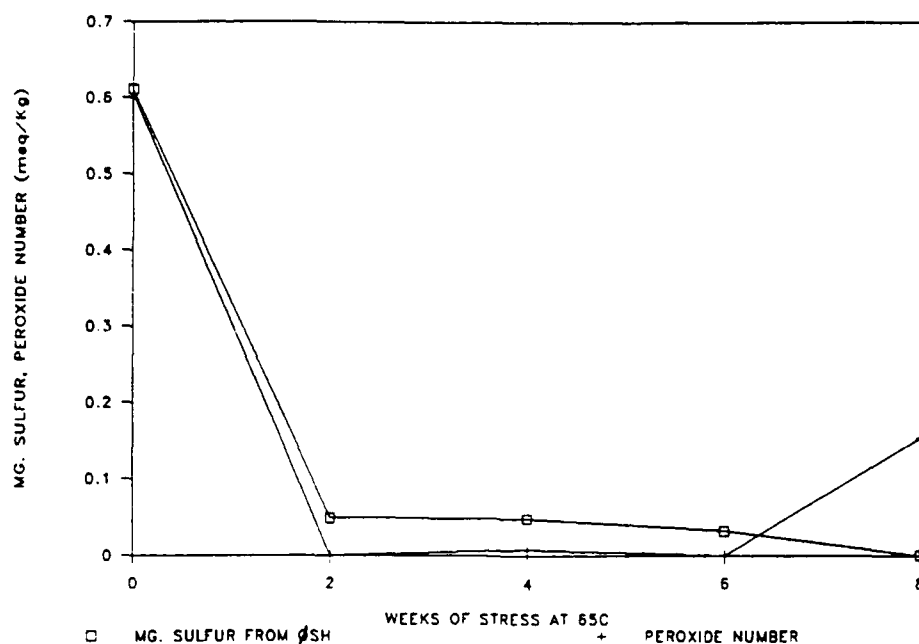


Figure 3. Sulfur concentration versus peroxidation for Shale-II JP-5 with 0.03% thiophenol.

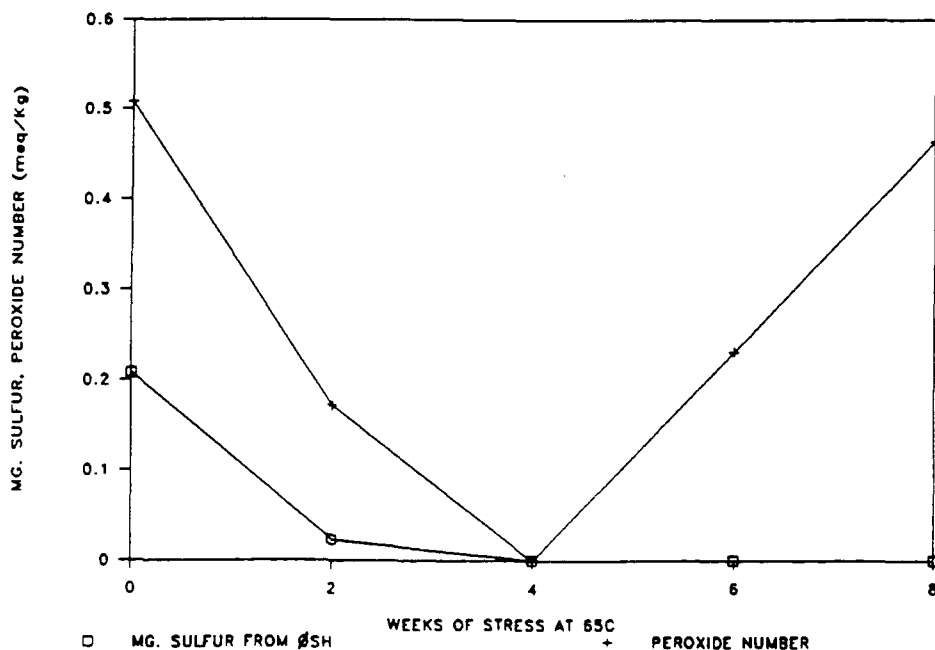


Figure 4. Sulfur concentration versus peroxidation for Shale-II JP-5 with 0.01% thiophenol.

samples did not decrease as rapidly or to the same extent as the concentrations in the other fuels. The sulfur concentration in the 0.03% sulfur-doped Shale JP-5 sample was depleted by the eighth week of the test while the concentration in the 0.01% doped sample was zero by the third week of the test. In the Hydrocracked Jet A blending stock samples there were low sulfur concentrations throughout the duration of the tests, with the 0.01% doped sample dropping to zero by week five. The 0.03% doped Jet A sample exhibited cyclic peroxide formation and a rapid decrease in sulfur concentration, while the 0.01% doped sample showed an immediate decrease in sulfur concentration during the first week of stress. Figures 3 and 4 provide a direct comparison of the sulfur concentration to the peroxidation of the samples doped with 0.03 and 0.01% added sulfur. According to this data, the concentration at which peroxidation was no longer controlled was about 0.03 mg of added sulfur for the 0.03%

Table VII. Sulfur Concentration vs Time for 0.03% Sulfur Dopant from Thiophenol

Shale-II JP-5		Jet A		Hydrocracked Jet A stock		Hydrofined Jet A stock	
week	mg of S	week	mg of S	week	mg of S	week	mg of S
0	0.61	0	0.60	0	0.60	0	0.60
1	0.13	1	0.17	1	0.17	1	0.31
2	0.05	2	0.03	2	0.12	2	0.20
3	0.06	3	0.01	3	0.01	3	0.21
4	0.05	4	0.01	4	0.05	4	0.19
5	0.05	5	0.01	5	0.03	5	0.18
6	0.03	6	0.01	6	0.05	6	0.13
7	0.03	7	0.01	7	0.01	7	0.10
8	0.00	8	0.01	8	0.00	8	0.10

doped sample. This concentration was reached at the end of 6 weeks of stress, and peroxidation began between the sixth and seventh week of the test. In the sulfur concentration versus peroxidation graph for the shale sample with

Table VIII. Sulfur Concentration vs Time for 0.01% Sulfur Dopant from Thiophenol

Shale-II JP-5		Jet A		Hydrocracked Jet A stock		Hydrofined Jet A stock	
week	mg of S	week	mg of S	week	mg of S	week	mg of S
0	0.21	0	0.20	0	0.21	0	0.20
1	0.03	1	0.00	1	0.01	1	0.09
2	0.02	2	0.00	2	0.00	2	0.12
3	0.00	3	0.00	3	0.01	3	0.05
4	0.00	4	0.00	4	0.00	4	0.07
5	0.00	5	0.00	5	0.00	5	0.06
6	0.00	6	0.00	6	0.00	6	0.04
7	0.00	7	0.00	7	0.00	7	0.03
8	0.00	8	0.00	8	0.00	8	0.05

0.01% added sulfur, peroxide inhibition stops in the fifth week of stress when the added thiophenol concentration was reduced to zero as measured by the sulfur detector. The comparison of sulfur concentration to peroxidation indicated that control or inhibition of peroxidation was lost at approximately 0.2 ± 0.1 mg of added sulfur in all fuel samples.

Conclusions

The effect of adding sulfur in the form of an aromatic thiol, thiophenol, was significant to peroxide formation.

Thiophenol has been found to act as an inhibitor or controller of peroxide formation in Jet A, Shale-II-derived JP-5, and petroleum-derived Jet A blending stocks. Hydrotreated jet fuels exhibited higher peroxide formation and concentration than other fuels. Hydrotreatment reduces the sulfur content of the fuel, which removes those naturally occurring sulfur compounds that possibly act as inhibitors to peroxide formation. There appeared to be a minimum concentration of sulfur as thiophenol above which peroxide formation was inhibited. If this concentration was decreased or consumed, peroxidation began.

In a mixture as complex as a fuel, when a sulfur dopant is present at a concentration of 0.10% or less, the sulfur compound reaction products are not possible to detect. Sulfur compound MS and hydrocarbon MS are quite similar, and the sulfur compounds are buried in the GC of the fuel. We suggest that since aromatic thiols are quite reactive in the presence of peroxide species, the thiophenol most likely undergoes oxidation by the peroxide.¹⁶ In model systems, in dodecane solvent, we found in our preliminary studies with hydroperoxides and sulfur model compounds that both aryl disulfides and oxidized sulfur species such as sulfoxides and sulfones were formed from thiophenol.

Registry No. Thiophenol, 108-98-5.

CHARACTERIZATION OF POLAR EXTRACTS FROM
TWO PETROLEUM-DERIVED FUELS

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ABSTRACT

Petroleum fuels of marginal stability have been used as a source of nitrogen-rich polar extracts. Polar compounds were isolated by mild acid extraction followed by silica gel adsorption. The extracts were characterized and identified by combined capillary column GC/MS. Both fuels were studied by two methods under accelerated storage conditions, bottle tests and oxygen overpressure. Bottle tests were conducted at 80°C for 14 days and the oxygen overpressure at both 65 and 43°C for 6 days and 4 weeks respectively. Filterable insolubles and adherent gum were measured for both methods. Peroxide numbers were determined by ASTM D3703-85 for both stressed and original fuel samples.

INTRODUCTION

As domestic and imported petroleum stocks decrease and petroleum again increases in cost, it is imperative to consider liquid fuel options. Several options can be explored:

(a) the relaxation of fuel specifications, (b) alternate sources of fuels, and (c) the use of lower quality or blended stocks. This paper deals with the study of two fuel blends that could be utilized as middle distillate fuels.

The bulk of the Navy's vehicles use middle distillate fuels; a kerosene type aircraft jet fuel, JP-5, for aircraft and Naval Distillate Fuel, NDF, for ships and boats.

Changes in fuel properties with time have been a continuing problem in the utilization of middle distillate fuels. Problems associated with the storage instability include: the formation of filterable sediments (FS) and gums as well as the production of peroxides and color bodies. The current trends toward lower grade petroleum crudes has created a pressing need for investigation into the fundamental nature of liquid fuel stability (Goetzinger et al., 1983; Frankenfild et al., 1982; Cooney et al., 1984; Beal et al., 1987).

Nitrogen containing aromatics have long been associated with storage instability (Goetzinger et al., 1983; Mushrush et. al., 1986; Beal et al., 1987), yet present knowledge is limited regarding the chemistry of their autoxidation in the complex fuel media. There are many approaches to the study of this problem. One approach involves the examination of model nitrogen compounds as dopants in otherwise stable base fuels. Although the results of fuel dopant studies are useful in screening nitrogen compound classes for potential activity,

the results must be interpreted with caution. For example, the particular stress test employed may have a great effect upon the results obtained. In addition, the question of interactive effects between species in fuels needs to be examined in greater detail, since it is likely that they may actually define the storage stability behavior of many fuels.

In this paper, two marginally stable low nitrogen petroleum jet fuels were examined. Polar extract components were isolated and characterized and the fuels studied by accelerated storage stability tests.

EXPERIMENTAL

Storage Test Techniques

The accelerated storage stability method used has been described in detail (Hazlett et al., 1983; Cooney et al., 1984). In summary, 300ml samples of filtered fuel were stressed in the dark in 500 ml screw-cap borosilicate brown bottles (teflon-lined caps). All samples were run in replicate and appropriate blank flask/filter holder corrections were applied. Both filterable sediment and adherent insolubles values were determined after stress. In general, fuel stability was defined by the amount of total insoluble material formed after stress. This quantity was equal to the sum of filterable insolubles and adherent insolubles. The

data presented in the Tables are in units of mg of insolubles per 100ml of fuel.

For tests using the oxygen overpressure method, 100 ml aliquots of filtered fuel were placed in borosilicate glass bottles in a closed steel reactor and the reactor pressurized to 100 psia with 99.5% oxygen (Hardy, et al., 1987). In separate experiments, the reactors were placed in thermostatted ovens at temperatures of 65°C or 43°C for times of 6 days and 4 weeks respectively. After aging and cooling, the amount of filterable insolubles and adherent gum was determined gravimetrically.

Peroxide numbers were determined in duplicate for samples of filtered fuel before and after stress by iodometric titration (ASTM D3703-85). Titrations were carried out using a Mettler DL20 Compact Titrator automatic titration system. This method removed the need to use starch indicator as described in ASTM D3703-85.

Instrumental Methods

The polar nitrogen compound extracts were examined by combined GC/MS (EI mode.) The GC/MS unit consisted of a Hewlett-Packard Model 5710 GC, an H-P Model 5982 mass spectrometer and a Ribermag SADR GC/MS data system. An all-glass GC inlet system was used in conjunction with a 0.31 mm x 50 m SP2100 (similar to OV-101) fused silica capillary

column (Hardy et al., 1985.) Operational parameters included: sample size - 2 to 3 microliters split at 60:1, column flow - 1.1 to 1.2 ml/min at a head pressure of 10.5 PSI, detector gain - 9 x Low, injection port - 250°C, temperature program - 70°C (2 min hold,) 4°C/min programmed temperature ramp to 220°C (16 min final hold.)

Nitrogen concentration levels in the fuel samples were determined with an Antek Model 720 nitrogen analyzer using a Dohrmann Model S-300 combustion furnace operating at 1000°C. Three-microliter samples were analyzed in quadruplicate (at the minimum) with the actual nitrogen concentration calculated by comparison with nitrogen calibration standards.

The sulfur content of the samples was examined using a Tracor Model 565 gas chromatograph equipped with a sulfur specific Hall electrolytic conductivity detector (ECD). An all-glass GC inlet system was used in conjunction with a 50m x 0.2mm i.d. wall-coated open tubular (OV-101) fused silica capillary column which was operated at a temperature program of 60°C for 8 min., and a ramp of 5°C/min to a final temperature of 260°C. Air was replaced with oxygen as the reaction gas in the ECD for improved resolution and baseline.

Nitrogen Compound Source Fuel

The low-nitrogen petroleum fuels Sun A (233ppm N) and Sun B (82ppm N) were refined and blended from both cracked and distillate stocks at the Sun Refinery in Marcus Hook, PA.

Extraction Procedure

As shown in Figure 1, the fuels were initially subjected to extraction with a 25% molar excess of 1.0 N HCl. The

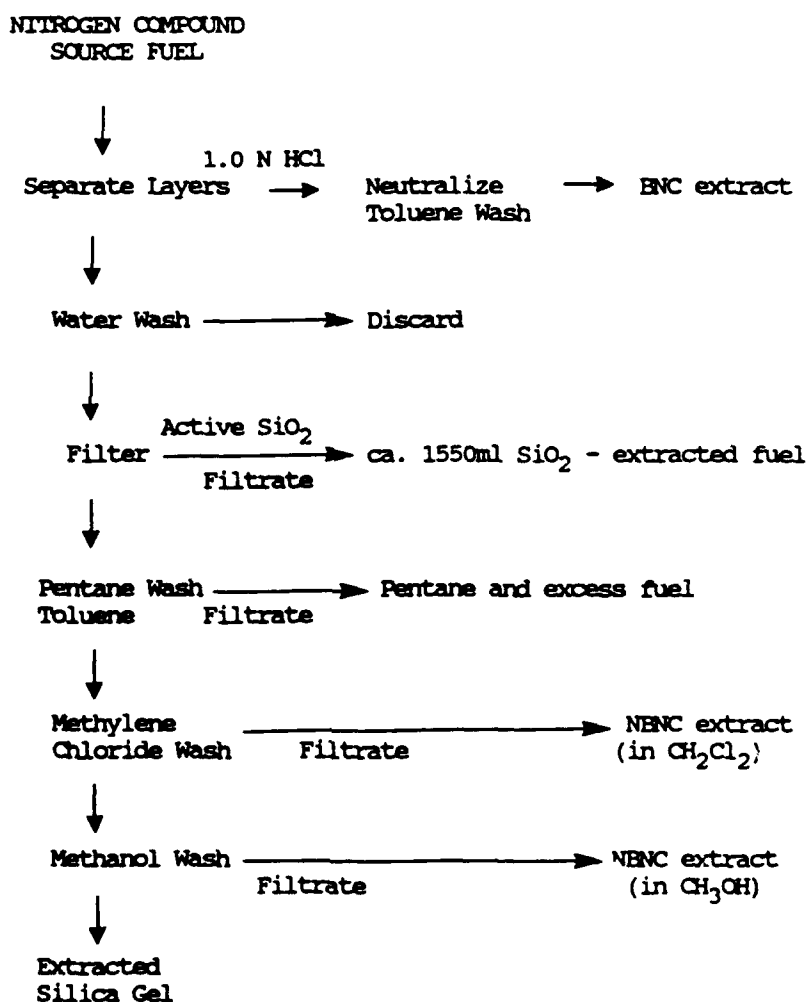


Figure 1
Nitrogen Compound Extraction Scheme

quantity of acid used was calculated by assuming that all of the nitrogen present in the fuels was basic or extractable. The single acid extraction was accomplished with 2 liters of fuel in a 4 liter separatory funnel. A portion of the fuel to be extracted was placed in the funnel with the appropriate quantity of 1.0 N HCl and shaken vigorously. The contents were then vigorously swirled for 5 min, allowed to stand 5 min, gently swirled for 5 min (to reduce the number of emulsion particles) and allowed to stand for 10 min. After careful separation of the layers, traces of acid were removed from the fuel sample by washing with water. The "basic" nitrogen compounds (BNC extracts) were isolated by neutralizing the combined aqueous acid extracts to pH 8-9 (NaHCO_3), extracting the mixture twice with toluene, drying the combined organic layer (anh. MgSO_4) and removing the solvent gently by rotary evaporation (verified by GC.)

The residual polar material (including non-basic nitrogen compounds, the "NBNC" extracts) was removed from the acid-extracted fuel by batch silica gel adsorption. Again, it was decided to employ a relatively mild separation technique to avoid extensive chemical alteration of the polar species present. Thus, 2 liters of fuel were treated once with 400g of fully activated Grade 923 silica gel (100-200 mesh, W. R. Grace) with stirring for a 3 hour period. Gravity filtration afforded ca. 1550 ml of silica extracted fuel (filtrate) and a

quantity of moist silica. Excess fuel was desorbed from the moist silica by several washings with pentane (ca. 2.5 L). The silica was next equilibrated several times with methylene chloride (8 x 500 ml.) The methylene chloride NBNC extracts were combined and retained. Following this treatment, the silica gel was treated with methanol (1 x 1 L). The methanol extract after separation was retained for further study and analysis (methanolic NBNC extract).

RESULTS AND DISCUSSION

The Naval Research Laboratory, as part of an effort to relate fuel composition to stability, has reported on the polar components and stability of high nitrogen fuels (Mushrush et. al., 1986; Cooney et. al. 1984, 1983, 1982; Hazlett et. al. 1983.) It was consequently of interest to examine the polar components and instability of low nitrogen containing fuels. Both fuels were subjected to simulated distillation analysis, ASTM D2887. Both Sun A and B fuels were found to be broad cut fractions. For Sun A, the IBP was 148°C, at 1% distilled 153°C, at 5% off 171°C, at 50% off 253°C, at 95% off 351°C, at 99% off 391°C and a FBP of 415°C. For Sun B, the IBP was 139°C, at 1% off 149°C, at 5% off 176°C, at 50% off 249°C, at 95% off 322°C, at 99% off 366°C and a FBP of 385°C.

Table I
NITROGEN ANALYSES FOR EXTRACTED NITROGEN
IN SUN A AND B FUELS

SAMPLE	N CONCENTRATION (ppm-w/v)	
	SUN A	SUN B
ORIGINAL FUEL	233	83
IN ACID EXTRACT	132	57
ISOLATED IN CH ₂ Cl ₂ WASH OF SILICA	27	19
ISOLATED IN CH ₃ OH WASH OF SILICA	53	8
TOTAL N RECOVERED IN FRACTIONS	212 (91%)	84 (101%)

Both fuels proved to be low in total organo-sulfur content. Sun A was found to have 0.09% and Sun B to contain 0.06% total organo-sulfur.

The separation scheme which was employed for the removal of polar, nitrogen-rich extract from the fuels studied is summarized in Figure 1. A single mild acid extraction was selected (3.7 equiv. of 1.0 N HCl) so that the opportunity for chemical changes in the fuel would be minimized. Many nitrogen heterocyclic compounds are known to be acid sensitive (Jones and Bean, 1977).

The HNC extract was obtained in toluene solution following neutralization of the acid wash. Subsequent treatment of the acid extracted fuel with activated silica gel afforded separate NENC extracts in methylene chloride and

methyl alcohol. The fuels and the three extracts for each were analyzed for soluble nitrogen content in order to assess a nitrogen balance. The nitrogen balance data, which appear in Table I, indicated that 91% of the nitrogen originally present in Sun A and 100% of the nitrogen present in Sun B was accounted for. With Sun A, several trial extractions (on a 10ml scale) were able to remove all of the nitrogen present. However, the actual batch extraction process was found to be far less efficient.

Examination of Nitrogen Compound Extracts

Compounds present in the ENC, NENC (CH_2Cl_2), and NENC (CH_3OH) extracts were examined by GC/MS. The conditions used permitted excellent separation of the compounds present in both fuels. Both total ion and selected ion counting techniques were employed, with peaks identified on the basis of fragmentation pattern and z-series (Hardy et. al., 1982; Burchill et. al., 1983.) Frequently, two or more compounds would be present in a peak so that the relative amount of each was approximated by the magnitude of the total ion count for a given fragmentation pattern. Peak areas were determined by integration of the total ion count over the entire peak. It is important to note that the percentages given in Tables II-V are not to be construed as "absolute" for the fuel extracts, since not every peak in the GC/MS spectrum could be identified and ionization efficiencies are not defined for most

Table II
EXAMINATION OF BNC EXTRACT FROM
SUN A AND B FUELS

GC FOUND CLASS	BNC EXTRACTS	
	SUN A AREA%	SUN B AREA%
I. <u>HYDROCARBONS</u>	<u>5.7</u>	<u>4.2</u>
A. ALKANES	1.0	0.7
B. BENZENES	2.1	0.9
C. TETRALINS	1.4	1.3
D. INDANS	1.2	—
E. NAPHTHALENES	1.3	—
II. <u>HETEROATOMIC COMPOUNDS</u>	<u>93.6</u>	<u>92.2</u>
A. PYRIDINES	64.3	66.9
B. PYRROLES	4.4	4.0
C. INDOLES	9.1	5.1
D. QUINOLINES	10.4	13.1
E. TETRAHYDROQUINOLINES	3.2	3.1
F. ACRIDINES	1.7	—
G. CARBAZOLES	0.5	—

compounds. The peaks which were examined in all GC/MS spectra of the extracts represented at least 95% of the total ion count and were thus representative of the total extracts. The results for the acid extractable material BNC for both Sun A and Sun B is given in Table II.

The hydrocarbon concentration for A showed 5.7% and 4.2% for B, while the heteroatomic compounds showed 93.6% for Sun A and 92.2% for Sun B. Sun A has approximately three times the nitrogen content of B, 233 vs 82 ppm. For the BNC extract from Sun A, one hundred and seventy-three well resolved major

peaks were analyzed and over 250 different distinct nitrogen compounds were identified. Substituted pyridines and anilines accounted for 64.3% of the compounds identified. Also present were substituted quinolines (10.4%), pyrroles (4.4%), indoles (9.1%), acridines (1.7%), and carbazoles (0.5%). Other heteroatomic compounds present include: tetrahydroquinolines, benzocinnolines, and dibenzothiophenes. For the Sun B fuel BNC extract, nitrogen heterocycles included pyridines/anilines (92.2%), quinolines (13.1%), indoles (5.1%), pyrroles (4.0%), tetrahydroquinolines (3.1%), and minor amounts of acridines, and carbazoles.

The pyridines/anilines which were in both the A and B BNC extracts were characterized principally by substituted long alkyl chains. For Sun B however, the pyridines appear to be more highly branched. The presence of substantial amounts of quinolines and the small quantity of tetrahydroquinolines is a reflection of the lack of hydrotreatment used during processing.

The major similarity between the two BNC fractions, other than the pyridine concentration was the presence of both indoles and pyrroles in this extract.

The NBNC (CH_3OH solubles from the silica gel treatment) extract for both Sun A and B is depicted in Table III. The hydrocarbon fraction was 31.6% for Sun A and 28.1% for Sun B. The heteroatomic fraction was 70.1% for Sun A and

Table III
EXAMINATION OF NENC (CH₃OH) EXTRACT
FROM SUN A AND B FUELS

COMPOUND CLASS	SUN A AREA%	SUN B AREA%
I. <u>HYDROCARBONS</u>	<u>31.6</u>	<u>28.1</u>
A. ALKANES	5.0	3.2
C. FLUORENES	5.5	6.1
E. PHENANTHRENE/ANTHRACENES	6.5	17.1
D. NAPHTHALENES	14.6	1.7
II. <u>HETEROATOMIC COMPOUNDS</u>	<u>70.1</u>	<u>70.9</u>
A. PYRIDINES	49.2	56.1
B. ACRIDINES	7.8	5.1
C. CARBAZOLES	6.7	7.2
D. QUINOLINES	4.1	2.0
E. TETRAHYDROQUINOLINES	1.2	—
F. INDOLES	1.2	0.5

70.9% for Sun B. The major components of both Sun A and B were substituted pyridines; 49.2% for Sun A and 56.1% for Sun B. Other compounds noted in Sun A were acridines (7.8%), carbazoles (6.7%), quinolines (4.1%), tetrahydroquinolines (1.2%), and indoles (1.2%). For Sun B other heteroatomic substances included: carbazoles (7.2%), acridines (5.1%), quinolines (2.0%), and indoles (0.5%). The results for these fractions seem to indicate a less efficient separation than the ENC fractions. The appearance of pyridines and quinolines in this extract can, however, be explained by an observation from the ENC extract. The Sun B, ENC extract, was found to contain more highly branched and consequently much less basic pyridines.

Table IV

EXAMINATION OF NENC (CH_2Cl_2) EXTRACT
FROM SUN A AND B FUELS

COMPOUND CLASS	SUN A AREA%	SUN B AREA%
I. <u>HYDROCARBONS</u>	<u>92.2</u>	<u>92.5</u>
A. ANTHRACENES	1.4	1.3
B. BENZENES	1.9	1.9
C. BIPHENYLS	6.9	4.8
D. DECALINS	0.3	0.3
E. FLUORENES	9.1	4.9
F. NAPHTHALENES	48.4	52.7
G. PHENANTHRENES	22.6	25.2
H. PYRENES	1.6	1.4
II. <u>HETEROATOMIC COMPOUNDS</u>	<u>7.7</u>	<u>7.6</u>
A. ACRIDINES	0.7	3.6
B. CARBAZOLES	6.1	3.2
E. QUINOLINES	0.8	0.4
C. DIBENZOTHIOPHENES	0.1	0.3
D. TETRAHYDROQUINOLINES	0.1	0.1

The NENC extract (CH_2Cl_2 solubles) from the silica gel treatment from both Sun A and B fuels is summarized in Table IV. The results in this table illustrate that overall, the separation scheme was efficient. The extracts consist primarily of hydrocarbons, 92% for both Sun A and B. The hydrocarbons present are primarily naphthalenes and phenanthrenes. For Sun A, 48% naphthalene and 23% phenanthrene and for B, the results were 53% and 25% respectively.

The heteroatomic constituents present were the less basic, multi-substituted carbazoles for both A and B along with acridines for Sun B. Minor components for both fuels

Table V

ACCELERATED STORAGE STABILITY FOR
FUELS SUN A AND SUN B

(Bottle Tests - Vented - mg/100ml, 80°C - 14 days)

INSOLUBLES	FUEL			
	Sun A		Sun B	
	Trial 1	Trial 2	Trial 1	Trial 2
Filterable Insolubles:	0.9	1.1	0.9	0.8
Adherent Insolubles:	0.8	0.8	0.9	0.7
Total Insolubles:	1.7	1.9	1.8	1.5
Peroxide Concentration ¹				
Before Stress ² :	0.58		0.57	
After Stress ² :	0.96		0.75	

¹meq. of active oxygen/kg fuel
²average of duplicates

included dibenzothiophenes, tetrahydroquinolines, and benzocinnolines.

Accelerated storage stability tests indicated that both Sun A and B fuels possessed marginal stability for jet fuels (i.e. greater than 1.0mg/100ml of total insolubles at 14 days/80°C). The accelerated storage stability results for both fuels are depicted in Table V. The peroxide concentrations, meq of active oxygen/kg fuel, are also listed in Table V. Before stress, the peroxide values were 0.58 for Sun A and 0.57 for Sun B. After stress, Sun A had increased to 0.96 and Sun B, 0.75. Sun A is approaching a level that has been

TABLE VI

ACCELERATED STORAGE STABILITY
Low Pressure Reactor

FUEL	Total Sediment (Mg/100ml Fuel)	
	43°C/4 weeks	65°C/6 days
Sun A	2.0 mg/100ml	1.0 mg/100ml
Sun B	1.5	0.7

defined as unstable (>1.0 meq active oxygen/kg fuel). Most freshly refined jet fuels analyzed at NRL have original peroxide levels of 0.1 meq/kg fuel or less. The initial values indicate that both fuels should be marginally stable.

Both fuels were also subjected to accelerated testing by a new technique developed at NRL and described elsewhere (Hardy et al., 1987). The method is termed LPR for Low Pressure Reactor. In brief the method consists of using 100ml of fuel in 125 ml bottles. The uncapped bottles are then placed in a steel reactor and pressurized to 100 psia with oxygen, purity 99.5%, and the reactor subsequently placed in a thermostated oven for the appropriate stress time period. The resulting sediments are then determined gravimetrically as described. The results for Sun A and B fuels are given in Table VI.

Fuels are graded on a Pass-Fail method for the LPR test procedure. The Fail value for the 43°C/4 week regimen is

5.0 mg/100ml of total sediment. The value for Sun A was 2.0 mg/100ml while for B it was 1.5 mg/100ml.

SUMMARY AND CONCLUSIONS

The polar extract components of two marginally stable low nitrogen petroleum JP-5 fuels were isolated, characterized and the fuels studied in the context of accelerated storage stability tests. Two storage stability methods were used: bottle tests and oxygen overpressure. By bottle tests, total insolubles for Sun A yielded 1.8mg/100ml of fuel and Sun B 1.7mg/100ml. By the low pressure oxygen reactor method Sun A gave 2.0 mg/100ml while B gave 1.5 mg/100ml at 43°C/4 weeks. For the 65°C/6 day regimen Sun A gave 1.0 and B gave 0.7 mg/100ml of sediment respectively.

The total nitrogen analysis for each fuel was determined by a chemiluminescent procedure and gave for Sun A 233 and for B 83 ppm-w/v.

Sun A and B fuels were subjected to a mild acid extraction followed by silica gel adsorption. A single mild extract separation was selected so that the opportunity for chemical changes would be minimized. The ENC extract contained 5.7% hydrocarbons and 93.6% heteroatoms for Sun A and 4.2% hydrocarbons and 92.2% heteroatoms for Sun B. The NBNC (CH₂Cl₂) extract gave for Sun A 92.0% hydrocarbons and

7.6% heteroatoms, and for Sun B 92.5% hydrocarbons and 7.6% heteroatoms. The NENC (CH_3OH) extract gave 31.6% hydrocarbons and 70.1% heteroatoms for Sun A while the B fuel yielded 28.1% hydrocarbons and 70.9% heteroatoms. The main class of heteratomic substances identified were pyridines. The pyridines identified in the ENC fraction were primarily mono-alkyl substituted while those in the NENC (CH_3OH) extract were highly branched.

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RECEIVED: August 12, 1988

ACCEPTED: September 1, 1988

LIQUID PHASE CO-OXIDATION OF THIOPHENOL AND STYRENE
BY OXYGEN AND t-BUTYL HYDROPEROXIDE

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ABSTRACT

Instability problems in both shale and petroleum derived middle distillate jet fuels have been correlated with the presence of peroxidic species. Although a good body of knowledge exists concerning the formation of peroxides in the liquid phase, relatively little is known about the reaction/decomposition pathways available when other functional groups are present. Since sulfur is the most abundant heteroatom present in jet fuels, the reaction of t-butyl hydroperoxide (tBHP) and/or oxygen with thiophenol in the presence of the active olefin, styrene, was examined in deaerated benzene at 120°C. The complex product mixture was analyzed by combined capillary column GC/MS. Major products included acetone, t-butanol and isobutylene from the tBHP. Thiophenol and styrene combined to form addition products. Phenyl disulfide was observed from the thiophenol. The results indicated that although the product slate was complex, it was possible to explain the product mix in terms of a few competing reactions.

INTRODUCTION

A detailed understanding of the influence of sulfur compounds on fuel instability is of continuing interest. Organo-sulfur compounds are present in refined fuels and petrochemicals. Thus, there is a heightened interest in the mechanism of interaction of organo-sulfur compounds with active olefins and the degradation of fuels under oxidizing conditions.

This observed degradation can be manifested in the fuel system by the formation of deposits on filters, in nozzles and on combustor surfaces (Hazlett and Hall, 1985; Taylor and Wallace, 1967; Scott, 1965; Taylor, 1974). These deposits are the consequence of free radical autoxidation reactions. Trace levels of sulfur compounds have been found to influence the deposit formation process. It has been shown that jet fuels low in sulfur content are relatively stable and that fuels of high sulfur content are fairly unstable (Taylor, 1976; Daniel and Heneman, 1983). Presently, it is not possible to relate the observed instability to specific sulfur species. Heteroatoms (oxygen, nitrogen and sulfur) and ash have been found to comprise 40 percent of such deposits (Nixon, 1962). The sulfur content of these deposits has been found to vary from 1 to 9% (CRC, 1979). Sulfur (0.4%) is the most abundant heteroatom present in the fuel itself. Deposits formed in jet

fuel in the presence of oxygen contained a greater percentage of sulfur than that present in the fuel itself (Wallace, 1964).

If sufficient oxygen is present, the hydroperoxide concentration will reach a high level. If the available oxygen is low, but the temperature is raised, the hydroperoxide level will be limited by free radical decomposition. In this situation fuel degradation can be associated with the reaction of hydroperoxides with the other moities in the fuel.

This paper is concerned with the reaction between a primary autoxidation product, a hydroperoxide, with thiophenol in the presence of the active olefin styrene. The reactions were carried out in deaerated benzene with t-butyl hydroperoxide or in benzene with an oxygen overpressure. The polymerization of styrene is a well studied reaction. The thrust of the present work, is not the major products, but the partially oxidized products that could further be implicated in oxidation reactions.

EXPERIMENTAL

Reagents. tert-Butyl hydroperoxide, tBHP, (90%), thiophenol and styrene were obtained from Aldrich Chemical Co. They were distilled in vacuo to 99.9% purity. Benzene (Aldrich Gold Label) was refluxed and distilled from calcium hydride.

CAUTION. Reactions involving peroxide species are inherently unstable. In our laboratory, we have successfully carried out the reduced pressure distillation of tBHP under the following conditions: small sample volume, 15 ml, and a temperature that did not rise above 30° C. HPLC grade uninhibited tetrahydrofuran, THF, was obtained from Fisher Scientific. Polystyrene molecular weight standards of 955, 1380 and 1850 were obtained from Pressure Chemical Company.

Method. The reactions were carried out in sealed borosilicate glass tubes. The reagents (typically $3-9 \times 10^{-4}$ mol of tBHP and 6×10^{-4} mol of both thiophenol and styrene in 0.6ml of solvent) were weighed into 6 in. long, 1/4-in. o.d. borosilicate glass tubes closed at one end and fitted at the other with a stainless steel valve via a Swagelok (teflon ferrules) fitting. The tube was attached to a vacuum system, cooled to 77K and subjected to several freeze-pump-thaw cycles. For those runs in oxygen, the solution was bubbled extensively with oxygen, a 40 - 45 psi over-pressure of oxygen was then added. The tube was then subsequently flame-sealed below the valve. The ullage volume (0.30 ml) was kept constant for all runs. The deaerated samples were warmed to room temperature and immersed in a Cole-Parmer fluidized sand bath. The temperature was controlled by a Leeds and Northrup Electromax III temperature controller. The total pressure during each run was estimated to be 5.1 atm for the runs in benzene solvent. After

the reaction period (15, 30, 60 min) the sealed tube was quenched to 77K and opened.

The samples were analyzed by combined GC/MS (EI mode). The GC/MS unit consisted of a Hewlett-Packard Model 5710 GC, a H-P Model 5982A mass spectrometer, and a Ribermag SADR GC/MS data system. An all glass GC inlet system was used in conjunction with a 0.31 mm x 50 m SP-2100 fused silica capillary column.

Gases formed during the reaction were analyzed using a Perkin-Elmer Model Sigma 2 gas chromatograph equipped with a 6 ft. 5A Molecular Sieve column. In this mode, the column was operated at 55C. The chromatogram was recorded and integrated on a Hewlett-Packard Model 3390A reporting integrator. An external standard was used for calibration. A gauge measured the pressure in the sample loop at the time of analysis.

Analysis for oligomeric polystyrene was performed using a Beckman microspherogel high-resolution, size exclusion column, coupled to a Beckman Model 100-A HPLC pump, equipped with a Rheodyne Model 7125 injector and a Waters Model 440 UV Absorbance Detector with a 254 nm filter. Unhibited THF, sparged with dry nitrogen, was used as the mobile phase. Peak integration and height measurements were performed with an Hewlett-Packard Model 3390-A integrator.

RESULTS AND DISCUSSION

At temperatures of 120° C or greater, tBHP decomposes rapidly by an autoinitiated pathway (Mosher and Durham, 1960). The major reaction pathway in the 120° C decomposition of tBHP involves attack by free radicals present in the solution. The detailed mechanism is complicated since free radicals are sensitive to structural, solvent and stereoelectronic effects.

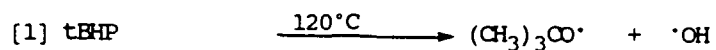
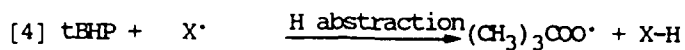
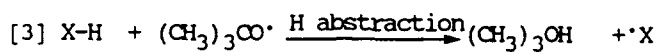
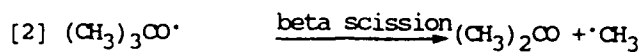
The results in Table 1 illustrate the product distribution for the tBHP, styrene, and thiophenol derived products. The quantities in the tables are expressed in terms of mole percent conversion from the moles of reactant originally present. Products derived solely from tBHP (for example acetone) are calculated based on the starting amount of tBHP. The same is true for products from the thiophenol (e.g., phenyldisulfide). Oxidation products are calculated based on the moles of styrene originally present.

From tBHP, the major product was t-butanol. Small amounts of acetone, methane, isobutylene and the tBHP radical termination product, di-t-butyl peroxide, were also observed.

tBHP products. The mechanism of autoinitiated t-butyl hydroperoxide decomposition can be depicted in Scheme I.

The greater yield of t-butanol compared to acetone, Table 1, definitively shows that hydrogen abstraction was favored

Scheme I

Self InitiationPropagationTermination

over β -scission under the conditions of this study. Solvent participation was noted by the formation of trace quantities of toluene and other substituted benzenes from benzene.

The reaction mechanism, initiation step, in the presence of molecular oxygen can be depicted by Scheme II.

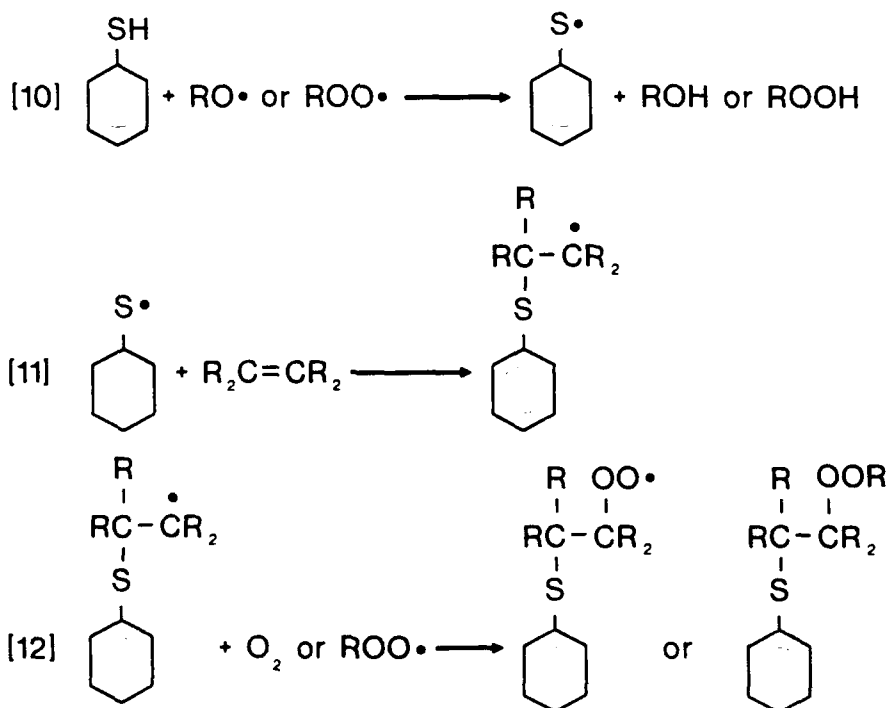
Scheme II

Initiation

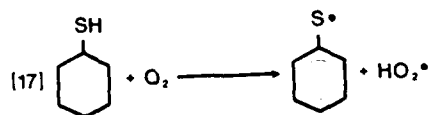
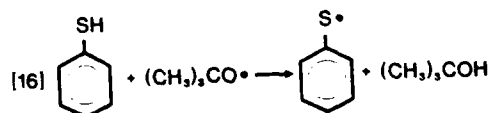
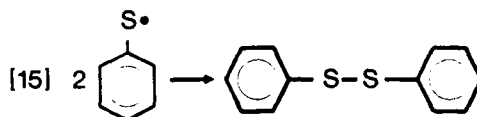
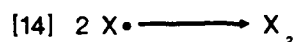
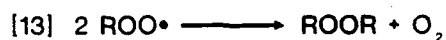


The reaction of the hydroperoxide, step [9], would then follow the same pathways as indicated for steps [1-6] in Scheme I. The radicals that result from either Schemes I or II could subsequently react with either the thiophenol and/or styrene that are present in the reaction mixture. This process can be described by Scheme III.

Scheme III



Styrene - thiophenol reaction products. The major product, Table 1, observed was the addition product 1-phenyl-2-phenylthiyl ethane. Its yield at 15 min was 41.3%, increasing to 71.2% at 30 min and decreasing to 68.3% at 60 min. Other products included: the 1-phenyl-1-phenylthiyl ethane isomer, 0.5% at 15 min increasing to 3.5% at 60 min; the dimer of styrene, 1,4-diphenyl butane, 0.2% at 60 min; phenyl-2-phenylethyl sulfoxide, 1.7% at 15 min increasing to 5.8% at 60



min; phenyl disulfide, 1.1% at 15 min increasing to 2.3% at 60 min;
1,4-diphenyl-2-phenylthiyl butane, 1.1% at 15 min

Table 1

Mole % Conversion for the Reaction of Styrene with Thiophenol and Oxygen or t-Butyl Hydroperoxide at 120°C

CONVERSION (MOLE%)				
	Reaction Time (minutes)			
	Molecular Oxygen			tBHP
	15	30	60	15
<u>Addition Products^a</u>				
1-phenyl-2-phenylthiyl ethane	41.3	71.2	68.3	62.4
1-phenyl-1-phenylthiyl ethane	0.5	1.5	3.5	1.4
phenyl-2-phenylethyl sulfoxide	1.7	4.9	5.8	3.9
phenyl disulfide	1.1	1.7	2.3	1.7
1,4-diphenyl-2-phenylthiyl butane	1.1	0.9	0.9	1.9
phenyl thiosulfonate	---	0.2	0.3	1.1
1,4-diphenyl butane	---	---	0.2	0.2
<u>Styrene Oligomers</u>				
polystyrene	---	---	1.0	1.0
<u>Unreacted</u>				
styrene	34.7	2.0	1.6	13.2
thiophenol	33.2	7.1	5.8	25.2
<u>tBHP Products</u>				
acetone	---	---	---	0.9
t-butanol	---	---	---	57.1
di-t-butyl peroxide	---	---	---	0.1
isobutylene	---	---	---	2.3
<u>Trace Products^b</u>				
	2.2	4.3	6.6	3.2

a. based on the starting moles of styrene

b. summation of small peaks

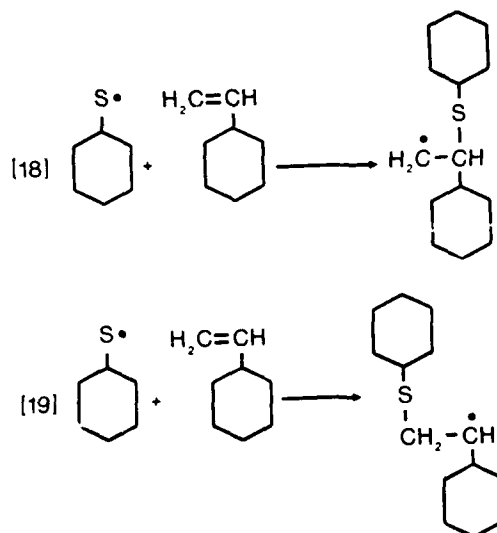
decreasing to 0.9% at 60 min and phenyl thiosulfonate, 0.3% at 60 min. Trace products (< 0.1% yield) included: phenyl-2 phenylethyl sulfone, styrene oxide, phenyl methyl sulfide and 2-ethyl toluene. The product slate was the same for both oxygen and tBHP, but the yields of individual components varied

significantly. In general, the tBHP reaction was faster as would be expected, than the reaction starting with oxygen. In the presence of tBHP, the major product, 1-phenyl-2-phenylthiylethane, increased to 62.4% at 15 min and the sulfoxide product was more than doubled at 3.9% for the same time period.

Styrene in the presence of oxygen or t-butyl hydroperoxide, was observed to undergo polymerization reactions to produce oligomeric polystyrene. Using high resolution, size exclusion chromatography, a standard curve was generated for the molecular weight standards as a function of retention volume. By this method, the average molecular weight of the oligomer was calculated to be approximately 1300. Using the 1380 molecular weight standard to generate a concentration standard curve, the mole percent conversion of monomeric styrene to oligomeric polystyrene was calculated. This resulted in 1.0 mole percent oligomer as shown in Table 1. In addition, there were some higher molecular weight oligomers that could not be quantitatively determined by this method.

The reaction of molecular oxygen or tBHP with thiophenol can proceed by the following chain mechanism, steps [16-17]. The t-butoxy radical is more reactive than the t-butyl peroxy radical and consequently is a more probable reactant in such a mechanism (Mushrush and Hazlett, 1985).

The thiyl radical can react by several different pathways. In a solution with a high molar concentration of styrene, the reaction would proceed as shown in steps [18-19].



Equation [19] was the preferred pathway since it resulted in the more thermodynamically stable radical. The major product, phenyl-2-phenyl thiyl ethane, then results by hydrogen abstraction. The other radical generated, equation [18], led to one of the observed minor products, diphenylthiyl ethane. Other pathways could involve the reaction of radicals generated in steps [11] or [12] with additional olefin to give products of high molecular weight.

The sulfoxide product, phenyl-2-phenylethyl sulfoxide, could result from several mechanisms. The most likely

mechanism however, would be the reaction of the hydroperoxide species with the sulfide formed in step [19]. Expansion of the sulfur valence shell is probable in the processes involved in this step. The resulting sulfoxide once formed is quite stable, as can be seen from the gradual increase in yield, Table 1, at extended reaction time.

The thiyl radical can also undergo a dimerization reaction to produce the disulfide, step [15], and subsequently more extensive oxidation to yield the thiosulfonate product.

CONCLUSION

Fuel deterioration can manifest itself in several ways, including the formation of insoluble deposits. Reactive species in fuels which may be involved include oxygen species, hydroperoxides, various classes of heteroatom compounds, sulfur species and active olefins. This paper specifically examined the t-butyl hydroperoxide and oxygen induced co-oxidation of styrene and thiophenol in benzene solvent at 120°C. Co-oxidation reactions offer one possible explanation for the increased heteroatom incorporation observed in these deposits.

A common slate of tBHP products was observed for all reaction times. The major product observed from tBHP was t-butanol. Other observed tBHP products included methane, acetone and isobutylene.

Co-oxidation of styrene and thiophenol in the presence of oxygen or tBHP at 120°C formed phenyl-2-phenylthiyl ethane as the major product. The styrene system also formed sulfoxides in appreciable yield. Styrene, oligomers were formed in about 1% yield at M.W. of about 1300 daltons with an indeterminate yield above 1300 daltons.

Thiophenol formed a significant amount of phenyl disulfide along with its oxidized product, phenyl thiol-sulfonate. No solvent incorporation was noted with any of the products.

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Received: December 8, 1989

Accepted: January 3, 1990

LIQUID PHASE OXIDATION STUDIES: CHEMICAL IONIZATION
OF ALKYL KETONES IN AN ION TRAP MASS SPECTROMETER

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ABSTRACT

The oxygen or hydroperoxide oxidation of various organo-sulfur compounds in both model and real fuels is an area that is presently under renewed investigation. Sulfur compounds of interest include thiols and disulfides in particular. Autoxidation reactions produce besides the expected sulfur oxidation products: sulfoxides, sulfones, thiosulfonates and sulfonic acids, small amounts of hydrocarbon oxygenates from the model fuel, dodecane. It was noted that the mass spectra of the oxygen species gave results that were instrument dependent. The results from an ion trap detector are quite different when compared to a dodecapole mass spectrometer.

INTRODUCTION

Liquid phase oxidation reactions of heteroatom species are intimately involved in the formation of sediments and gums in middle distillate fuels (C. R. C., 1988; Mushrush, et.al.,

1987; Mayo and Ian, 1987; Hazlett, 1980; Scott, 1965). Deposit formation in some fuels is triggered by autoxidation reactions and can be closely linked to active oxygen species such as hydroperoxides (Watkins, et. al., 1989). Although slight thermal degradation is found to occur under nonoxidizing atmospheres, the presence of oxygen or active oxygen species, hydroperoxides, will greatly accelerate oxidative instability reactions. If sufficient oxygen is present, the hydroperoxides will reach a high level. At elevated temperatures however, the hydroperoxide concentration will be lowered by free radical decomposition. These free radical decomposition reactions of hydroperoxides result in the formation of ketones and alcohols (Mosher and Durham, 1960; Mushrush and Hazlett, 1985). In a study of the mass spectra of the autoxidation products of dodecane, the mass spectral results obtained via an ion trap detector and a dodecapole mass spectrometer were quite different. In particular, the generation of the $(M+1)^+$ ion from ketones as detected by the ion trap detector failed to exhibit a concentration dependency, although such a dependency was confirmed for the dodecapole detector.

EXPERIMENTAL

Instrumental Methods Product identification was obtained by combined GC/MS (EI mode). The GC/MS unit consisted of a

Hewlett-Packard Model 5890 GC coupled to a Finnigan MAT ion trap detector, ITD. An all glass GC inlet system was used in combination with a 0.2mmx50m OV-101 fused-silica capillary column. Operational parameters included: sample size - 0.5 microliter, injector split at 60:1, column flow - 1mL/min at a head pressure of 30 psi, detector gain - 10^5 (dynode voltage 800 to 2900v computer controlled), injection port - 200°C, temperature program - 70°C (2 min hold), 6°C/min programmed temperature rise, 240°C (25 min final hold). The mass spectra were compared with those obtained from a dodecapole GC/MS (EI mode) instrument. The GC/MS unit consisted of a Hewlett-Packard Model 5710 GC, a HP Model 5928A mass spectrometer and a Ribermag SADR GC/MS data system. An all glass GC inlet was used in conjunction with a 0.31mmx50m SP2100 (similar to OV-101) fused-silica capillary column. Operational parameters included: sample size - 1 to 2 microliters, injection split at 60:1, column flow - 1.1 to 1.2 mL/min at a head pressure of 10.5 psi, detector gain - 9 on "Low" scale, injection port - 220°C, temperature program - 70°C (2 min hold), 4°C/min programmed temperature rise, 220°C (16 min final hold).

Reagents n-Hexyl disulfide and n-dodecane were supplied by Aldrich Chemical Co. and purified by reduced pressure distillation. Model dodecanones and dodecanols were supplied by J.T. Baker and Chemical Samples Co. They were used as received.

A typical run consisted of a dodecane solvent (150 mL) with a maximum of 0.3% (w/w) sulfur added as hexyl disulfide. The solution was then reacted at 100°C in a sealed 100 psi air or pure oxygen atmosphere. The reaction mixture was quenched, titrated for peroxide species and analyzed by combined capillary column GC/MS for oxidized sulfur and dodecane products.

RESULTS AND DISCUSSION

Hydrocarbons in an oxidizing environment produce as a primary product, hydroperoxides. Long chain alkyl hydroperoxides are usually not observed due to their labile bonds. However, their decomposition products, alcohols and ketones are the observed reaction products. The major observed products from the oxygen induced oxidation of hexyl disulfide in dodecane solvent at 100°C included: thiolsulfinates, thiol-sulfonates, disulfones and all the dodecanone and dodecanol isomers. These compounds were confirmed by retention time and silylation of model mixtures of model dodecanones and dodecanols (Mushrush, et. al., 1987). In a kinetic study of the competitive oxidation rates of heteroatoms with hydrocarbons, mass spectra results for aliphatic ketones were detected with an ion trap detector that were quite different from those determined with a dodecapole instrument.

The mass spectrum of the dodecanones detected with an EI ion trap detector differed significantly from those determined with an EI dodecapole instrument. It is well known that oxygen moieties, i.e. ethers and ketones, can form an $(M+1)^+$ ion in an EI source of a standard quadrapole or dodecapole mass spectrometer when high concentrations or large sample sizes are employed (Silverstein, et. al., 1974). This has been attributed to bimolecular collisions in the (EI) ion chamber rather than an intramolecular rearrangement or collisions with a reagent CI gas. With large sample sizes, a hydrogen transfer from a neutral molecule with the parent radical ion to form an $(M+1)^+$ ion was observed to occur in the dodecapole GC/MS unit. This $(M+1)^+$ species was also observed with the ion trap detector. However, alkyl ketones were observed to routinely show the $(M+1)^+$ ion regardless of the concentration or sample size in the ITD. Figure 1 depicts the ITD mass spectrum of 3-dodecanone (1000 ppm) in heptane contrasted with the 3-dodecanone (10 ppm) mass spectrum that results from the oxidation of the dodecane reaction mixture. These concentrations correspond to an analyte concentration in the ion trap detector of approximately 7 ng and 0.1 ng respectively. The $(M+1)^+$ species at m/z 185 was evident in both spectra obtained under identical ion trap conditions. There are several explanations for this observation. Scheme 1 depicts a plausible mechanism for the formation of an $(M+1)^+$

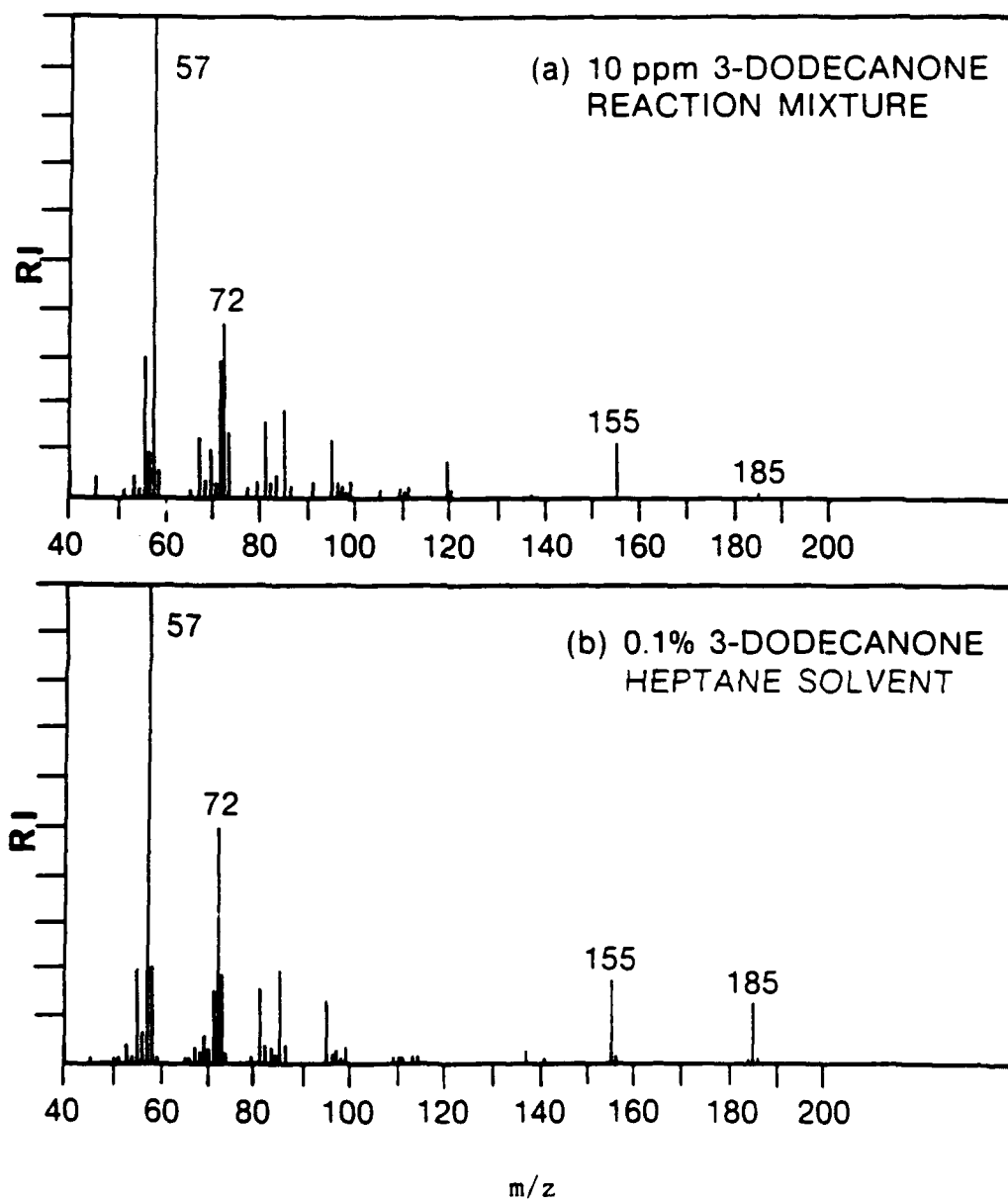
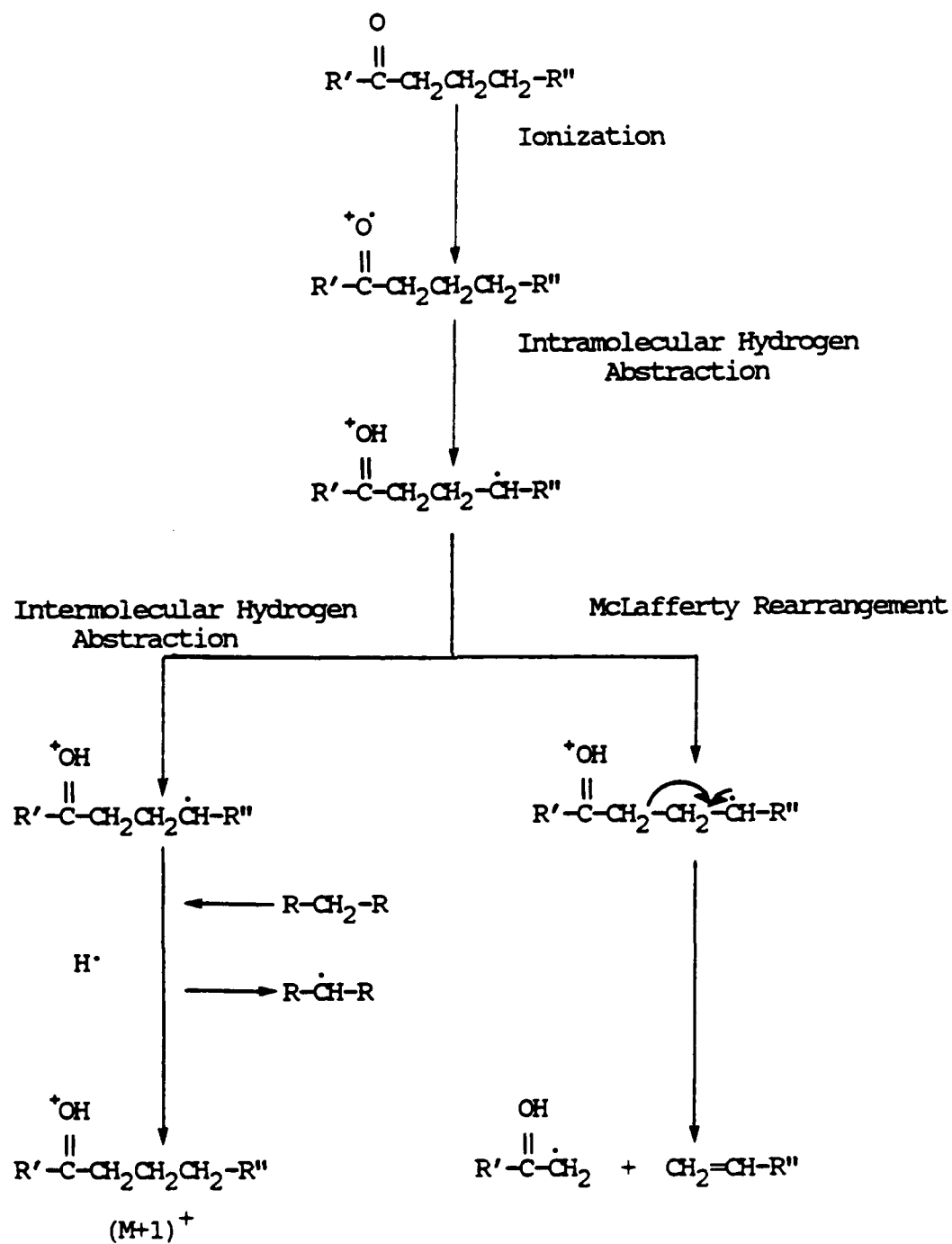


Figure 1

ITD Mass Spectra of (a) 3-Dodecanone at 10 ppm from the autoxidation reaction mixture of dodecane, hexyl disulfide and 100 psi oxygen at 100°C, and (b) 3-Dodecanone at 1000 ppm in heptane.



Scheme 1

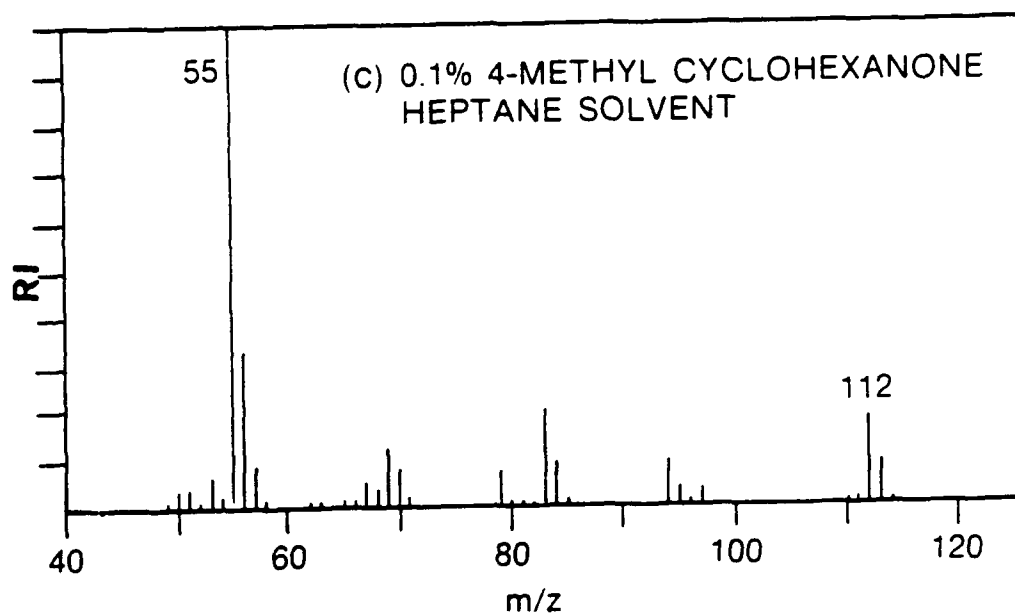


Figure 2

ITD Mass Spectra of (c) 4-Methylcyclohexanone at a concentration of 1000 ppm in heptane.

ion. A typical McLafferty rearrangement could be invoked as in a standard EI source at high sample concentrations (Milne, 1971). This does not appear to be the entire explanation based on the fact that even at low sample concentrations, the $(M+1)^+$ ion was still observed in the ion trap detector. An additional check using 4-methylcyclohexanone at a concentration of 1000 ppm in heptane solvent was made as depicted in Figure 2. This compound even at the high concentration in the ion

trap detector was not able to undergo the McLafferty rearrangement and yet a prominent $(M+1)^+$ ion was formed. An alternative explanation was that the ion trap detector EI source operation allows intermolecular hydrogen abstraction from a neutral sample species regardless of source pressure and even of sample concentration. An $(M+1)^+$ ion formation mechanism for 4-methylcyclohexanone in the ion trap detector could not be explained by the McLafferty rearrangement. However, where molecular geometry allows, both the McLafferty rearrangement and the ion trap detector source operation effect are operational simultaneously.

CONCLUSIONS

Autoxidation reactions of hydrocarbons result in alcohols and ketones as primary reaction products. It was noted in the mass spectral study of the oxidation products of dodecane that the mass spectrum differed when an EI source ion trap detector mass spectrum was compared to that of an EI source dodecapole mass spectrometer. The generation of an $(M+1)^+$ ion from ketones in an ion trap detector failed to exhibit concentration dependencies. Concentration dependency was confirmed for the dodecapole detector. Two explanations are offered to explain the observed results. First, a typical McLafferty

rearrangement can be invoked for the dodecapole detector. Secondly, it is proposed that the ion trap detector EI source operation allows intermolecular hydrogen abstraction from other neutral species regardless of the source pressure and concentration effects. The mass spectra of ketones must be interpreted with caution when an EI source ion trap detector is employed.

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RECEIVED: January 10, 1990 ACCEPTED: January 25, 1990

Preprints, Fuel Chemistry Division

American Chemical Society

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Vol. 35, No. 4

ACCELERATED PEROXIDE FORMATION IN JET FUEL USING
CONVENTIONAL AND OXYGEN OVERPRESSURE METHODS

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INTRODUCTION

In recent years the quality of petroleum feedstocks used by refineries has decreased. This has necessitated the use of more severe refinery processes in order to produce jet fuels of higher thermal stability and cleanliness. Unfortunately, these processes remove species that inhibit the formation of hydroperoxides during storage. As a result the storage stability of some jet fuel products, as measured by hydroperoxide formation, has decreased.

Hydroperoxides in jet fuel have a deleterious effect on elastomers in aircraft fuel systems. (1-3) This problem was first recognized in the early 1960s when an unusually large number of flexible fuel manifold hose failures occurred in aircraft operating in the Far East. (4) To investigate the cause for these failures, a rubber immersion test was developed to distinguish between good and bad fuels. Rubber samples were immersed in jet fuel at $100 \pm 1^\circ\text{C}$ and their rate of deterioration, from visual inspection, was recorded. Peroxides, which were known to cause rapid deterioration of elastomers, were monitored during the immersion test. The peroxides in a fuel as received were designated existent peroxides. The peroxides that formed after the fuel was heated to 100°C for 100 hours were designated potential peroxides. In general, as the concentration of potential peroxides in a fuel increased, the failure time for a rubber sample decreased. (4)

During the 1970s and 1980s, additional hydroperoxide induced elastomer failures in aircraft fuel systems occurred. In one instance the failure resulted in the loss of an aircraft. As a result of these failures, a cooperative program was initiated to develop a method to predict a jet fuel's tendency to form hydroperoxides during storage. Six laboratories participated and seven fuels, some of which contained a phenolic antioxidant, were included in the first Coordinating Research Council, Inc., (CRC) cooperative interlaboratory testing (round robin).

A procedure similar to the rubber immersion test was used. Fuel samples were stressed in capped brown borosilicate glass bottles at 100°C for up to 168 hours. The fuel samples were periodically analyzed for hydroperoxide concentration at intermediate intervals by ASTM D3703-78. (5) The results indicated that this procedure had fair repeatability and poor reproducibility. The participants concluded that additional work was needed to achieve better values.

Prior to further developmental work, it was suggested that testing at 100°C may not be indicative of peroxidation at ambient conditions. To verify this possibility, an experiment was performed in which four

fuels from the first round robin were stressed at 43°C, 65°C, and 80°C. Aliquots of the fuels were periodically removed for peroxide analysis. Peroxidation rates at these temperatures were compared to the rates obtained at 100°C in the first interlaboratory round robin.

The fuel samples were, unfortunately, stressed in capped bottles. This limited the amount of oxygen available to the samples. At higher temperatures, 80°C and 100°C for instance, the frequency at which aliquots were removed allowed for more frequent replenishment of atmospheric oxygen. At the lower temperatures where aliquot removal was less frequent, oxygen starvation led to a decrease in the peroxidation rate. This suppression of peroxidation rate in turn led to the erroneous conclusion that peroxidation occurs by a different mechanism at elevated temperatures. In further studies, therefore, the temperature at which fuels were stressed was limited to 65°C.

Two additional interlaboratory round robins were performed. This work culminated in a set of standard test conditions that are useful in research studies. (6) These conditions, however, have serious limitations for fuel quality use. These include the duration, 4 weeks, and the limitation as a Go/No Go (pass/fail) test. The use of a pass/fail criterion does not allow fuels to be ranked relative to each other. Furthermore, under these conditions antioxidant additives cannot be easily or quickly tested for their relative effectiveness. Clearly a more rapid and meaningful test must be developed.

This paper describes experiments that compare fuels stressed at 65°C in capped and vented bottles. Also described is a method for distinguishing between various antioxidant additives using a serial dilution technique.

EXPERIMENTAL

Five fuels were used in this study and included: Three JP-5 blending stocks; coded Fuel #1, #2, and #3; Shale II, a finished JP-5 jet fuel; and n-dodecane. The n-dodecane was treated with silica gel to remove polar species that may have influenced peroxidation rate. This was done by adding 250g of 100-200 mesh activated silica gel to two liters of n-dodecane. The mixture was magnetically stirred for six hours. Two liters of each sample were prefiltered through a pair Gelman type A/E glass fiber filters prior to accelerated aging.

Two sets of each sample were prepared. The first set remained exposed to atmospheric oxygen, and the second set remained tightly capped for the duration of the test. For each anticipated hydroperoxide analysis period, two 125mL brown borosilicate glass bottles each containing a 100mL sample were prepared. The duplicate samples were initially to be analyzed for hydroperoxide concentration in duplicate every two weeks for eight weeks. This was later modified and single samples were analyzed in duplicate for up to twelve weeks. The samples were stressed in an oven at 65°C for the duration of the test.

Phenolic antioxidant experiments were performed using a serial dilution technique. Two pure compounds, 2,6-di-t-butyl-4-methyl phenol (26dtb4mp) and 2,4-di-t-butyl phenol (24dtbp), were used in this study.

Stock solutions were prepared by dissolving 24mg of an additive in 1.0L Fuel #1. This is the maximum concentration allowed in JP-5 jet fuel by MIL-T-5624N. (7) Aliquots of the stock solution were diluted to 100mL, with an appropriate volume of neat Fuel #1, in 125mL brown borosilicate glass bottles. A series of samples for each additive were produced with concentrations between 24.0mg/L and 0.3mg/L.

An entire sample set of either additive, including a 100mL additive-free Fuel #1 aliquot, was simultaneously stressed in a low pressure reactor (LPR) at 100°C and an oxygen overpressure of 793kPa. (8) After 24 hours under these conditions, the samples were removed and analyzed for peroxide concentration.

A Mettler DL20 automatic titrator was used for peroxide determinations. Analyses were performed according to ASTM D3703-85: the Standard Test Method for Peroxide Number of Aviation Turbine Fuels. (5)

RESULTS

The results of accelerated aging at 65°C in capped bottles are shown in Figure 1a. It can be seen that four of the samples approached hydroperoxide concentrations of approximately 90ppm. The fifth sample, Shale II JP-5, continued slow peroxidation for the duration of the test. The results of accelerated aging at 65°C in vented bottles is shown in Figure 1b. It can be seen that three samples, Fuels #1, #2, and #3, produced extremely high concentrations of hydroperoxides under these conditions. In Figure 1c the peroxidation of n-dodecane and Shale II JP-5 in vented bottles is shown with an expanded ordinate.

Comparison of Figures 1a and 1b shows that peroxidation rate in the capped bottles is significantly reduced. This is a result of the limitation of atmospheric oxygen. Although not apparent from these figures, the hydroperoxide concentration in the two sets of fuels significantly differed at two weeks. At four weeks Fuel #3 had the highest hydroperoxide concentration in both sets of fuels. It can be seen, however, that the concentration in the vented sample was nearly eight times that of the capped sample. After four weeks, the hydroperoxide concentration in Fuel #3 continued to increase in the vented bottle. In the capped bottle, however, the concentration of hydroperoxides remained relatively constant. This indicates that oxygen starvation has occurred.

In Figure 1b it can be seen that Fuels #1 and #2 also exhibited a tendency to form high concentrations of hydroperoxides. Both of these fuels undergo a relatively slow rate of peroxidation for six weeks. After six weeks, both fuels rapidly form hydroperoxides. In the vented bottle, Fuel #1 undergoes peroxidation at a linear rate until ten weeks. In the capped bottle, however, Fuel #1 peroxidizes at much slower rate. Unlike Fuel #3, Fuel #1 slowly approaches what appears to be a limit of approximately 100ppm.

Similar characteristics are exhibited by Fuel #2. In the vented bottle this fuel undergoes a rapid rate of peroxidation after six weeks. The peroxide concentration continues to increase for the duration of the test. In the capped bottle, however, Fuel #2

peroxidizes at a much slower rate finally reaching a concentration limit similar to that of Fuels #1 and #3. These results indicate that accelerated aging in capped bottles not only limits the amount of hydroperoxides formed, but reduces the rate at which peroxidation occurs.

Figure 1c shows the rate of peroxidation for n-dodecane and Shale II JP-5 in vented bottles. Both fuels exhibited a relatively slow and linear peroxidation rate. When compared to Figure 1a, it can be seen that Shale II exhibited similar characteristics in capped bottles. The Shale II sample reached a maximum hydroperoxide concentration of 28ppm in the vented bottle. In the capped bottle the maximum concentration formed is approximately 18ppm. In general, the rate of hydroperoxide formation in the capped bottles was approximately $68.6 \pm 7.8\%$ of the rate in vented bottles for the Shale fuel. This again shows that accelerated aging in capped bottles reduces peroxidation rate.

The rate of hydroperoxide formation in n-dodecane in capped bottles seemed to exhibit a periodicity. This was much less apparent in the vented samples. The maximum concentration of hydroperoxides formed was similar in both sets of samples. It is expected that after twelve weeks the hydroperoxide concentration in the capped n-dodecane sample would remain constant.

A cursory examination of phenolic antioxidant effects at 100°C and 793kPa oxygen for 24 hours was also performed. It is well known that hindered phenols significantly reduce liquid phase free-radical autoxidation of hydrocarbon fluids. (9-11) The relative effectiveness of these compounds has been shown to be structure dependent. (9) In general, the presence of a t-butyl group in the 2-position or both the 2- and 6-position increases its effectiveness as an antioxidant. The presence of an alkyl group in the 4-position also leads to an increase in its antioxidant properties. If the alkyl group in the 4-position possesses α -branching, such as a t-butyl or an isopropyl group, however, the additive's antioxidant characteristics are diminished. (9)

Figure 2a shows the effect of 26dtb4mp in Fuel #1 using the serial dilution technique. It can be seen that this additive exhibits an antioxidant effect to concentrations as low as 0.3mg/L. Figure 2b shows the effect of 24dtbp in Fuel #1. It can be clearly seen that under these conditions, 24dtbp is a significantly less effective antioxidant than 26dtb4mp as would be expected.

Figure 2c is a side-by-side comparison of the effect of the two additives. This shows that 26dtb4mp is approximately 20 times more effective than 24dtbp at various concentrations, e.g., 0.3mg of 26dtb4mp is as effective as 6.0mg of 24dtbp; 0.6mg of 26dtb4mp is as effective as 12.0mg of 24dtbp, etc. These results show that under these conditions it is possible to evaluate the effect of various antioxidants relative to each other.

SUMMARY

In the past additive-free fuels have been ranked relative to each other by the length of their induction period. This period is

characterized by slow peroxidation until a readily discernible change in rate occurs, i.e., the "breakpoint". Antioxidants have also been compared by their ability to increase the induction period in a particular fuel. Unfortunately at higher temperatures the induction period for additive-free fuels is either minimal or non-existent. This renders its measurement quite subjective. Furthermore, the end of the induction period, or breakpoint, often occurs at hydroperoxide concentrations higher than are allowed by MIL-T-5624N. (7) The use of the breakpoint as a criterion for ranking fuels or additives is, therefore, not appropriate.

The rate at which a fuel approaches the military specification peroxide limit, 8ppm, would be more useful. For example, a fuel with a longer induction period than another fuel is not necessarily better. If the first fuel's induction period rate is greater, it will reach the specification limit sooner. Unfortunately, the use of induction period rate also presents problems. At lower temperatures the induction period for additive-free fuels is long enough to objectively measure an induction period rate. At higher temperatures, 100°C and 120°C for instance, the induction period rate measurement, like its length, is too subjective.

If more objective measurements of induction period rates are desired, it is necessary to remove and titrate samples for hydroperoxide concentration at very frequent intervals. At 100°C and 120°C, it may be necessary to analyze fuel samples every 30 minutes, or less. For additive-free fuels, or fuel samples obtained from field activities, these labor intensive induction period rate measurements are necessary.

For antioxidant evaluations, the use of the serial dilution technique has advantages over induction period rate and length measurements. First, it is not a subjective test. All samples of a particular fuel and additive combination are stressed under exactly the same conditions. The technique is not concerned with either the length or rate of the induction period. It simply compares the concentration effect of various antioxidants on peroxidation in a given fuel. Second, the technique is far less labor intensive. These advantages make this technique useful for further antioxidant evaluations.

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ACCELERATED PEROXIDE FORMATION 12 Wks @ 65C & Atm. Air (Capped Bottle)

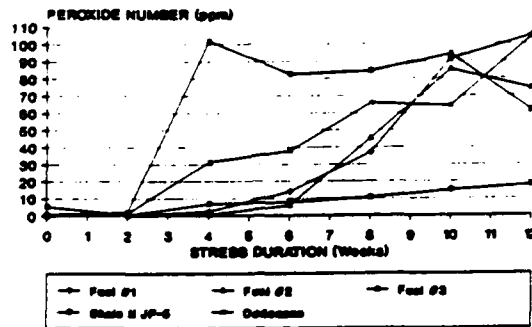


FIGURE 1a

ACCELERATED PEROXIDE FORMATION 12 Wks @ 65C & Atm. Air (Vented Bottle)

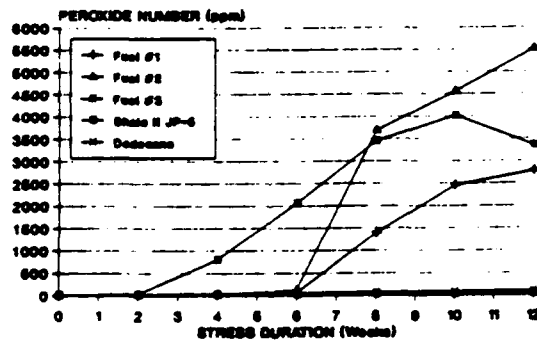


FIGURE 1b

ACCELERATED PEROXIDE FORMATION 12 Wks @ 65C & Atm. Air (Vented Bottle)

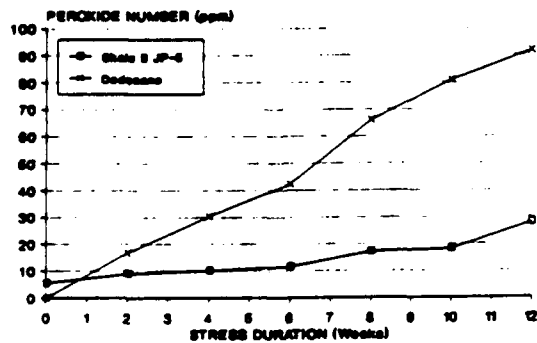


FIGURE 1c

2,6-di-t-Butyl-4-Methyl Phenol
LPR @ 100C & 793kPa Oxygen

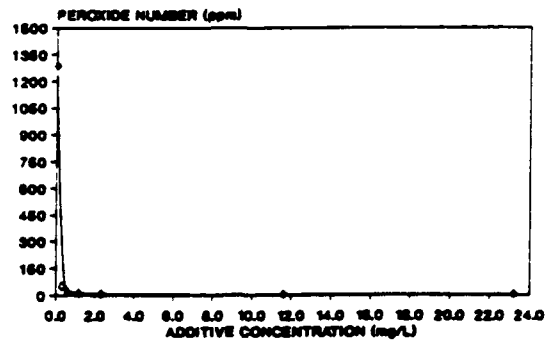


FIGURE 2a

2,4-di-t-Butyl Phenol
LPR @ 100C & 793kPa Oxygen

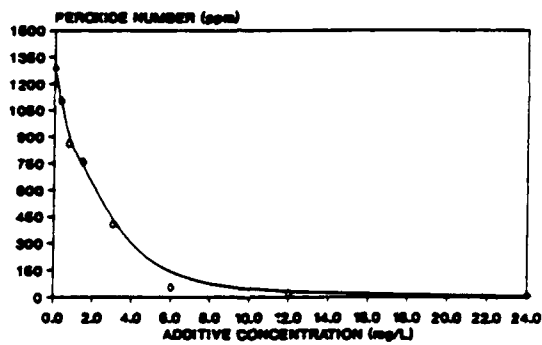


FIGURE 2b

PHENOLIC ANTIOXIDANT EFFECT
LPR @ 100C & 793kPa Oxygen

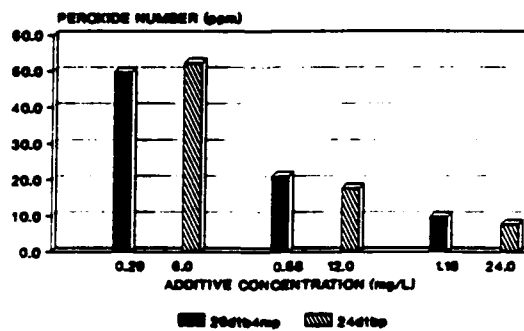


FIGURE 2c

GC-TR-86-1628

LITERATURE REVIEW OF CETANE
NUMBER AND ITS CORRELATIONS

PREPARED FOR
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UNDER CONTRACT NO. N00014-86-C-2288

PREPARED BY
GEO-CENTERS, INC.
7 WELLS AVENUE
NEWTON CENTRE, MA 02159

MAY 1987



REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution unlimited.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) GC-TR-87-1628			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION GEO-CENTERS, INC.		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) 7 Wells Avenue Newton Center, MA 02159			7b. ADDRESS (City, State, and ZIP Code)		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Naval Research Laboratory		8b. OFFICE SYMBOL (If applicable) 6181		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. N00014-86-C-2288	
8c. ADDRESS (City, State, and ZIP Code) 4555 Overlook Avenue, S.W. Washington, D.C. 20375-5000			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO. 63724N	PROJECT NO. R0838	WORK UNIT ACCESSION NO 61-0079
11. TITLE (Include Security Classification) LITERATURE REVIEW OF CETANE NUMBER AND ITS CORRELATIONS					
12. PERSONAL AUTHOR(S) Pande, Seetar G.					
13a. TYPE OF REPORT Progress		13b. TIME COVERED FROM 7/86 TO 3/87		14. DATE OF REPORT (Year, Month, Day) 1987 May	
15. PAGE COUNT 62					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Cetane Number, Cetane Indices, Predicted Cetane Number, Correlations, Distillation Temperatures, Density, Aniline Point, Physical Properties, Physico-Chemical Properties.		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
This review covers the standard method of determining cetane number (engine test, ASTM D613) and alternative methods, which comprise 1 engine test method and 33 cetane indices (predictive equations of cetane number). Of the alternative methods, emphasis is given to those which appear or had appeared promising as good predictors of cetane number. The various cetane indices are categorized according to the type of parameters employed viz, physical properties (e.g., the calculated cetane index, ASTM D976, an approved alternative method to ASTM D613), chemical composition/structure, and physico-chemical properties (e.g., spontaneous ignition tests). Of the physical properties, the combination of distillation temperature(s) and density appear to afford good correlations between cetane index and cetane number. Furthermore, these two parameters continue to feature in the replacement equations of D976. For indices based on a single property, aniline point gives the best prediction.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL Robert N. Hazlett			22b. TELEPHONE (Include Area Code) (202) 767-3559		22c. OFFICE SYMBOL 6180-825:SGP:drs

18. (Cont.) predictability, regression analyses.

19. (Cont.)

Evaluations were based on regression analyses of cetane number vs cetane index as well as on the predictability of the cetane indices as defined by arbitrary criteria imposed on the results. Relatively good correlations with cetane number were observed for most of the cetane indices that were based on distillation temperature(s) and density ($R^2 = \sim 0.8$). The lowest correlation with cetane number was exhibited by a trial cetane index that was based on refractive index and density ($R^2 = 0.45$, for 26 of the 28 fuel set).

ASTM D976-80 exhibited the lowest % overprediction but exhibited a tendency to underpredict on these fuels. Furthermore, none of the cetane indices appear to exhibit significant improvement over ASTM D976-80. However, the most promising of the published cetane indices was Ingham's proposed equation for replacement of D976-80; nevertheless, it exhibited a tendency to overpredict on these fuels. Of the trial correlations, the most promising was the modified ASTM D976-80 cetane index. This equation employs the same formulation as D976-80 but differs from it, in that its mid-distillation temperature term is the average of 10, 50, and 90% distillation temperatures.

GC-TR-86-1628-1

EVALUATION OF CETANE INDICES
FOR MARINE FUELS

PREPARED FOR
NAVAL RESEARCH LABORATORY
4555 OVERLOOK DRIVE, S.W.
WASHINGTON, D.C. 20375-5000
UNDER CONTRACT N00014-86-C-2288

PREPARED BY
GEO-CENTERS, INC.
7 WELLS AVENUE
NEWTON CENTRE, MA 02159

NOVEMBER 1987



GEO-CENTERS, INC.

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release. Distribution unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
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8a. NAME OF FUNDING/SPONSORING ORGANIZATION Naval Research Laboratory	8b. OFFICE SYMBOL (If applicable) Code 6180	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) 4555 Overlook Avenue, S. W. Washington, DC 20375-5000		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO. 62760N	PROJECT NO. -
		TASK NO. -	WORK UNIT ACCESSION NO. 61-0079
11. TITLE (Include Security Classification) EVALUATION OF CETANE INDICES FOR MARINE FUELS (U)			
12. PERSONAL AUTHOR(S) Pande, Seetar G.			
13a. TYPE OF REPORT Progress	13b. TIME COVERED FROM 4/87 TO 9/87	14. DATE OF REPORT (Year, Month, Day) November 1987	15. PAGE COUNT 78
16. SUPPLEMENTARY NOTATION Progress report on one phase of NRL Contract No. N00014-86-C-2288			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		Evaluation, published cetane indices, trial correlations, fuel physical properties, compositional analysis, commercial marine-fuels, cetane numbers, evaluation method	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) In this study, 14 cetane indices were evaluated with respect to their correlations with cetane number. Most of the evaluations were performed on a 28 fuel set taken from a worldwide survey of commercial marine fuels obtained in 13 different countries. Cetane numbers of the fuels ranged from ~ 41-57. Of the 14 cetane indices, 9 were published cetane indices and 5 were trial correlations. The published cetane indices included ASTM D976-80, Ingham et al.'s proposed equation for replacement of D976-80 (their distillation temperatures/density equation), Ingham et al.'s aniline point equation, the Canadian General Standards Board cetane index, the Collins and Unzelman equation, the Ethyl Corp. equation, the SWRI cetane index for fuels containing aromatics, as well as the Diesel Index and ASTM D976-66 for comparison purposes. The trial cetane indices included 4 correlations based on established parameters and 1 correlation based on refractive index and density.			
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Evaluations were based on regression analyses of cetane number vs cetane index as well as on the predictability of the cetane indices as defined by arbitrary criteria imposed on the results. Relatively good correlations with cetane number were observed for most of the cetane indices that were based on distillation temperature(s) and density ($R^2 = \sim 0.8$). The lowest correlation with cetane number was exhibited by a trial cetane index that was based on refractive index and density ($R^2 = 0.45$, for 26 of the 28 fuel set).

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Cetane Number Predictions of a Trial Index Based on Compositional Analysis

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Received October 24, 1988. Revised Manuscript Received March 1, 1989

Continuing revision of the Calculated Cetane Index (ASTM D976), which is based on physical properties, focuses on the need for a Calculated Cetane Index based on fuel composition rather than physical properties. To address this need, the development of a new cetane index was investigated by using multiple linear regression analysis. The trial index was based on percent straight chain and branched chain saturates, and percent monocyclic and dicyclic aromatics, as determined by a combination of HPLC and proton NMR analyses. The 53 fuels that comprised the fuel set were obtained from a worldwide survey, and their cetane numbers ranged from approximately 43 to 64. For the same fuel set, the trial index was evaluated on its percent predictability and R^2 value, relative to those of three published cetane indices. For the fuels examined, the preliminary cetane index based on compositional analysis appears promising: it exhibited similar percent predictions and lower percent overprediction than the recent Calculated Cetane Index, ASTM D4737-87.

Introduction

An accurate and reliable method of measuring cetane number, i.e. the ignition quality of diesel fuels, is important since diesel fuel is the primary mobility fuel used in the U.S. Navy's ships and boats as well as in the nation's trucks, buses, etc. The standard method of determining cetane number is the engine test, ASTM D613.¹ However, for convenience purposes, most refineries rely on the approved alternative method of determining cetane number, viz., the Calculated Cetane Index.² This is a predictive equation of cetane number and is based on bulk properties, namely, distillation temperature(s) and density of the fuel.³⁻⁶

Historically, the need for greater accuracy in predicting cetane number led to several revisions of the original cetane index, which was recommended in 1944.⁶ These revisions include ASTM D976-66³ and ASTM D976-80.⁴ Also, to resolve problems of biases observed with ASTM D976-80, improvement equations for ASTM D976-80 were formulated.^{7,8} However, the ASTM D976 method was recently replaced by a more complex equation, ASTM D4737-87.⁵ Like the indices preceding it, D4737-87 is based

on similar bulk properties, viz., 10, 50, and 90% distillation temperatures and density.

Continuing revision of the Calculated Cetane Index is likely indicative of fuel compositional changes such as changes in the crudes' composition or refinery operations or both, for the ignition characteristics of a fuel are related to its chemical composition.⁹⁻¹² Consequently, an index based on compositional analysis would be better predictive of cetane number than calculated cetane indices based on physical properties. The National Research Council of Canada (NRCC) has developed a cetane index based on parameters involving combinations of physical properties that, on modeling, relate to the chemical structure of diesel fuels.¹² Although the NRCC index was found to be an improvement over existing indices and was proposed¹² as an alternative to ASTM D976-80 and the Canadian General Standards Board cetane index,¹³ it is lengthy and involves six measurements, one of which is aniline point. This also detracts from its merits since aniline is toxic.

In formulating cetane indices based on compositional analysis, it is important to identify and quantify the various types of hydrocarbons present in diesel fuels. Several indices based on the different types of carbons, as well as on hydrogen type distribution, have been reported. Determination of different types of carbons was based on proton NMR^{11,12,14} or carbon-13 NMR^{15,16} analysis; hy-

(1) ASTM Method D-613, Standard Test Method for Ignition Quality of Diesel Fuels by the Cetane Method. In *Annual Book of ASTM Standards, Part 47, Test Methods for Rating Motor, Diesel, Aviation Fuels*; ASTM: Philadelphia, PA, 1980.

(2) Military Specification MIL-F-16884H, Fuel, Naval Distillate: Amendment 2, Section 4.5.1.

(3) ASTM Method D-976-66, Standard Test Method for Calculated Cetane Index of Distillate Fuels. In *Annual Book of ASTM Standards, Part 23, Petroleum Products and Lubricants*; ASTM: Philadelphia, PA, 1976.

(4) ASTM Method D-976-80, Standard Test Method for Calculated Cetane Index of Distillate Fuels. In *Annual Book of ASTM Standards, Petroleum Products, Lubricants, and Fossil Fuels*; ASTM: Philadelphia, PA, 1988; Vol. 05.01.

(5) ASTM Method D-4737-87, Standard Test Method for Calculated Cetane Index by Four Variable Equation. In *Annual Book of ASTM Standards, Petroleum Products, Lubricants, and Fossil Fuels*; ASTM: Philadelphia, PA, 1988; Vol. 05.03.

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drogen type distribution was based on proton NMR analysis.^{17,18}

A disadvantage of cetane indices based solely on conventional NMR analysis for identification and quantification of the different types of hydrocarbons is that overlap of several chemical structures in the same spectral region can cause anomalous results.¹⁸ Thus, there is need for a cetane index based on improved compositional analysis.

In this paper, the development of a new cetane index was investigated to address this need. The trial index was based on percent straight-chain and branched-chain saturates and percent monocyclic and dicyclic aromatics as determined by a combination of HPLC and conventional proton NMR analyses. Evaluation of the index was based on percent predictions, over/underpredictions, as defined by specific criteria and on regression analysis. The percent predictabilities of this index and its correlation coefficient with cetane number, R^2 , were compared with those of three other published indices including ASTM D4737-87.

Experimental Section

Fuel Set. The fuel set comprised 53 fuels obtained from a worldwide survey involving 38 countries.¹⁹ Classification of the fuels as documented²⁰ were as follows: (a) 27 samples of commercial marine gas oil of which 3 were duplicates for quality analysis/quality control purposes, with cetane numbers of these fuels ranging from approximately 45 to 64; (b) 22 samples of Navy distillate fuel (F-76) with cetane numbers ranging from approximately 48 to 56; (c) 4 samples of commercial heavy marine gas oil with cetane numbers ranging from 43 to 56; Note: in Tables I and II, for the same class of fuels, fuels were ranked in descending order of cetane number.

Fuel Composition. Two types of compositional analyses were performed, which were as follows.

Proton NMR Analysis. Analysis based on proton NMR was performed by Southwest Research Institute (SwRI) using a JEOL FX 90Q Fourier transform NMR spectrometer. Sample concentration was 33% in deuterated chloroform (v/v) with tetramethylsilane as the internal standard; the NMR tube was 5 mm in diameter. The NMR integrations for specific chemical shifts, as reported by Bailey et al.,¹⁸ were measured by Geo-Centers Inc.

HPLC Analysis. The method employed was based on the liquid chromatography/differential refractive index detection method developed by Sink, Hardy, and Hazlett.²¹ By this method, the fuels were separated into three compound classes, viz., saturates, monocyclic aromatics, and dicyclic aromatics (% v/v). Fuels were analyzed on a silica gel column (Whatman M9 10/25 μ m Partail PAC semiprep, 25 cm long, 9 mm i.d.) with polar amino cyano groups as the bonded stationary phase and Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane) as the mobile phase.

Analysis of all fuels except one (C-M-88) was done at least in triplicate (see Table IA). The results given in Table I are average values of replicate analyses. Repeatability was good for most of the fuels including those fuels that were recoded for quality analysis/quality control purposes. Thus, the standard deviation for approximately 80% of the fuels was within $\pm 0.1\%$. This can be considered as within the experimental error of the method. For approximately 17% of the fuels, their standard deviations were within $\pm 1.2\%$, and for approximately 2% of the fuels, the standard deviation was 4%. Standard deviations of $\pm 2-4\%$ may be attributed to the assigned vs the true base line in the automatic integration of those peaks. However, such problems are readily

Table I. HPLC Compositional Analysis of Worldwide Survey II Fuels

fuel ID ^a	cetane no. ^b	CH ₂ :CH ₃ (proton NMR data) ^c	% compn (v/v) ^d		
			saturates	mono- cyclic aromatics	dicyclic aromatics
A. 27 Samples of Commercial Marine Gas Oil (Ranked in Order of Measured Cetane Number)					
C-M-21	64.4	2.02	92	5	3
C-M-45	59.5	2.05	84	13	3
C-M-26	59.0	1.77	81	15	4
C-M-37 (A)	56.7	1.82	88	10	2
C-M-30 (A)	56.6	1.77	88	10	2
C-M-28	55.9	1.73	85	13	2
C-M-18	55.1	1.56	84	14	3
C-M-11	53.3	1.87	79	14	8
C-M-42	53.0	1.83	81	11	8
C-M-19	52.3	1.67	81	15	4
C-M-34	52.0	1.74	72	21	7
C-M-24	51.8 (49.6)	1.89	75	21	4
C-M-33	51.8	1.47	81	15	4
C-M-20 (B)	51.0	1.53	80	17	3
C-M-17 (C)	50.9	1.41	80	17	3
C-M-48	50.8	1.60	82	15	3
C-M-39 (B)	50.4	1.62	81	17	3
C-M-43	49.8 (48.5)	1.24	85	12	3
C-M-29	49.7	1.51	85	12	3
C-M-49	49.7	1.51	78	20	2
C-M-38 (C)	49.3 (51.7)	1.51	78	19	3
C-M-23	48.6	1.58	78	19	2
C-M-14	47.5	1.39	84	14	2
C-M-88	47.4	1.60	77 ^e	15 ^e	8 ^e
C-M-13	47.1	1.54	73	24	4
C-M-36	45.5	1.22	84	13	3
C-M-25	45.3	1.65	76	16	8
B. 22 Samples of Naval Distillate Fuel and 4 Samples of Commercial Heavy Marine Gas Oil (for the Same Fuel Class, Fuels Ranked in Order of Measured Cetane Number)					
N-F-72	56.3	1.67	81	17	2
N-F-55	54.0	1.40	85	11	3
N-F-71	53.9	1.62	83	14	3
N-F-53	53.9	1.48	84	12	5
N-F-73	53.2	1.71	83	13	4
N-F-63	53.1	1.77	80	17	3
N-F-83	53.0	1.58	81	15	4
N-F-66	52.7	1.61	80	18	2
N-F-59	52.1	1.34	85	12	3
N-F-61	52.0	1.70	79	18	3
N-F-64	51.9	1.55	81	17	2
N-F-56	51.8	1.68	72	24	4
N-F-57	51.6	1.68	77	19	4
N-F-81	51.6	1.47	84	13	3
N-F-77	51.0	1.41	81	18	1
N-F-52	50.8	1.57 (1.48) ^f	81	16	3
N-F-80	50.6 (51.2)	1.52	80	17	3
N-F-82	50.3	1.36	83	14	3
N-F-79	50.0	1.58	81	15	4
N-F-74	49.6	1.52	81	14	5
N-F-54	49.5 (49.6)	1.49	80	16	4
N-F-78	48.6 (48.2)	1.41	83	14	3
C-H-23	55.6	1.65	81	17	2
C-H-30	49.6	1.75	83	14	3
C-H-21	48.7 (47.9)	1.69	75	18	7
C-H-36	43.1	1.27	79	19	2

^a Fuels with the identical letter in parentheses are identical. Key: N = Navy; F = F-76 (Naval distillate fuel); C = commercial marine gas oil; H = heavy marine gas oil. ^b Cetane numbers in parentheses are the values obtained on recoding the same fuel. ^c This ratio is a measure of the straight- to branched-chain saturates. ^d Average of analysis performed at least in triplicate unless otherwise noted. ^e Average of analysis performed in duplicate. ^f Value obtained on repeat NMR analysis.

resolved with the improved automatic integrators that are commercially available today.

Included in Table I are the CH₂:CH₃ proton ratios obtained from the proton NMR data. This is a semiempirical ratio and was included as a means of fractionating the percent total saturates

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(21) Sink, C. W.; Hardy, D. R.; Hazlett, R. N. Naval Research Laboratory Memorandum Report 5497, Part 2; NRL: Washington, DC, Dec 1984.

Table II. Cetane Indices Values and Predictabilities* of Worldwide Survey II Fuels

fuel ID ^a	cetane no.	cetane index value			compr anal. trial cetane index (R ² = 0.692)
		ASTM D4737-87	ASTM D976-80	SwRI	
A. 27 Samples of Commercial Marine Gas Oil (Ranked in Order of Measured Cetane Number)					
C-M-21	64.4	68.2 OP	62.9 P	69.2 OP	62.6 P
C-M-45	59.5	59.3 P	56.3 UP	62.3 OP	59.0 P
C-M-26	59.0	56.6 UP	54.1 UP	57.0 P	54.0 UP
C-M-37 (A)	56.7	55.9 P	53.2 UP	60.3 OP	58.5 P
C-M-30 (A)	56.6	56.2 P	53.4 UP	58.6 P	57.9 P
C-M-28	55.9	55.8 P	54.8 P	57.3 P	56.0 P
C-M-18	55.1	54.1 P	54.4 P	56.0 P	52.7 UP
C-M-11	53.3	52.0 P	49.4 UP	55.5 OP	53.1 P
C-M-42	53.0	54.3 P	52.5 P	57.3 OP	53.8 P
C-M-19	52.3	55.4 OP	51.9 P	54.9 OP	52.6 P
C-M-34	52.0	52.9 P	51.3 P	54.5 OP	48.6 UP
C-M-24	51.8	52.1 P	51.7 P	53.7 P	52.5 P
C-M-33	51.8	47.7 UP	46.8 UP	52.5 P	50.2 P
C-M-20 (B)	51.0	52.6 P	52.2 P	53.4 OP	50.7 P
C-M-17 (C)	50.9	51.0 P	51.0 P	50.2 P	49.2 P
C-M-48	50.8	53.5 OP	53.5 OP	54.0 OP	52.4 P
C-M-39 (B)	50.4	52.1 P	51.9 P	53.7 OP	52.4 P
C-M-43	49.8	49.4 P	49.9 P	47.0 UP	47.8 P
C-M-29	49.7	51.4 P	50.5 P	52.3 OP	52.4 OP
C-M-49	49.7	54.8 OP	52.7 OP	51.9 OP	49.9 P
C-M-38 (C)	49.3	51.0 P	50.9 P	50.6 P	49.4 P
C-M-23	48.6	52.5 OP	52.9 OP	52.6 OP	50.9 OP
C-M-14	47.5	47.4 P	48.4 P	48.5 P	50.1 OP
C-M-88	47.4	48.9 P	47.1 P	50.1 OF	49.0 P
C-M-13	47.1	50.1 OP	50.4 OP	48.9 P	47.6 P
C-M-36	45.5	48.2 OP	47.2 P	44.4 P	47.3 P
C-M-25	45.3	43.1 UP	44.2 P	45.0 P	48.9 OP
B. 22 Samples of Naval Distillate Fuel and 4 Samples of Commercial Heavy Marine Gas Oil (for Same Fuel Class, Fuels Ranked in Order of Measured Cetane Number)					
N-F-72	56.3	55.4 P	53.5 UP	55.3 P	53.3 UP
N-F-55	54.0	53.7 P	52.3 P	51.9 UP	50.6 UP
N-F-71	53.9	54.6 P	53.5 P	55.6 P	53.3 P
N-F-53	53.9	52.8 P	50.8 UP	51.3 UP	51.0 UP
N-F-73	53.2	53.8 P	52.2 P	55.5 OP	54.2 P
N-F-63	53.1	52.2 P	52.3 P	55.1 P	53.8 P
N-F-83	53.0	52.0 P	51.6 P	52.8 P	51.8 P
N-F-66	52.7	55.1 OP	54.3 P	54.4 P	52.2 P
N-F-59	52.1	53.3 P	53.0 P	51.7 P	49.5 UP
N-F-61	52.0	53.4 P	52.8 P	53.5 P	52.6 P
N-F-64	51.9	52.9 P	52.7 P	53.4 P	51.4 P
N-F-56	51.8	53.7 P	53.5 P	53.2 P	48.9 UP
N-F-57	51.6	51.8 P	52.0 P	53.2 P	51.1 P
N-F-81	51.6	51.7 P	51.3 P	51.7 P	51.5 P
N-F-77	51.0	51.4 P	51.7 P	50.8 P	49.8 P
N-F-52	50.8	53.3 OP	53.0 OP	54.2 OP	51.7 P
N-F-80	50.6	52.3 P	51.7 P	52.5 P	50.8 P
N-F-82	50.3	51.2 P	50.3 P	48.8 P	49.6 P
N-F-79	50.0	54.3 OP	53.3 OP	54.4 OP	51.7 P
N-F-74	49.6	50.3 P	49.8 P	51.9 OP	50.4 P
N-F-54	49.5	51.1 P	50.6 P	51.2 P	50.1 P
N-F-78	48.6	52.3 OP	51.4 OP	50.7 OP	49.9 P
C-H-23	55.6	59.2 OP	54.6 P	57.7 OP	53.0 UP
C-H-30	49.6	53.8 OP	52.7 OP	57.7 OP	55.2 OP
C-H-21	48.7	48.7 P	47.1 P	51.0 OP	49.4 P
C-H-36	43.1	49.6 OP	44.8 P	45.0 P	46.6 OP

*Based on the criteria imposed: P = prediction; OP = overprediction; UP = underprediction. ^bSamples with identical letters in parentheses are identical. Key: N = Navy; F = F-76 (Naval distillate fuel); C = commercial marine gas oil; H = heavy marine gas oil.

into percent straight- and percent branched-chain saturates.

Cetane Indices. The indices that were evaluated included three published cetane indices and the trial cetane index. Their formulations are given below. Lotus 1-2-3 was employed in development of the new trial cetane index. Thus the trial cetane index was based on the equation obtained on multiple linear

regression analysis of cetane number vs the pertinent parameters examined.

Published Cetane Indices. 1. Calculated Cetane Index (CCI) by a Four-Variable Equation. ASTM D4737-87^b (replacement of D976-80):

$$\text{CCI} = 45.2 + (0.0892(\text{T10N})) + [(0.131 + 0.901B)(\text{T50N})] + [(0.0523 - 0.420B)(\text{T90N})] + [0.00049((\text{T10N})^2 - (\text{T90N})^2)] + 107B + 60.0B^2$$

where D = density at 15 °C in g/mL, $B = \exp(-3.50(\text{DN}))-1$, $\text{DN} = D - 0.850$, $\text{T10N} = \text{T10} - 215$, $\text{T50N} = \text{T50} - 260$, and $\text{T90N} = \text{T90} - 310$. T10, T50, and T90 refer to the distillation temperatures in °C of 10, 50, and 90% recovered distillate, respectively.

2. Calculated Cetane Index (CCI) of Distillate Fuels. ASTM D976-80:^c

$$\text{CCI} = 454.74 - 1641.416D + 774.74D^2 - 0.554(\text{T50}) + 97.803(\log \text{T50})^2$$

where D = density at 15 °C in g/mL and T50 = distillation temperature in °C of 50% recovered distillate.

3. Southwest Research Institute (SwRI) Cetane Index.¹⁸

$$\text{PCN} = 9.49 - 0.0298\text{DHH}_{\text{CH}_3} + 0.0896\text{DHH}_{\text{CH}_2} + 0.000097\text{DHS}^2 - 0.038\text{DHH}_a$$

where PCN = predicted cetane number, H = wt % hydrogen content, D = density, H_{CH_3} = % methyl protons of the total number of protons, H_{CH_2} = % methylene protons of the total number of protons, S = sum of % (methyl, methylene, and methine) protons, and H_a = % α protons (protons immediately adjacent to an aromatic ring).

Because of its simplicity, the SwRI index was selected over other indices that are based on a similar carbon/hydrogen type distribution and also exhibited good correlations with cetane number. For example, the best equation proposed by Gulder and Glavinovski¹⁷ involves 14 coefficients as opposed to 4 for the SwRI index.

Parameters. Those parameters employed in the formulation of the published indices were determined by the National Institute of Petroleum and Energy (NIPER). These include 10, 50, and 90% distillation temperatures, density, and wt % hydrogen. Cetane number measurements were determined by Phillips Petroleum Co. These data were obtained through private communication.²⁰ A summary of the analytical results obtained on characterization of the worldwide survey fuels has been published by Shaver et al.¹⁹

Trial Correlation Based on Compositional Analysis. This involved HPLC analysis by which percent total saturates, monocyclic and dicyclic aromatics were determined. Also, proton NMR analysis from which the previously determined percent total saturates was subdivided into percent straight- and branched-chain saturates. This fractionation of the percent total saturates was based on the ratio of CH_2 to CH_3 proton types, since these proton types are representative of straight-chain and branched-chain saturates, respectively.¹² Formulation of this trial index for the 53 fuel set is as follows. Equation obtained on regression analysis ($R^2 = 0.692$):

$$\text{CI} = 49.321 + 0.568(\% \text{ straight-chain saturates}) - 0.600(\% \text{ branched-chain saturates}) - 0.317(\% \text{ monocyclic aromatics}) - 0.582(\% \text{ dicyclic aromatics})$$

Standard error of the cetane number estimate was 2.11.

Results and Discussion

Cetane index values of the three published indices and the trial index, based on their respective parameters, are given in Table II. Included in this table are the predictabilities of the various cetane indices for the fuels examined. Predictability of the indices was based on the following adopted criteria: Cetane indices whose predictive ranges (i.e., cetane index minus cetane number) were within ± 2 cetane numbers were designated as being predictive of cetane number; those whose predictive ranges

Table III. Determination of Percent Predictability of Cetane Indices of Worldwide Survey II Fuels

predictive range (CI - CN)*	% predictability for specific predictive ranges for 53 fuels			
	ASTM D4737-87	ASTM D976-80	SwRI cetane index	compn anal. trial cetane index $R^2 = 0.69\%$
predictions within				
0 to +1.0	22.6	20.8	7.5	28.3
-0.1 to -1.0	20.8	20.8	11.3	17.0
+1.1 to +2.0	20.8	17.0	28.3	15.1
-1.1 to -2.0	3.8	11.3	5.7	11.3
tot. 0 to ± 2.0	67.9	69.8	52.8	71.7
overpredictions within				
+2.1 to +3.0	9.4	7.5	24.5	5.7
+3.1 to +4.0	9.4	5.7	9.4	3.8
+4.1 to +5.0	3.8	1.9	5.7	0.0
>+5.0	3.8	0.0	1.9	1.9
tot. +2.1 to >+5.0	26.4	15.1	41.5	11.3
underpredictions within				
-2.1 to -3.0	3.8	1.9	5.7	11.3
-3.1 to -4.0	0.0	9.4	0.0	3.8
-4.1 to -5.0	1.9	3.8	0.0	1.9
<-5.0	0.0	0.0	0.0	0.0
tot. -2.1 to <-5.0	5.7	15.1	5.7	17.0

*Cetane index - cetane number.

were +2.1 to >+5.0 were designated as overpredictive, and those whose predictive ranges were -2.1 to <-5.0 were designated as underpredictive.

On the basis of their frequency of predictions, over/underpredictions, the percent predictabilities of the various indices for specific predictive ranges were then determined (see Table III). Table IV gives the percent prediction, overprediction, and underprediction of the three published indices and the trial index, along with their corresponding R^2 values. The indices were ranked primarily on their percent predictions and secondarily on their tendency not to overpredict, since overpredictions can pose a problem to the consumer but underpredictions will not. Note, although R^2 values are the conventional method of evaluating cetane indices, the indices were not ranked on their R^2 values since evaluations based solely on such values can be misleading.

On the basis of high percent prediction and low percent overprediction coupled with high R^2 values, for the fuel set examined, the trial index based on compositional analysis appears to be a better predictor of cetane number than ASTM D4737-87, the new calculated cetane index, and slightly better than ASTM D976-80 (see Table IV). Correlation of the trial index with cetane number is shown graphically in the plot of predicted cetane number vs measured cetane number for the trial index (see Figure 1).

This trial index based on compositional analysis is to be regarded as a preliminary formulation. Regression analysis of a fuel set that is larger and comprises fuels of more diverse composition is necessary before a definitive formulation can be derived. The use of proton NMR to

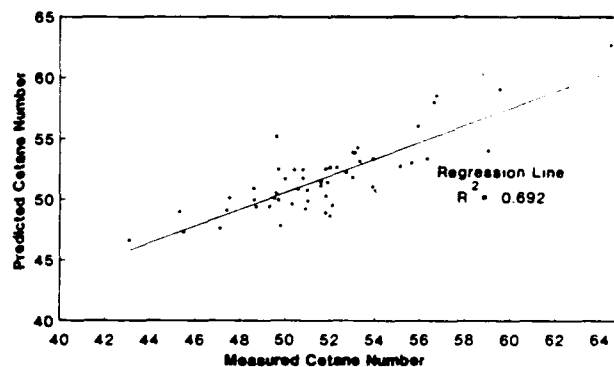


Figure 1. Predicted vs measured cetane number based on HPLC/proton NMR analysis for 53 fuels.

estimate the ratio of straight-to branched-chain composition of the accurately determined percent saturates greatly improved the R^2 value from 0.24 to 0.69 for the 53 fuels examined. The semiempirical ratio probably worked so well because the sum of the percent CH_2 and CH_3 NMR integrals was in good agreement with the percent total saturates determined by HPLC, to a first approximation. For example, on comparison of the data, approximately 90% of the fuels exhibited an agreement within 0-6% between the total percent saturates and the total percent CH_2 and CH_3 NMR integrals. The ratio of straight- to branched-chain saturates as factored by using proton NMR analysis should be verified by using the urea extraction method, for example.

Furthermore, sulfur-, nitrogen-, and oxygen-containing compounds in fuels can significantly affect cetane number.¹⁵ Consequently, consideration should be given to their content in fuels as well as to the olefin and naphthenic content, when a definitive cetane index is formulated on the basis of compositional analysis. Nevertheless, despite this trial index being a preliminary formulation, it is indicative of the promising predictability of a cetane index based on a very simple fuel compositional analysis.

The disparity between high R^2 value and poor predictability as exhibited by the SwRI cetane index (see Table IV) is indicative of the limitation of evaluations based solely on regression analysis. Also, the tendency of ASTM D4747-87 to overpredict has been observed with other fuel sets examined by us.

Conclusions

A trial index based on compositional analysis involving percent straight-chain and branched-chain saturates, as well as percent monocyclic and dicyclic aromatics, appears promising, particularly from the viewpoint of high percent prediction and low percent overprediction. In the establishment of a definitive cetane index based on compositional analysis, the following needs to be addressed: (1) fuel sets containing a larger number of fuels with more diverse composition; (2) analysis of the heteroatom content

Table IV. Evaluation of Cetane Indices of Worldwide Survey II Fuels (Indices Ranked Primarily on High Percent Predictions and Secondarily on Tendency Not to Overpredict)

cetane index	parameters	meas of % predictability ^a			R^2 values for 53 fuels ^a
		predict	over- predict	under- predict	
trial: based on compn anal.	% branched- and straight-chain saturates and monocyclic and dicyclic aromatics	72	11	17	0.692
ASTM D 976-80	T50, density	70	15	15	0.664
ASTM D4737-87 (replacement of D976-80)	T10, T50, T90, density	68	26	6	0.715
Southwest Research Inst.	proton type, density, % hydrogen	53	41	6	0.775

^aThe 53 fuels include 27 MGOs, 22 F-76s, and 4 HMGs.

of the fuels as well as the percent olefins and naphthenics; (3) verification of the differentiation of the total percent saturates into percent straight-chain and branched-chain saturates obtained from proton NMR analysis by using other analytical techniques including ^{13}C high-resolution NMR performed on the saturate fraction isolated during the HPLC analysis.

Acknowledgment. We gratefully acknowledge funding support of this work from the Office of Naval Research. We also thank B. D. Shaver (David Taylor Research and Development Center, Annapolis, MD) for providing the documented data on the fuels and B. K. Bailey (Southwest Research Institute, San Antonio, TX) for providing the NMR spectra.

GENERAL PAPERS (POSTER SESSION)
PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
MIAMI BEACH MEETING, SEPTEMBER 10 - 15, 1989

A RIGOROUS AND PRACTICAL EVALUATION OF PUBLISHED CETANE INDICES

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INTRODUCTION

Cetane number is an important index for characterizing the ignition quality of diesel fuels. The standard method for determining cetane number is an engine test, ASTM D613. However, for convenience purposes, most refineries rely instead on the ASTM approved alternative method - the Calculated Cetane Index, which is a predictive equation of cetane number. Continuing revision of the Calculated Cetane Index reflects the need for a reliable predictor of cetane number. Revisions include ASTM: D976-66, D976-80, and D4737-87 - the proposed ASTM replacement equation of D976-80. In addition, other cetane indices have been proposed to address problems associated with ASTM D976-80, such as, over/under-predictability and limitations in its applicability.

In this study, a rigorous and practical evaluation of six important published cetane indices was performed. Since cetane indices are predictive equations of cetane number, the approach employed was as follows: 1) determine their degree of predictabilities based on the rigorous and practical criteria adopted by us (1) in a previous evaluation of a trial cetane index based on compositional analysis; and 2) use a fuel set that: a) was not employed in deriving the cetane indices formulations and b) contained fuels with a wide range of cetane numbers. The world-wide survey fuels employed meet these requirements for five of the six cetane indices evaluated. The R^2 values obtained on regression analysis of cetane index vs. cetane number were also determined as well as the corresponding standard error of the Y estimate.

The evaluation performed in this study gives an independent assessment for five of the six cetane indices examined. The exception refers to the modified CCAI equation which was derived from the fuel set employed in this study. This was necessary because the CCAI equation requires a correction factor in order to be a meaningful predictor of cetane number. Despite this requirement, we included it in our study because of the simplicity of the measurements employed and hence its possible application for emergency refueling onboard ship. Compared with the calculated cetane indices, the CCAI equation is apparently also applicable to a wider range of fuels including residual fuels.

EXPERIMENTAL

Fuel Sets

The fuel set comprised 76 fuels taken from a world-wide survey involving 43 countries. For quality analysis/quality control purposes, the fuel set comprised a few fuels that were duplicates or triplicates. Classification of these fuels were as follows: a) 36 samples of commercial marine gas oil (MGO) with cetane numbers ranging from approximately 37 to 64; b) 28 samples of Naval Distillate Fuel (F-76) with cetane numbers ranging from approximately 48 to 56; c) 6 samples of commercial heavy marine gas oil (HMGO) with cetane numbers ranging from approximately 43 to 56; and d) 6 samples of commercial marine diesel fuel (MDF) with cetane numbers ranging from 44 to 60.

Measurement of Fuel Properties

Cetane number measurements were determined by Phillips Petroleum Co. Other properties employed in the determination of the cetane indices were measured by the National Institute of Petroleum and Energy, (NIPER, Oklaboma). The viscosity measurements at 50°C required by the CCAI equation were not available and were determined graphically by plotting the viscosity values at 40° and 100°C, which were available, on ASTM Viscosity/Temperature Chart paper.

Cetane Indices

Those evaluated include the following 6 cetane indices

1. ASTM D4737-87 - the proposed ASTM replacement of ASTM D976-80.
2. ASTM D976-80 - a current calculated cetane index.
3. Ethyl equation (2) - an improvement equation of ASTM D976-80.
4. National Research Council of Canada (NRCC) cetane index (3) - this was reported to be a significant improvement over existing indices.
5. Canadian General Standards Board (CGSB) cetane index (4) - this was found to predict cetane number better than ASTM D976-80 and was reported to be applicable to diesel fuels containing synthetic distillates as well as conventional petroleum distillates.
6. A modified Calculated Carbon Aromaticity Index (CCAI) obtained on regression analysis of CCAI values vs. cetane number for the corresponding 76 fuels employed. A correlation between CCAI and ignition delay for petroleum distillates and residual fuels has been reported by Zeelenberg et al. (5). However, these authors did not report (5) the CCAI formulation. The CCAI is based on two simple measurements, viz. viscosity and density - both of which are specification requirements on fuel procurement. In contrast, the Calculated Cetane Indices are based on distillation temperature(s) which is not a specification requirement, and on density. The formulation for the CCAI equation examined was obtained via private communication (6) and is given below:

$$CCAI = D - 81 - 141 \log \log (V + 0.85)$$

where: D is the Density in mg/l at 15°C, and V is the kinematic viscosity in cSt at 50°C.

The above equation appears to be a simplified version of the CCAI formulation cited by David and Denham (7).

Evaluation of Cetane Indices

The cetane indices were comparatively evaluated based on the %-predictability method previously adopted by us (1) and is described below for convenience. The conventional method of evaluation was also employed. This includes linear regression analysis to determine the correlation of fit between cetane index and cetane number for the fuels examined i.e., the R^2 values; and the standard error of the Y estimate - both these statistical functions were determined by standard analysis of variance.

Evaluation Method Based on %-Predictability

This method offers both a qualitative and quantitative assessment of cetane indices. To qualitatively assess the cetane indices, their predictive ranges (PR), for the fuels examined, were first determined, where: PR = Cetane Index minus Cetane Number for that fuel. Predictability was then determined based on the following criteria: PR within +/- 2 cetane numbers were defined as predictions; PR greater than +2 cetane numbers were defined as overpredictions, and PR less than -2 cetane numbers, as underpredictions.

The above criteria were based on the reproducibility limits allowed by ASTM D613 for determining cetane number which are 2.5 to 3.3 for cetane number range, 40 to 56, respectively. These limits were interpreted as being +/- 1.3 to 1.7 for the same cetane number range. Consequently, the criteria for predictions being +/- 2 cetane numbers may be considered to be both rigorous and practical. In addition, by defining the criteria for predictability in this way, multiple or averaged cetane number determinations for each fuel evaluated are unnecessary.

Based on the qualitative assessment described above, percent predictabilities of the cetane indices were then determined from their frequency of predictions, overpredictions, and underpredictions, for the fuel sets examined. Finally, for evaluation of the cetane indices based on percent predictability, the indices were ranked in order of best to worse primarily on their %-predictions and secondarily, on their tendency not to overpredict. This order was adopted for the following reasons: In evaluating the predictability of cetane indices, it is obvious that first, a high percent prediction is desirable and second, overpredictions will pose a problem to the consumer, but underpredictions will not. Ideally, the best indices should try to minimize both over- and under- predictions.

RESULTS AND DISCUSSION

Summarized in Table I are the following results for the fuels examined: the percent-predictions, overpredictions, and underpredictions of the various cetane indices; their respective R^2 values on regression analysis of cetane index vs. cetane number for the 76 fuel set; and their corresponding standard error of the % estimate. The parameters for each index are also given. Based on the adopted evaluation method, for the same fuel set, the following were observed: The indices which ranked highest in this evaluation include the ASTM D976-80 and the modified CCAI equation - both these indices exhibited similar predictabilities. Formulation for the modified CCAI equation is included in the footnotes of Table I. However, except for the Ethyl equation, in general, the indices examined exhibited fairly similar percent predictions (62 to 68%); also, their

TABLE 1
EVALUATION OF CETANE INDICES: RANKED ON PREDICTABILITY
For 76 World-Wide Survey Marine Fuels^a

Cetane Index	Parameters	Measure of % Predictability			R ² Values	Standard Error of the Y Est.
		Predict	Over-Predict	Under-Predict		
ASTM D 976-80	TS0, Density	68	17	15	0.683	2.8
Modified CCAI Equation ^b	Density, Viscosity	66	18	16	0.650	2.9
Canadian General Standards Board (CUSB)	T10, TS0, T90, Density Aniline Point, Viscosity	64	11	25	0.654	3.3
ASTM D4737-87 (Replacement of D976-80)	T10, TS0, T90, Density	64	29	7	0.730	3.1
National Research Council of Canada (NRCC)	T10, TS0, T90, Density Aniline Point, Viscosity	62	10	28	0.685	3.3
Ethyl Equation	TS0, Density	28	67	5	0.665	4.2
ASTM D1737-87 (Replacement of D976-80)	T10, TS0, T90, Density	70 ^c	25 ^c	5 ^c	0.649 ^c	4.1

a. Unless otherwise stated, The 76 fuels includes: 38 MGOs, 28 F-76s, 6 HMGs, and 6 MDEs.

b. CCAI Modified Equation = $-(0.3658 \times \text{CCAI}) + 345.0876$

c. For 63 of the 76 fuels and includes only those fuels which meet the application range specified by this index viz, 28 MGOs, 28 F-76s, 3 HMGs, and 3 MDEs.

standard errors of the Y estimate were similar (approximately 3). In addition, the R^2 values of all the indices were similar (approximately 0.7).

Nevertheless, differences among the indices appear to be in their percent- overpredictions and underpredictions. Indices which exhibited a tendency to overpredict include the Ethyl equation (87%) and to a lesser extent, the ASTM D4737-87 (29%). A similar tendency of ASTM D4737-87 to overpredict (25%) was also observed for the 63 fuel set, which comprised only those fuels that were within the recommended range of application specified by this index (see Table I). Indices which exhibited a tendency to underpredict include the CGSB (25%) and NRCC (28%). Both these indices employ the same six parameters in their formulations, but despite the more complex equation of the NRCC index, it exhibited similar predictabilities as the CGSB cetane index.

CONCLUSIONS AND RECOMMENDATIONS

Based on the fuel set examined and the rigorous and practical evaluation method employed, ASTM D4737-87 does not appear to be a better predictor of cetane number than ASTM D976-80, the index it is intended to replace. Indices that exhibited a tendency to overpredict include the Ethyl equation and to a lesser extent, the ASTM D4737-87. In view of ASTM D4737-87 being the ASTM proposed replacement of ASTM D976-80, such a tendency to overpredict should be monitored in future evaluations by using fuel sets such as the one employed in this study vis. fuel sets which do not comprise fuels used in deriving its formulation.

The modified CCAI equation appears to be a similar predictor of cetane number as ASTM D976-80. The promising predictability of the modified CCAI equation coupled with the two simple measurements required for the CCAI determination indicate that a new modified CCAI equation, based on a larger fuel set which comprised fuels of more diverse molecular composition would be particularly useful in cases of emergency re-fueling including combat scenarios.

Cetane indices which exhibited a tendency to underpredict include the CGSB cetane index and the NRCC cetane index. Despite the complexity of the NRCC index, it exhibited similar predictabilities as the CGSB index.

Use of the predictability method of evaluation was particularly advantageous in identifying the tendency of an index to overpredict or underpredict. This is important since such information is not obtained from the conventional method of evaluation involving R^2 values and the standard error of the Y estimate calculated by standard analysis of variance.

ACKNOWLEDGMENTS

We thank R. N. Hazlett (Naval Research Laboratory, Washington, D.C.) for helpful discussions and B. D. Shaver (David Taylor Research Center, Annapolis, MD) for providing the documented data on the fuels.

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A practical evaluation of published cetane indices

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(Received 25 May 1989; revised 27 September 1989)

Six published cetane indices were comparatively evaluated using a per cent predictability method, which was both rigorous and practical. The conventional linear regression analysis method was also employed. The indices evaluated included ASTM D976-80, ASTM D4737-87 (the proposed replacement of ASTM D976-80), the National Research Council of Canada (NRCC) cetane index, the Canadian General Standards Board cetane index (CGSB), the Calculated Carbon Aromaticity Index (CCAI), and the Ethyl equation. The fuel set, which was obtained from a worldwide survey, comprised 63 fuels and included only those fuels that met the application range specified by ASTM D4737-87 (the index which was most restrictive towards fuel properties). Cetane numbers of the fuels ranged from ≈ 45 to 57, with one fuel having a cetane number of 37. For the fuel set examined, based on the criteria imposed for determining predictability, the following were observed: ASTM D4737-87 exhibited a tendency to overpredict and did not appear to be an improvement over ASTM D976-80; both the NRCC and the CGSB cetane indices exhibited a tendency to underpredict; and a modified CCAI equation appeared promising as a predictor of cetane number.

(Keywords: diesel; fuel; cetane number)

Cetane number is important for characterizing the ignition quality of diesel fuels. The standard method for determining cetane number is an engine test, ASTM D613. However, for purposes of convenience, most refineries rely instead on the ASTM approved alternative method – the calculated cetane index, which is a 'non-engine' predictive equation of cetane number. The need for greater accuracy in predicting cetane number has led to two revisions of the original calculated cetane index, ASTM D976-66. The revisions are ASTM D976-80, and ASTM D4737-87 (the proposed replacement equation of D976-80). In addition, other cetane indices have been proposed to address problems associated with ASTM D976-80, such as over/under-predictability and limitations in its applicability. Continuing revision of the calculated cetane index is likely indicative of fuel compositional changes such as changes in crudes' composition and/or changes in refinery operations. Thus, there is need for a reliable predictor of cetane number.

In this study, six important published cetane indices were evaluated using a percentage predictability method that was both rigorous and practical. Since cetane indices are predictive equations of cetane number, the approach employed was as follows:

1. Determine their degrees of predictability, based on the rigorous and practical criteria adopted^{1,2} in previous evaluations of cetane indices.
2. Use a fuel set that: was not employed in deriving the cetane indices formulations; and comprised fuels that met the application range specified by ASTM D4737-87 (the most restrictive of the six cetane indices towards fuel properties).

The worldwide survey fuels employed met these requirements for five of the six cetane indices evaluated. The R^2 values obtained on regression analysis of cetane

index versus cetane number were also determined, as well as the corresponding standard error of the Y estimate.

The evaluation performed in this study gives an independent assessment for five of the six cetane indices examined. The exception is the modified CCAI equation, which was derived from the fuel set employed in this study. This was necessary because the CCAI equation requires a correction factor to be a meaningful predictor of cetane number. Despite this requirement, it was included in this study because of the simplicity of the measurements employed and hence its possible application for emergency re-fueling onboard ship. Compared with the calculated cetane indices, the CCAI equation is apparently also applicable to a wider range of fuels: residual fuels for which it was developed³ as well as distillate fuels.

EXPERIMENTAL

Fuel sets

The fuel set comprised 63 fuels taken from a worldwide survey involving 37 countries. For quality analysis/quality control purposes, the fuel set comprised a few fuels that were duplicates or triplicates. Classification of these fuels was as follows: 29 samples of commercial marine gas oil (MGO) with cetane numbers ranging from ≈ 45 to 57 with one fuel having a cetane number of 37; 28 samples of Naval Distillate Fuel (NATO F-76 type) with cetane numbers ranging from ≈ 48 to 56; 3 samples of commercial heavy marine gas oil (HMGO) with cetane numbers ranging from ≈ 48 to 50; and 3 samples of commercial marine diesel fuel (MDF) with cetane numbers ranging from ≈ 48 to 52.

Measurement of fuel properties

Cetane number measurements were determined by Phillips Petroleum Co. Other properties employed in the determination of the cetane indices were measured by the National Institute of Petroleum and Energy (NIPER, Oklahoma). The viscosity measurements at 50°C required by the CCAI equation were not available, and were determined graphically by plotting the viscosity values at 40°C and 100°C (which were available) on ASTM viscosity/temperature chart paper.

Cetane indices

The following six cetane indices were evaluated:

1. ASTM D4737-87 – the proposed ASTM replacement for ASTM D976-80;
2. ASTM D976-80 – a current calculated cetane index;
3. Ethyl equation⁴ – an improved version of ASTM D976-80;
4. National Research Council of Canada (NRCC) cetane index⁵, which was reported to be a significant improvement over existing indices;
5. Canadian General Standards Board (CGSB) cetane index⁶, which was found to predict cetane number better than ASTM D976-80 and was reported to be applicable to diesel fuels containing synthetic distillates as well as conventional petroleum distillates;
6. A modified calculated carbon aromaticity index (CCAI) obtained on regression analysis of CCAI values versus cetane number for a 76 fuel set².

A correlation between CCAI and ignition delay for petroleum distillates and residual fuels has been reported by Zeelenberg *et al.*³. The CCAI is based on two simple measurements, namely viscosity and density, both of which are specification requirements on fuel procurement. In contrast, the calculated cetane indices are based on distillation temperature, which is not a specification requirement, and on density. The formulation for the CCAI equation examined is given below:

$$\text{CCAI} = D - 81 - 141 \log \log (V_k + 0.85)$$

where D is the density (kg m^{-3}) at 15°C, and V_k is the kinematic viscosity ($\text{mm}^2 \text{s}^{-1}$) at 50°C. This equation appears to be a simplified version of the CCAI formulation cited by David and Denham⁷.

Evaluation of cetane indices

The cetane indices were comparatively evaluated based on the percentage predictability method adopted previously^{1,2}, which is described below for convenience. The conventional method of evaluation was also employed. This includes linear regression analysis to determine the correlation of fit between cetane index and cetane number for the fuels examined, i.e. the R^2 values; and the standard error of the Y estimate. Both these statistical functions were determined by standard analysis of variance.

Evaluation method based on percentage predictability

This method offers both a qualitative and quantitative assessment of cetane indices. To qualitatively assess the cetane indices, their predictive ranges (PR) for the fuels examined were determined, where $\text{PR} = \text{cetane index} - \text{cetane number}$ for that fuel. Predictability was then determined based on the following criteria: PR within ± 2 cetane numbers were defined as predictions;

PR greater than $+2$ cetane numbers as overpredictions; and PR less than -2 cetane numbers as underpredictions.

The above criteria were based on the reproducibility limits allowed by ASTM D613 for determining cetane number, which are 2.5–3.3 for the cetane number range 40–56. These limits were interpreted as being ± 1.3 – 1.7 for the same cetane number range. Consequently, the criteria for predictions being ± 2 cetane numbers may be considered to be both rigorous and practical. In addition, by defining the criteria for predictability in this way, multiple or averaged cetane number determinations for each fuel evaluated are unnecessary.

Based on the qualitative assessment described above, per cent predictabilities of the cetane indices were then determined from their frequency of predictions, overpredictions, and underpredictions, for the fuel sets examined. Finally, for evaluation of the cetane indices based on per cent predictability, the indices were ranked in order of best to worst, first on their percentage predictions, and then on their tendency not to overpredict. This order was adopted because in evaluating the predictability of cetane indices, it is obvious that: first, a high per cent prediction is desirable; and second, overpredictions will pose a problem to the consumer, but underpredictions will not. Ideally, the best indices should try to minimize both over- and underpredictions.

RESULTS AND DISCUSSION

Cetane index values for the indices examined are given in Table 1. The fuels were ranked in order of their measured cetane numbers. Table 1 also includes the predictabilities of the cetane indices for the fuels employed (predictability being based on the criteria described earlier). The per cent predictability of the six cetane indices for specific predictive ranges are given in Table 2. Summarized in Table 3 are the following results for the fuels employed: the per cent predictions, overpredictions, and underpredictions of the various cetane indices; their respective R^2 values on regression analysis of cetane index versus cetane number for the 63 fuel set; and their corresponding standard error of the Y estimate. The parameters for each index are also given.

Based on the adopted evaluation method, for the same fuel set, the following observations were made: the indices that ranked highest in this evaluation included the modified CCAI equation and ASTM D976-80 – both these indices exhibited similar predictabilities. Formulation for the modified CCAI equation is included in the footnotes of Tables 1–3. However, except for the Ethyl equation, the indices examined generally exhibited fairly similar per cent predictions (65–73%) and similar standard errors of the Y estimate (≈ 4). The R^2 values of all the indices were also similar (≈ 0.6).

Nevertheless, differences among the indices appear to be in their per cent overpredictions and underpredictions. Indices that exhibit a tendency to overpredict include the Ethyl equation (70%) and, to a lesser extent, ASTM D4737-87 (25%). Indices that exhibit a similar tendency to underpredict include CGSB and NRCC ($\approx 25\%$). Both these indices employ the same six parameters in their formulations, but despite the more complex equation of the NRCC index, it exhibits predictabilities similar to the CGSB cetane index. The predictabilities of

Table 1 Cetane indices values and predictabilities^a of worldwide survey fuels

Fuel ID ^b	Cetane no. ASTM D613	ASTM D4737-87	ASTM D976-80	Ethyl eqn.	NRCC cetane index	CGSB cetane index	Modified ^c CCAI eqn.
C-M-37 (A)	56.7	55.9 P	53.2 UP	56.8 P	54.2 UP	54.9 P	53.0 UP
C-M-30 (A)	56.6	56.2 P	53.4 UP	57.0 P	53.6 UP	53.9 UP	53.1 UP
N-F-72	56.3	55.4 P	53.5 UP	57.2 P	53.1 UP	52.7 UP	53.8 UP
C-M-28	55.9	55.8 P	54.8 P	59.2 OP	53.2 UP	53.2 UP	54.8 P
C-M-18	55.1	54.1 P	54.4 P	58.6 OP	52.0 UP	53.7 P	53.7 P
N-F-86 (B)	54.2	55.1 P	54.2 P	58.3 OP	52.3 P	52.4 P	52.4 P
N-F-55	54.0	53.7 P	52.3 P	55.3 P	53.0 P	52.6 P	53.0 P
N-F-53	53.9	52.8 P	50.8 UP	53.1 P	51.9 P	50.4 UP	50.9 UP
N-F-71	53.9	54.6 P	53.5 P	57.1 OP	52.8 P	52.4 P	53.4 P
C-M-11	53.3	52.0 P	49.4 UP	50.9 UP	51.9 P	50.1 UP	49.7 UP
N-F-73	53.2	53.8 P	52.2 P	55.2 P	52.9 P	51.7 P	52.3 P
N-F-63	53.1	52.2 P	52.3 P	55.3 OP	49.7 UP	49.8 UP	51.8 P
C-M-42	53.0	54.3 P	52.5 P	55.7 OP	52.9 P	52.3 P	51.4 P
N-F-83	53.0	52.0 P	51.6 P	54.2 P	50.2 UP	49.8 UP	51.3 P
N-F-66 (B)	52.7	55.1 OP	54.3 P	58.5 OP	52.3 P	52.5 P	53.9 P
C-M-19	52.3	55.4 OP	51.9 P	54.7 OP	53.7 P	51.1 P	52.1 P
N-F-59	52.1	53.3 P	53.0 P	56.4 OP	52.1 P	51.6 P	54.1 P
N-F-61	52.0	53.4 P	52.8 P	56.1 OP	49.6 UP	49.6 UP	52.2 P
C-M-34	52.0	52.9 P	51.3 P	53.8 P	50.6 P	51.6 P	51.0 P
N-F-64	51.9	52.9 P	52.7 P	55.9 OP	50.7 P	51.4 P	52.9 P
C-D-33	51.9	52.4 P	52.7 P	56.0 OP	49.8 UP	49.9 P	52.1 P
N-F-56	51.8	53.7 P	53.5 P	57.1 OP	50.5 P	51.2 P	52.8 P
C-M-33	51.8	47.7 UP	46.8 UP	47.1 UP	45.8 UP	46.3 UP	52.7 P
C-M-24 (C)	51.8	52.1 P	51.7 P	54.5 OP	48.6 UP	48.5 UP	50.8 P
P-W-6 (D)	51.7	51.0 P	50.9 P	53.1 P	48.7 UP	48.7 UP	51.2 P
N-F-57	51.6	51.8 P	52.0 P	54.9 OP	48.7 UP	48.8 UP	51.1 P
P-W-4	51.6	56.7 OP	53.8 OP	57.7 OP	56.1 OP	53.2 P	53.9 OP
N-F-81	51.6	51.7 P	51.3 P	53.8 OP	49.7 P	49.9 P	51.4 P
P-W-7 (E)	51.2	51.0 P	51.1 P	53.5 OP	49.3 P	49.6 P	51.9 P
C-M-20 (F)	51.0	52.6 P	52.2 P	55.1 OP	49.8 P	50.0 P	51.9 P
N-F-77	51.0	51.4 P	51.7 P	54.4 OP	48.1 UP	48.5 UP	51.7 P
C-M-17 (D)	50.9	51.0 P	51.0 P	53.3 OP	48.7 UP	48.7 UP	51.1 P
N-F-52	50.8	53.3 OP	53.0 OP	56.4 OP	49.7 P	49.7 P	52.6 P
C-M-48	50.8	53.5 OP	53.5 OP	57.3 OP	49.9 P	50.8 P	52.4 P
N-F-80 (E)	50.6	52.3 P	51.7 P	54.4 OP	50.0 P	49.7 P	52.2 P
N-F-85 (E)	50.6	52.0 P	51.4 P	53.9 OP	49.9 P	49.7 P	52.1 P
C-M-39 (F)	50.4	52.1 P	51.9 P	54.7 OP	48.7 P	48.8 P	51.8 P
N-F-82	50.3	51.2 P	50.3 P	52.2 P	49.9 P	49.4 P	50.0 P
C-H-87	50.2	54.6 OP	54.7 OP	59.1 OP	51.5 P	51.4 P	53.1 OP
C-D-23	50.1	53.9 OP	51.3 P	53.9 OP	52.6 OP	52.2 OP	53.7 OP
N-F-79	50.0	54.3 OP	53.3 OP	56.9 OP	51.2 P	50.8 P	52.7 OP
C-M-47	49.9	52.4 OP	51.6 P	54.3 OP	50.5 P	50.1 P	50.5 P
C-M-43 (G)	49.8	49.4 P	49.9 P	51.7 P	47.8 P	49.9 P	48.6 P
C-M-29	49.7	51.4 P	50.5 P	52.6 OP	50.2 P	50.6 P	51.0 P
C-M-49	49.7	54.8 OP	52.7 OP	56.0 OP	51.1 P	49.4 P	52.3 OP
N-F-74 (H)	49.6	50.3 P	49.8 P	51.5 P	54.6 OP	56.1 OP	50.0 P
P-W-5 (I)	49.6	50.7 P	50.6 P	52.7 OP	49.5 P	49.5 P	50.7 P
P-W-1 (C)	49.6	52.1 OP	51.8 OP	54.6 OP	48.5 P	48.4 P	50.8 P
N-F-54 (I)	49.5	51.1 P	50.6 P	52.8 OP	49.4 P	49.3 P	50.5 P
N-F-84 (H)	49.4	50.5 P	50.0 P	51.9 OP	53.7 OP	54.8 OP	50.1 P
C-M-38 (D)	49.3	51.0 P	50.9 P	53.1 OP	48.6 P	48.6 P	51.1 P
C-M-87	49.3	50.1 P	49.7 P	51.4 OP	48.6 P	47.4 P	49.9 P
C-H-21 (J)	48.7	48.7 P	47.1 P	47.6 P	47.5 P	48.5 P	46.8 P
N-F-78 (K)	48.6	52.3 OP	51.4 OP	53.9 OP	50.8 OP	50.4 P	51.3 OP
C-M-23	48.6	52.5 OP	52.9 OP	56.3 OP	49.4 P	49.9 P	52.3 OP
P-W-8 (G)	48.5	49.7 P	50.0 P	51.9 OP	47.8 P	49.7 P	48.7 P

Table 1 *Contd.*

Fuel ID ^a	Cetane no. ASTM D613	ASTM D4737-87	ASTM D976-80	Ethyl eqn.	NRCC cetane index	CGSB cetane index	Modified ^c CCAI eqn.
P-W-3 (K)	48.2	52.5 OP	51.5 OP	54.1 OP	51.0 OP	50.5 OP	51.2 OP
C-D-12	48.0	43.1 UP	44.2 UP	43.6 UP	42.1 UP	42.2 UP	42.3 UP
P-W-2 (J)	47.9	49.2 P	47.3 P	47.9 P	48.3 P	49.5 P	47.0 P
C-M-13	47.1	50.1 OP	50.4 OP	52.4 OP	46.2 P	46.0 P	49.8 OP
C-M-36	45.5	48.2 OP	47.2 P	47.8 OP	46.3 P	47.1 P	47.6 OP
C-M-25	45.3	43.1 UP	44.2 P	43.5 P	45.3 P	46.9 P	42.1 UP
C-M-89	37.0	37.4 P	38.7 P	36.4 P	36.2 P	35.6 P	38.5 P

^aBased on the criteria imposed: P = prediction; OP = overprediction; UP = underprediction^bSamples with the same letters in parentheses are identical: C = commercial; M = marine gas oil; N = navy; F = F-76 (naval distillate fuel); H = heavy marine gas oil; D = marine diesel fuel^cModified CCAI eqn. = $-(0.3656 \times \text{CCAI}) + 345.0875$ (this regression equation was derived from a 76 fuel set)

Table 2 Determination of percentage predictability of cetane indices (worldwide survey II fuels)

Predictive range ^a (CI-CN)	Predictability (%) for specific predictive ranges (for 63 fuels)					
	ASTM D4737-87	ASTM D976-80	NRCC cetane index	CGSB cetane index	Ethyl eqn.	Modified ^b CCAI eqn.
Predictions within:						
0 -1.0	25.4	25.4	11.1	7.9	6.3	23.8
-(0.1-1.0)	17.5	19.0	23.8	23.8	3.2	17.5
1.1-2.0	23.8	19.0	6.3	12.7	12.7	19.0
-(1.1-2.0)	3.2	7.9	23.8	25.4	3.2	12.7
Total: $\pm(0-2.0)$	69.9	71.3	65.0	69.8	25.4	73.0
Overpredictions within:						
2.1-3.0	11.1	9.5	4.8	3.2	17.5	12.7
3.1-4.0	6.3	4.8	0.0	0.0	20.6	3.2
4.1-5.0	4.8	3.2	4.8	0.0	12.7	0.0
> 5.0	3.2	0.0	0.0	3.2	19.0	0.0
Total: (2.1->5.0)	25.4	17.5	9.6	6.4	69.8	15.9
Underpredictions within:						
-(2.1-3.0)	1.6	1.6	15.9	11.1	1.6	3.2
-(3.1-4.0)	0.0	7.9	6.3	9.5	0.0	6.3
-(4.1-5.0)	3.2	1.6	0.0	0.0	3.2	0.0
-(>5.0)	0.0	0.0	3.2	3.2	0.0	1.6
Total: -(2.1->5.0)	4.8	11.1	25.4	23.8	4.8	11.1

^aCetane index-cetane number^bModified CCAI = $-(0.3656 \times \text{CCAI}) + 345.0875$ Table 3 Evaluation of cetane indices: ranked on predictability for 63 worldwide survey marine fuels^a

Cetane index	Parameters	Predictability (%)			R^2 values	Standard error of the Y est.
		Predict	Overpredict	Underpredict		
Modified CCAI eqn. ^b	Density, viscosity	73	16	11	0.601	3.9
ASTM D976-80	T_{50} , density	71	18	11	0.579	3.9
Canadian General Standards Board (CGSB)	T_{10} , T_{50} , T_{90} , density aniline point, viscosity	70	6	24	0.551	4.3
ASTM D4737-87 (replacement of D976-80)	T_{10} , T_{50} , T_{90} , density	70	25	5	0.649	4.1
National Research Council of Canada (NRCC)	T_{10} , T_{50} , T_{90} , density aniline point, viscosity	65	10	25	0.572	4.3
Ethyl equation	T_{50} , density	25	70	5	0.572	5.7

^aThe 63 fuel set includes only those fuels that meet the application range specified by this index and comprise: 29 MGOs, 28 F-76s, 3 HMGOs, and 3 MDFs^bModified CCAI eqn. = $-(0.3656 \times \text{CCAI}) + 345.0875$; where $\text{CCAI} = D - 81 - 141 \log \log (\text{visc} + 0.85)$; D = density in g l^{-1} at 15°C , and visc = kinematic viscosity (cSt) at 50°C

Table 4 Repeatability of cetane numbers and cetane indices (worldwide survey fuels)

Fuel ID ^a	Cetane no. ASTM D613	Repeatability						
		Cetane no. ASTM D613	ASTM D4737-87	ASTM D976-80	Ethyl eqn.	NRCC cetane index	CGSB cetane index	Modified CCAI eqn.
C-M-37 (A)	56.7	0.1	0.3	0.2	0.2	0.6	1.0	0.1
C-M-30 (A)								
N-F-86 (B)	54.2	1.5	0.0	0.1	0.2	0.0	0.1	1.5
N-F-66 (B)								
C-M-24 (C)	51.8	2.2	0.0	0.1	0.1	0.1	0.1	0.0
P-W-1 (C)								
P-W-6 (D)	51.7	2.4	0.0	0.1	0.2	0.1	0.1	0.1
C-M-17 (D)								
C-M-38 (D)								
P-W-7 (E)	51.2	0.6	1.3	0.6	0.9	0.7	0.1	0.3
N-F-80 (E)								
N-F-85 (E)								
C-M-20 (F)	51.0	0.6	0.5	0.3	0.4	1.1	1.2	0.1
C-M-39 (F)								
C-M-43 (G)	49.8	1.3	0.3	0.1	0.2	0.0	0.2	0.1
P-W-8 (G)								
N-F-74 (H)	49.6	0.2	0.2	0.2	0.4	0.9	1.3	0.1
N-F-84 (H)								
P-W-5 (I)	49.6	0.1	0.4	0.0	0.1	0.1	0.2	0.2
N-F-54 (I)								
C-H-21 (J)	48.7	0.8	0.5	0.2	0.3	0.8	1.0	0.2
P-W-2 (J)								
N-F-78 (K)	48.6	0.4	0.2	0.1	0.2	0.2	0.1	0.1
P-W-3 (K)								

^aFuels with the same letter in parentheses are identical

the six indices for the 63 fuel set, a subset of a 76 fuel set², are similar to the results obtained for the 76 fuel set. The 76 fuel set included 13 fuels that were not within the application range specified by ASTM D4737-87, i.e. they either exceeded the fuel properties or the cetane number specification ranges.

Repeatability

Cetane numbers. Of the eleven fuels examined in duplicate or in triplicate, the repeatabilities of seven fuels were within 1 cetane number; two fuels were within 1.5 cetane numbers; and the remaining two fuels were within 2.5 cetane numbers (see Table 4). Although four of the eleven fuels exceeded the repeatability limits for ASTM D613 (which are 0.6–0.9 for cetane number range 40–56), the average repeatability for the 11 sets of replicate fuels was 0.9. Nevertheless, the poor repeatability of the ASTM D613 method poses an identical problem for all evaluations of cetane indices and emphasizes the need for an improved method of determining cetane number, especially since ASTM D613 is the reference method for evaluating cetane indices.

Cetane indices. For most indices repeatability was very good, with differences ranging from 0 to 0.5 cetane number. Differences of ≥ 1 were observed more for those indices that employed aniline point in their formulations, namely the NRCC and CGSB cetane indices (see Table 4). The average repeatability of the indices ranged from ≈ 0.2 to 0.5 cetane number.

CONCLUSIONS

Based on the rigorous and practical method of evaluation employed, and for the fuel set examined, which comprised

fuels that met the application range specified by ASTM D4737-87 (the most restrictive property equation), the following observations were made: ASTM D4737-87 does not appear to be a better predictor of cetane number than ASTM D976-80, the index it is currently intended to replace as an ASTM standard. Indices that exhibit a tendency to overpredict include the Ethyl equation and, to a lesser extent, ASTM D4737-87. In view of ASTM D4737-87 being the proposed replacement of ASTM D976-80, such a tendency to overpredict should be monitored in future evaluations by using fuel sets such as the one employed in this study, i.e. fuel sets that do not comprise fuels used in deriving the formulation.

The modified CCAI equation appears to predict similar cetane numbers as ASTM D976-80. The promising predictability of the modified CCAI equation, coupled with the two simple measurements required for the CCAI determination, indicate that a new modified CCAI equation, based on a larger fuel set comprising fuels of more diverse molecular composition, would be particularly useful in cases of emergency re-fueling, including possible military applications.

Cetane indices which exhibit a tendency to underpredict include the CGSB cetane index and the NRCC cetane index. Despite the complexity of the NRCC index, the predictabilities exhibited were similar to those exhibited by the CGSB index.

Use of the predictability method of evaluation was particularly advantageous in differentiating those cetane indices that tended to overpredict from those that tended to underpredict. This is important since such information is not obtained from the conventional method of evaluation involving R^2 values and the standard error of the Y estimate calculated by standard analysis of variance.

ACKNOWLEDGEMENTS

The authors thank R. N. Hazlett (Naval Research Laboratory, Washington, DC) for helpful discussions and B. D. Shaver (David Taylor Research Center, Annapolis, MD) for providing the documented data on the fuels.

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ABSTRACT

11th International Symposium on
Column Liquid Chromatography
Amsterdam, The Netherlands
July, 1987

Determination of Corrosion Inhibitor/Lubricity Additives
in Middle Distillate Fuels by
Size Exclusion Chromatography

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This paper describes the improvements in our previously published method for qualitatively and quantitatively determining commercial corrosion inhibitors in aircraft turbine fuels. Improvements include a significant scale down of the initial fuel volume and extractant volumes. Also discussed will be a method of external standard calibration using pure components. The results for the actual concentration of active ingredients in ten commercial corrosion inhibitors will be presented. In addition, the possibility of using the technique to assess the lubricity of aircraft turbine fuels by measuring the amount of high molecular weight base extractables will be discussed. The final analysis is achieved by high resolution size exclusion chromatography and quantitation at the 2 ppm (w/w) level is possible.

ABSTRACT

194th National Meeting of
The American Chemical Society
Division of Analytical Chemistry
New Orleans, Louisiana
September, 1987

Analysis of Corrosion Inhibitor Depletion in Fuel Handling and Storage Systems

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A series of experiments were performed to elucidate physical and chemical characteristics of high molecular weight dicarboxylic acid corrosion inhibitor/lubricity enhancers. Topics to be discussed will include the effect of different surfaces on the adsorption of the dimer acid as well as the effect the dimer acid has on the coalescence of water from middle distillate jet fuels. Fuel samples were analyzed using a modified version of a previously developed method for determining corrosion inhibitor concentration.

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DETERMINATION OF CORROSION INHIBITOR/LUBRICITY ENHANCER ADDITIVES IN JET FUELS BY SIZE-EXCLUSION CHROMATOGRAPHY

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(First received August 3rd, 1987; revised manuscript received October 30th, 1987)

SUMMARY

Improvements in techniques for the qualitative and quantitative determination of commercial corrosion inhibitor/lubricity enhancer additives which contain linoleic acid derivatives are described. These include a procedural modification to use 100-, rather than 250-ml volumes of sample and extractant, and an external calibration using known pure compounds. Quantitative results for concentrations of active ingredients in six commercial corrosion inhibitors are given. The extraction technique has also been used as a possible compositional assessment of the lubricity of jet fuels by quantification of the higher-molecular-weight acidic components via high-resolution size-exclusion chromatography. Quantification of the corrosion inhibitor additive is possible at levels as low as 2 ppm (v/v) in jet fuel.

INTRODUCTION

An analytical scheme to efficiently extract and quantify the active ingredients of corrosion inhibitor additives by size exclusion chromatography has been previously described¹. The method was shown to be useful in the concentration range between 1 and 35 ppm (v/v). This includes the concentration range of interest for U.S. military jet fuels in which these additives are mandatory for lubricity improvement². This work describes significant improvement in the extraction step and in the quantification of the fatty acid dimer ingredients of these additives.

Fuel lubricity is known to vary from fuel to fuel³⁻⁷. It appears likely that lubricity enhancement is a function of composition and may be specifically related to the concentration of base extractables of sufficiently high molecular weight. The lubricity of distillate fuels is generally defined in the U.S. as the resistance to wear scar on a ball in contact with a rotating cylinder which is partially immersed in a particular fuel³. Although still in its development, the ball on cylinder lubricity evaluator

(BOCLE) device has been shown to be useful in diagnosing field problems. In practice, it is used to rank fuels by means of a wear scar diameter measurement varying between 0.25 and 0.80 mm. The mandatory corrosion inhibitor additives have been shown to be quite influential in improving the lubricity of a particular fuel (lowering its wear scar diameter measurement). Since the extraction technique employed in removing the corrosion inhibitor additives was highly efficient and quantitative, the technique was tried on corrosion inhibitor-free fuels of known lubricity (as measured by the BOCLE) to investigate whether there might be a connection between fuel composition and the measured lubricity.

An additional application of the method was the quantitative determination of the active ingredient, the fatty acid dimer, in each corrosion inhibitor. This information may be useful in future lubricity testing in setting limits for addition of these materials as lubricity enhancers in jet fuels.

EXPERIMENTAL

Equipment

Samples were analyzed on a Beckman-Altex Microspherogel column Model 255-80 (50 Å pore size, 30 cm × 8.0 mm I.D.). Fisher HPLC-grade uninhibited tetrahydrofuran (THF) was used as the mobile phase. The THF was periodically sparged with dry nitrogen. Peak integration was performed on a Hewlett-Packard Model 3390-A integrator. Samples were injected into a Rheodyne Model 7125 loop/valve injector. A Beckman Model 100-A HPLC pump was used for solvent delivery and a Waters Model 401 differential refractometer for detection.

Method

Fuel samples are prepared for analysis by extraction with 0.2 *M* aqueous sodium hydroxide. For determination of additive concentration as low as 1 ppm (v/v) of active ingredient, equal volumes of fuel and aqueous base are used. The minimum volume of fuel necessary is 100 ml. The two phases are shaken well together for 1 min. After the two phases have been allowed to separate, the aqueous phase is recovered and acidified with concentrated hydrochloric acid to pH 2. The acidified aqueous phase is then back-extracted with an equal volume of methylene chloride which is recovered and allowed to evaporate to dryness at ambient temperature. The material left in the beaker after evaporation is collected by thoroughly rinsing the beaker with small portions of THF and allowing it to collect in the corner of the beaker. It is finally taken up in 2.0 ml of THF and transferred to a glass vial with a PTFE-lined cap. Using these volumes, additive recovery is $94 \pm 1\%$ based on replicate analyses of fuel samples spiked with known additive concentrations in the range of interest. Additive recovery of 100% is possible if volumes are increased by 50%.

The analytical method was applied to include JP-5 jet fuel field samples. For those samples which were found to contain a fatty acid dimer of molecular weight 562 (dilinoleic acid, DLA) as active ingredient, quantification was based on comparison with standard solutions of EMPOL 1010, a product which contains approximately 97% DLA and 1–3% of the monomer and trimer acids⁸.

Further, six additives from the corrosion inhibitor qualified products list⁹ were analyzed to determine their DLA concentration by comparison with EMPOL 1010.

Samples of each additive and EMPOL 1010 were prepared in THF to concentrations of 2500 ppm (v/v). Duplicate injections of the additive samples and triplicate injections of the EMPOL standard were made. Peak height comparisons, which have been found to yield satisfactory results in related experiments, were made using the HP 3390-A integrator¹⁰.

The EMPOL comparator method was used to determine the concentration of the DLA rather than the total additive in extracted fuel samples. Samples extracted from fuels were compared with a standard curve generated from EMPOL 1010 samples for a working range of 1 to 10 ppm of DLA concentration. Thus, by comparing chromatograms of DLA obtained from fuel samples with those obtained from EMPOL 1010 standards, it is possible to quantify the DLA concentration. All EMPOL data were based on a DLA concentration of 97%.

Our analytical technique was also applied to a series of eight additive-free U.S. Navy JP-5 fuels. Comparisons were made between chromatograms obtained for the base extractables of the various additive-free fuels by size-exclusion chromatography, and their respective BOCLE measurements. The BOCLE results were provided by the Naval Air Propulsion Center (NAPC), Trenton, NJ, U.S.A. and were obtained using the accepted method developed for this test¹.

RESULTS AND DISCUSSION

Quantification of DLA

Nine approved military specification corrosion inhibitors were used in this study and are coded A-J in Table I. The molecular weights of the active ingredient, or dimer acid, for these additives were determined by size-exclusion chromatography. Additives A-F were found to contain a substance whose molecular weight was 561 ± 13 . This corresponds very closely with the molecular weight of DLA which is 562. Additives G and J contain an active ingredient with a considerably lower (430) molecular weight, while additive H contains a substance whose molecular weight was substantially higher (678) than the others.

TABLE I

DLA CONCENTRATION IN APPROVED MILITARY SPECIFICATION CORROSION INHIBITORS

N.D. = not determined: different composition.

Corrosion inhibitor additive	Percent DLA in additive
A	54
B	52
C	40
D	38
E	42
F	62
G	N.D.
H	N.D.
J	N.D.

Dimer concentrations for those additives whose highest-molecular-weight component corresponds well with the DLA in EMPOL 1010 are also summarized in Table I. The range of DLA present varies from 62% (v/v) to 38% (v/v). Since individual additives cannot be identified once they are extracted from fuel¹, quantification as ppm (v/v) of corrosion inhibitor additive concentration is not possible without the use of a comparator standard of similar composition. However, any additive which contains DLA or other dimer acid with a similar molecular weight can be quantified on the basis of the dimer acid concentration *versus* the EMPOL standard curve (Fig. 1).

In a similar fashion, it is possible to provide quantitative information on the level of corrosion inhibitor present in a fuel without knowing which additive was used. For those additives which contain active substances of much lower or higher molecular weight (G-J, Table I), quantification could be done by using, as a comparator standard, one of the additives which contains a similar substance. Since the number of corrosion inhibitor additives in this category is small when compared to the other group (A-F, Table I), this should yield satisfactory results.

Fig. 2 shows a size-exclusion chromatogram obtained for a JP-5 sample obtained from a fuel tank at the Patuxent River (MD, U.S.A.) Naval Air Station and is known to contain corrosion inhibitor. This experiment was performed prior to the procedural change and thus a 250-ml volume of the sample was used. It was extracted, concentrated, and an aliquot was injected onto the size-exclusion column following the method described previously¹. The peak height comparison with the EMPOL standard curve yielded a concentration of 1.9 ppm (v/v) of DLA. Depending on which was used, the concentration of corrosion inhibitor expressed as total additive

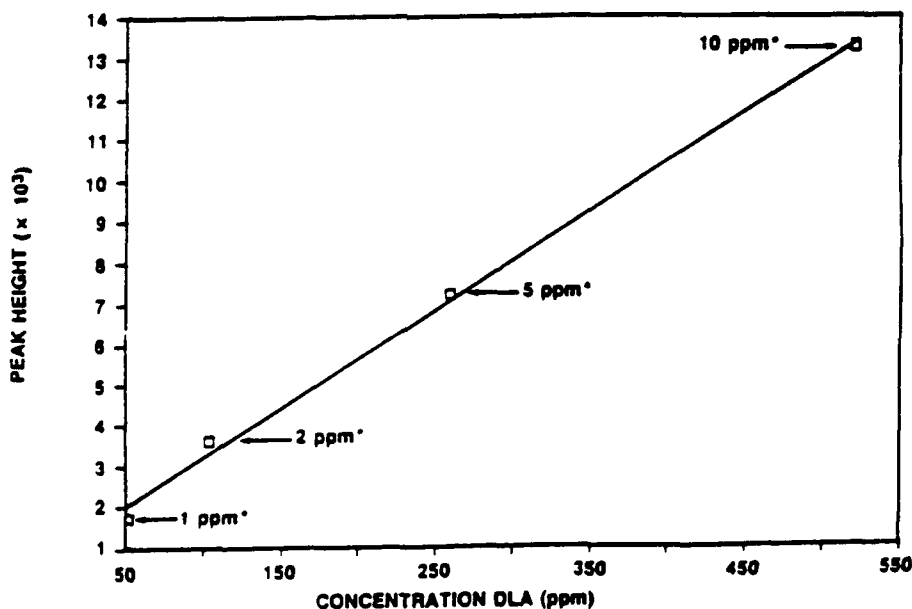


Fig. 1. DLA (EMPOL 1010) standard curve. The astensks denote the effective concentration in fuel before extraction.

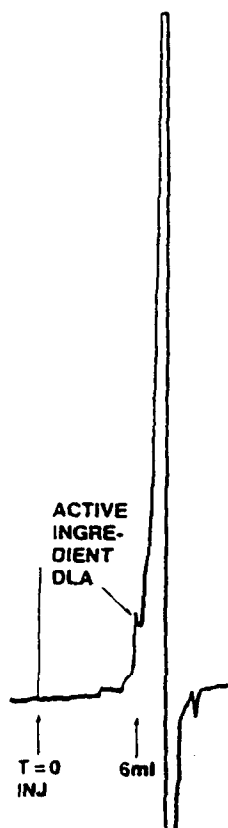


Fig. 2. Size-exclusion chromatogram of a Naval Air Station JP-5 sample from tank storage. The marked peak is active ingredient DLA. The minimum concentration determined from the external calibration graph and the active ingredient list was 4.8 ppm (w/v).

would vary between 3.1 and 5.0 ppm (v/v). Other samples run during the course of this study yielded comparable results.

Lubricity studies

A series of eight additive-free JP-5 type jet fuels was extracted and analyzed by size-exclusion chromatography following our usual procedure. Samples of each were sent to NAPC for lubricity evaluation using the BOCLE. Fig. 3 and 4 show size-exclusion chromatograms for the eight fuels. The higher-molecular-weight region of interest as seen on the chromatogram is the area with a retention volume between 6.0 ml and 7.5 ml. We focused attention particularly on the peak which is well defined on several of the chromatograms and is centered near 7.0 ml. This corresponds to a molecular weight of approximately 280. The height of this peak or deviation from baseline at 7.0 ml was measured for each fuel chromatogram and is reported, together with the corresponding BOCLE results, in Table II.

Comparison of the chromatographic and BOCLE results are quite interesting. Those fuels (Nos. 1, 2, 3, 4) which have substantial, well-defined chromatographic peaks at 7.0 ml have lower wear scar diameters and, hence, greater lubricity than do

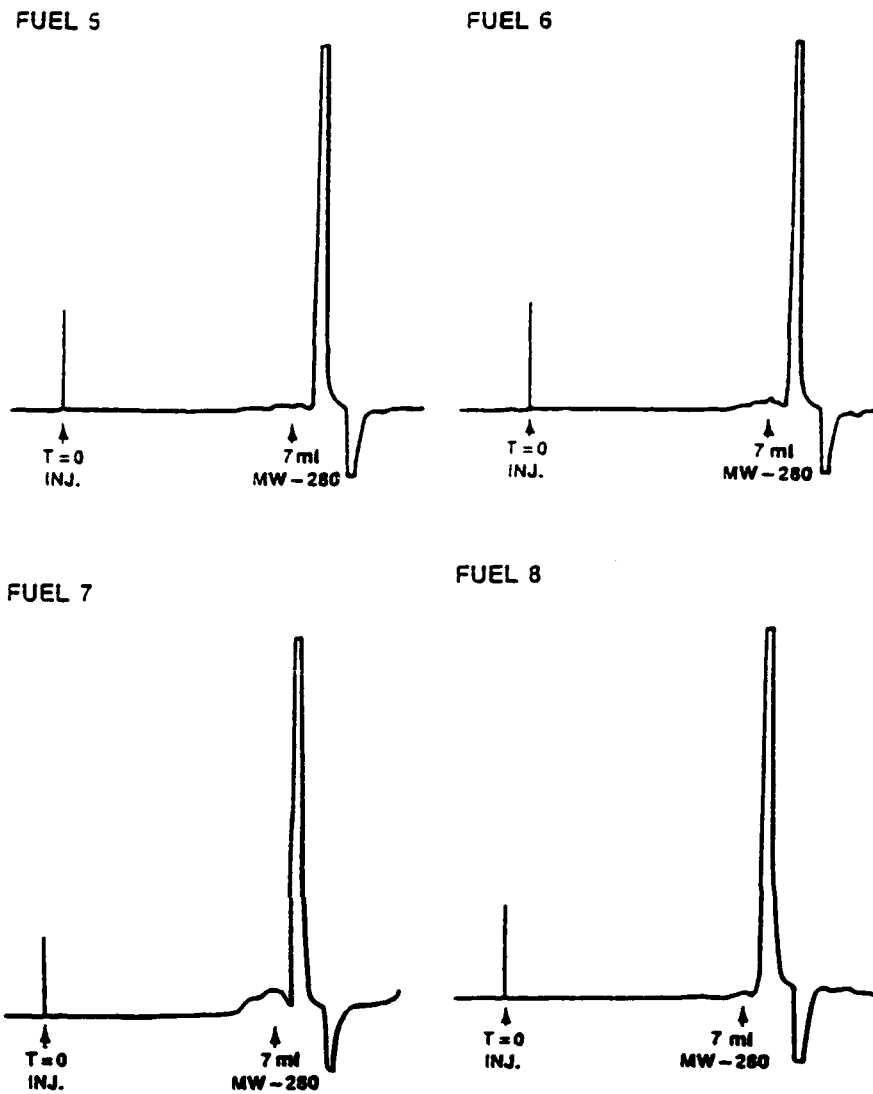


Fig. 3. Size-exclusion chromatograms of base extractables of low-lubricity (additive-free) fuels.

TABLE II
SUMMARY OF PEAK HEIGHT AND BOCLE DATA FOR LUBRICITY STUDIES

<i>JP-5 fuel</i>	<i>Peak height at 7 ml (mm)</i>	<i>BOCLE (Wear Scar Diameter, mm)</i>
1	> 200	0.23
4	59	0.28
3	27	0.27
2	25	0.26
8	2	0.41
7	14	0.36
6	4	0.35
5	3	0.34

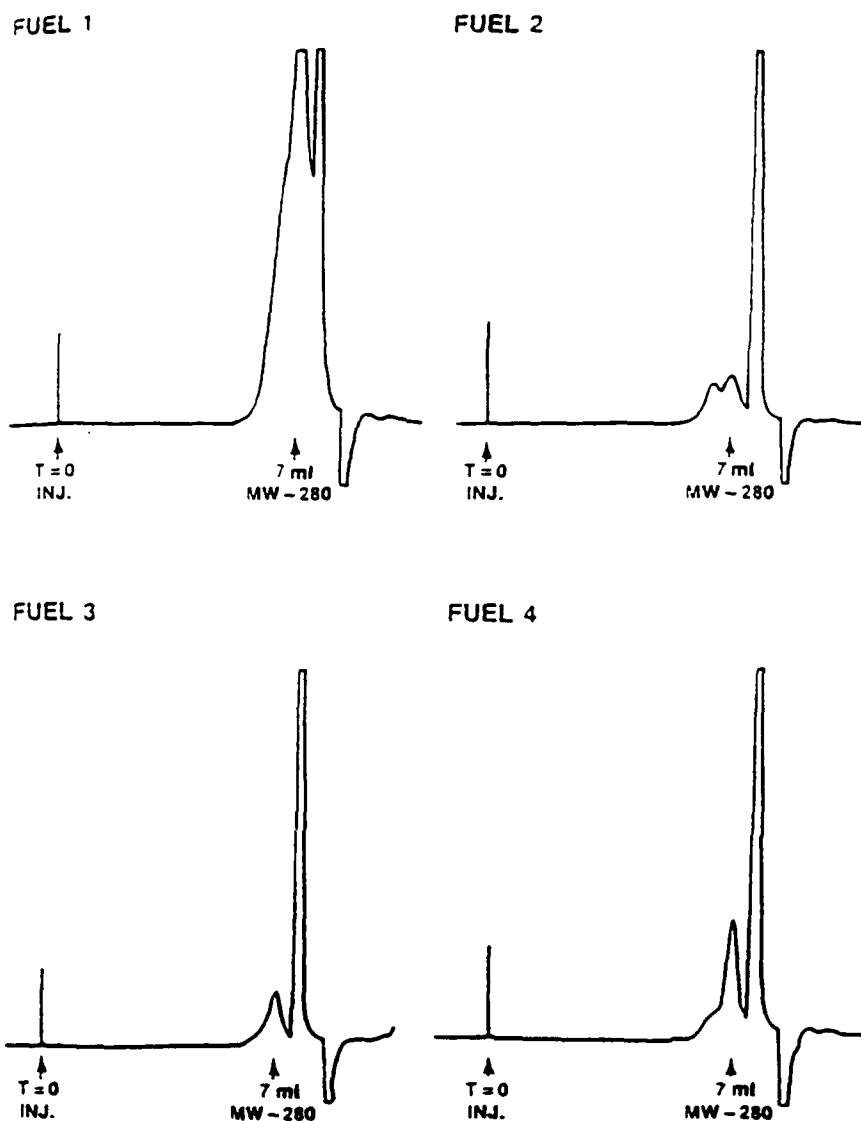


Fig. 4. Size-exclusion chromatograms of base extractables of high-lubricity (additive-free) fuels.

the others (Nos. 5, 6, 7, 8). The "break" in BOCLE results exhibited between the two groups of fuels is significant as is the difference in chromatographic data. While the peak we use as an indicator has not yet been identified, its apparent molecular weight (280) is the molecular weight range of linoleic acid. Since high-molecular-weight acids are known to increase fuel lubricity³, we suggest that it is likely that the chromatographic peak corresponds to an acid or acids.

CONCLUSIONS

A method for quantifying corrosion inhibitor additive levels in Navy jet fuels

has been modified to enable the concentration of DLA to be determined regardless of which additive is present. The method was applied to field samples obtained from the Patuxent River Naval Air Station.

Results obtained from extracted samples of a series of additive-free JP-5 type fuels, which were subsequently analyzed by size-exclusion chromatography, were compared with BOCLE results. Higher lubricity fuels, as measured by the BOCLE contained acidic components in the molecular weight range of linoleic acid. These results are very encouraging and indicate that chemical separation and chromatography may be useful in future lubricity testing.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of Mr. James Peluso of the Naval Air Propulsion Center for providing the BOCLE data. Part of the work was funded by the Naval Air Propulsion Center and the Naval Research Laboratory under contract N00014-86-M-0247.

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ABSTRACT

9th Rocky Mountain Regional Meeting
of The American Chemical Society
Las Vegas, Nevada
March, 1988

Lubricity Properties of Jet Fuel as a Function of Composition

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Due to more severe refining processes of less desirable feedstocks, the lubricity properties of jet fuel products have decreased. As a result, it is mandatory that a lubricity enhancer/corrosion inhibitor is added to all U.S. military jet fuels to assure adequate lubricity. While this additive is effective in increasing lubricity, it is expensive and decreases the ability to coalesce water from fuel. The naturally occurring components in fuel which have been shown to impart lubricity are of interest to us. Analyses of fuels by high resolution size exclusion chromatography indicate that high molecular weight acidic species play a significant role in increasing lubricity. In addition, high molecular weight acidic species were doped into low lubricity fuels and a corresponding increase in lubricity was measured using the Ball on Cylinder Lubricity Evaluator (BOCLE).

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08 November 1988

DETERMINATION OF MANDATORY ADDITIVE LEVELS IN U.S. NAVY JP-5

FINAL REPORT: NRL CONTRACT N00014-86-M-0247

by

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20375-5000

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified			1b RESTRICTIVE MARKINGS None		
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE					
4 PERFORMING ORGANIZATION REPORT NUMBER(S)			5 MONITORING ORGANIZATION REPORT NUMBER(S)		
6a NAME OF PERFORMING ORGANIZATION Southeastern Massachusetts University		6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION NRL		
6c ADDRESS (City, State, and ZIP Code) Old Westport Road; N. Dartmouth, MA 02747			7b ADDRESS (City, State, and ZIP Code) Code 6180; Washington D.C. 20375-5000		
8a NAME OF FUNDING/SPONSORING ORGANIZATION Naval Research Laboratory		8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-86-M-0247		
8c ADDRESS (City, State, and ZIP Code) Code 6180 Washington, D.C. 20375-5000			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO. 62765N	PROJECT NO.	TASK NO.
11 TITLE (Include Security Classification) Determination of Mandatory Additive Levels in U.S. Navy JP-5					
12 PERSONAL AUTHOR(S) Wechter, Margaret A., Black, Bruce H. (GEO-CENTERS, Inc.), Hardy, Dennis R. (NRL)					
13a TYPE OF REPORT Final	13b TIME COVERED FROM 3/5/86 TO 8/31/87	14 DATE OF REPORT (Year, Month, Day) 1988, Nov. 8		15 PAGE COUNT 25	
16 SUPPLEMENTARY NOTATION					
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Jet Fuels, Additives, Antioxidants, Corrosion Inhibitors, Lubricity		
FIELD	GROUP	SUB-GROUP			
19 ABSTRACT (Continue on reverse if necessary and identify by block number) A method which efficiently extracts military approved corrosion inhibitors from aircraft turbine fuels was used to determine the molecular weights of active ingredients in nine of these additives. The method was refined to use smaller extraction volumes and a comparator standard method was developed so that quantification of active ingredient (typically dilinoleic acid) could be accomplished regardless of additive source. The extraction/chromatography technique was applied successfully to the analysis of field samples for corrosion inhibitor content. Base extraction and subsequent back extraction followed by analysis by size exclusion chromatography was used to relate the polar compound content of a number of fuels to their lubricity as determined by the Ball - on - Cylinder Lubricity Evaluator. This feasibility study yielded extremely promising results. A series of experimental techniques was applied to attempt to quantify totally hindered phenol antioxidants in jet fuels. Quantification in the range of interest was not possible.					
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION U		
22a NAME OF RESPONSIBLE INDIVIDUAL D. R. Hardy			22b TELEPHONE (Include Area Code) (202) 767-3555	22c OFFICE SYMBOL	

Determination and Use of Isothermal Adsorption Constants of Jet Fuel Lubricity Enhancer Additives

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Code 6180, Naval Research Laboratory, Washington, DC 20375-5000

In order to assess the hypothesis of adsorptive loss of surface-active carboxylic acid lubricity enhancer additives from jet fuel, adsorption constants for a variety of materials were determined. These materials included 70:30 copper/nickel alloy, cold-rolled steel, zinc-plated steel, and glass. Care was taken to determine the adsorption at additive concentrations below 4 ppm (v/v) and surface area to volume ratios of 0.1–0.001 cm⁻¹. Given the worst case surface area to volume ratio for a typical fuel pipeline, approximately 0.4 cm⁻¹, a fuel with a lubricity additive concentration of 9 ppm would lose less than 3% by adsorption on pipeline walls.

At present, a lubricity enhancer additive is required in U.S. military jet fuel (JP-4 and JP-5). The required concentration range is between 9 and 22.5 ppm (QPL-25017-14, 1984). This additive was previously used to decrease corrosion to fuel-handling and -storage systems (Goodger and Vere, 1985). The additive is effective as a corrosion inhibitor due to its surface-active nature, usually imparted by an organic acid or alcoholamine. The acid forms a monolayer boundary which hinders surface attack by dissolved oxygen and free water.

This additive's current important use is to increase the lubricity of low-lubricity jet fuel (Vere, 1969; Moses et al., 1984; Petrarca, 1974; Hillman et al., 1977; Grabel, 1977; Masters et al., 1987). Qualitatively, lubricity is defined as the relative abilities of two fluids, which have the same viscosity, to resist wear and friction (Moses et al., 1984; Goodger and Vere, 1985). Lubricity is recognized as one of the most critical properties degraded by refining processes such as hydrotreatment and clay treatment. These processes effectively remove the trace polar compounds that naturally impart lubricity (Biddle et al., 1987; Masters

et al., 1987; Vere, 1969; Moses et al., 1984; Petrarca, 1974; Goodger and Vere, 1985; Grabel, 1977).

A number of problems associated with the use of low-lubricity fuels have occurred in the past 20 years. Aircraft components which derive lubrication from fuel have been experiencing increased wear and mechanical failure. Since this additive is surface active and also contains a long hydrocarbon chain structure, it was serendipitously found to impart increased lubricity to fuels that had been severely processed in order to improve thermal stability. In early 1966, the Air Force designated corrosion inhibitor as a mandatory additive in JP-4 and, hence, JP-5 as a lubricity enhancer.

More recent fuel lubricity problems have been experienced by military aircraft (Biddle et al., 1987; Moses et al., 1984; Grabel, 1977). These recent fuel lubricity related problems are believed to be a result of lubricity additive loss from fuel. It has been postulated that corrosion inhibitor, added as a fuel lubricant at the refinery, may be depleted from the fuel during storage and handling by adsorption. Once below a critical minimum, the additive would be unable to achieve its intended purpose.

In the late 1970s, a series of experiments were performed in the United Kingdom to measure the adsorption of the active ingredient in most lubricity enhancer additives

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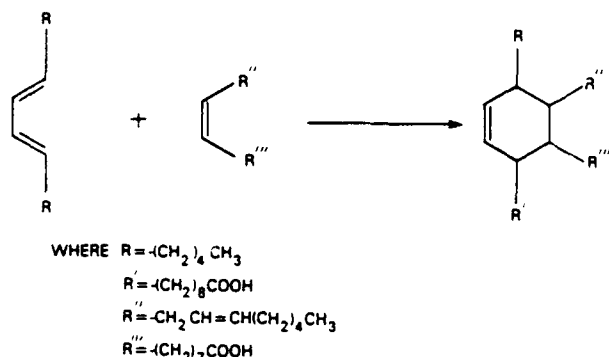


Figure 1. 1,4-Cycloaddition (Diels-Alder) reaction for the formation of dilinoleic acid.

(Dacre et al., 1977, 1979; Dacre and Wheeler, 1980; Wheeler and Dacre, 1980). This compound is an organic acid with a molecular weight of 562. It is prepared by a 1,4-cycloaddition (Diels-Alder) reaction of two linoleic acid molecules. The product is a monocyclic compound with a molecular weight twice that of linoleic acid and, hence, is given the name dilinoleic acid (DLA). It possesses two carboxylic acid groups which are believed to be the points of attachment to active surface sites. Figure 1 is an example of a typical 1,4-cycloaddition reaction for the formation of one possible isomer of DLA.

The adsorption of linoleic acid and trilinoleic acid (TLA), both of which may be present in some lubricity enhancer additives, was also investigated. TLA, which is also a product of the Diels-Alder reaction, may possess either a partially unsaturated fused dicyclic ring structure or two isolated partially unsaturated cyclohexyl rings. It has a molecular weight approximately 3 times that of linoleic acid.

Their investigation attempted to simulate the environment of high-temperature fuel pumps in aircraft. Metal disks and powder of the materials found in fuel pumps were used as adsorption surfaces. *n*-Dodecane was chosen as a model fuel for adsorption studies. The work was carried out in a high surface area to model fuel volume regime. This results in greater loss of additive per unit volume of model fuel and is not representative of actual conditions encountered.

Carbon-14-labeled linoleic acid was used to synthesize DLA and TLA. For experiments using powders, adsorption was measured as a decrease in additive concentration in *n*-dodecane by a liquid scintillation method. Adsorption of linoleic acid and its derivatives onto disks was determined directly by an end-window Geiger counter on the disks.

The results of that work showed DLA to have the highest affinity for the materials studied. This is due to the two carboxylic acid groups on the molecule which are believed to be the points of attachment. While TLA possesses three carboxylic acid groups, steric hindrance between molecules is believed to decrease surface adsorption.

More recently, others have measured the depletion of DLA from a representative fuel by using base extraction and analysis by high-resolution size exclusion chromatography (Black, 1986; Wechter, 1986; Hardy et al., 1986; Black et al., 1988). Varying masses and, hence, varying surface areas of stainless steel wool were used as an adsorption surface. The estimated surface area to volume ratio was approximately 2.5 cm^{-1} . The equilibration of DLA between fuel and metal surfaces was found to be very rapid. Adsorption was also found to be surface area de-

pendent. The use of steel wool, however, provided only a crude control of surface area, and the surface area to volume ratio was also much higher than field conditions.

This paper investigates the adsorption of DLA onto various materials where surface area is more accurately measured. The surface area to model fuel volume is closer to what would be encountered in actual field operations. The materials chosen are commonly found in field and laboratory operations and included 70:30 copper/nickel alloy, cold-rolled steel, zinc-plated steel, and glass. The adsorption experiments were carried out using a model fuel prepared in the laboratory which simulated JP-5. Polar compounds, which would interfere with analysis or actually compete with DLA for adsorption, were excluded by silica gel washing.

Experimental Section

Reagents. HPLC-grade uninhibited tetrahydrofuran (THF) and HPLC-grade methylene chloride were obtained from Fisher Scientific. The model JP-5 fuel was prepared using technical grade (99.7% purity) *n*-dodecane obtained from Phillips 66 Co. Other constituents of the model fuel were obtained from Fisher Scientific. These compounds included indan, decalin, *tert*-butylbenzene, and cyclohexylbenzene. Dilinoleic acid (DLA), 97% purity, was obtained from Emery Chemical, Division of National Distiller (trade name EMPOL 1010).

Equipment and Materials. Samples were analyzed by using a Beckman-Altex Microspherogel high-resolution, size exclusion column, Model 255-80 (50-Å pore size, 30-cm $\times$ 8.0-mm i.d.). Uninhibited THF was used as the mobile phase. The THF was periodically sparged with dry nitrogen to inhibit formation of hazardous peroxides. The injector was a Rheodyne Model 7125. A Beckman Model 100-A HPLC pump was used for solvent delivery and a Waters Model 401 differential refractometer for detection. Peak integration or height measurements were performed by a Hewlett-Packard Model 3390-A integrator. The following materials were used for adsorptive surfaces: (1) steel, 304-O steel, mild, SAE 1010 cold rolled; (2) copper/nickel alloy, 304-I cupro-nickel 70/30, MIL-C-12726D, composition 70-30; (3) zinc, 304-OZn steel, SAE 1010 cold rolled, zinc plated, QQ-Z-325. These materials were obtained from The Metaspac Co., San Antonio, TX. Each had a 280-grit surface finish and were received as small metal coupons measuring approximately 7.6 cm $\times$ 1.3 cm $\times$ 0.15 cm. An additional material studied was borosilicate glass. For this experiment, Fisher Finest microscope slides were obtained from Fisher Scientific.

Method. The model fuel was prepared in a 5-gal, epoxy-lined can. A substantial quantity of 35-60-mesh-grade silica gel was added to the model fuel prior to the addition of DLA to remove polar compounds. These compounds can interfere with the chromatographic analysis as well as compete with the additive for surface adsorption. The final composition of the model fuel was determined by gas chromatographic analysis. The results of the analysis are found in Table I.

The adsorption experiments were carried out in 1-gal, epoxy-lined steel containers with a contact surface area of approximately 900 cm^2 . Before beginning adsorption studies for the materials of interest, it was necessary to determine the effect of the epoxy surface on DLA depletion. To accomplish this, a 2500-mL volume of model fuel, to which approximately 4 ppm of DLA had been freshly added, was placed in the container. A 100-mL aliquot of model fuel was immediately removed and extracted to determine the initial DLA concentration. Earlier experiments have shown the standard error of a single deter-

Table I. Results of Gas Chromatographic Analysis of Model JP-5 Jet Fuel

component	vol %
dodecane	72.6
indan	2.7
decalin	13.2
<i>tert</i> -butylbenzene	4.6
cyclohexylbenzene	6.9
total	100.0

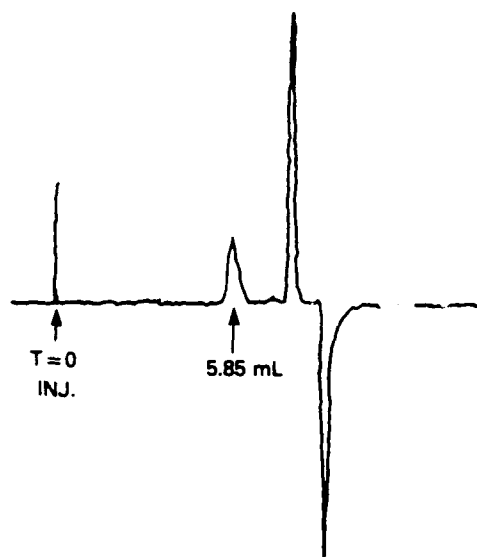


Figure 2. Representative chromatogram of 2.4 ppm dilinoleic acid extracted from model JP-5 jet fuel.

mination to be approximately 8%.

Figure 2 is a representative chromatogram of DLA extracted from the model fuel. DLA has a molecular weight of 562 and is the first component to elute. Its elution volume is approximately 5.85 mL. This peak is well resolved from lower molecular weight peaks. These lower molecular weight peaks were not extracted from the model fuel but are artifacts of the mobile phase and detector.

Additional 100-mL aliquots were also removed and analyzed at 1 h, 1 day, 1 week, and 2 weeks. No appreciable decrease in additive concentration was measured after 1 h; hence, adsorption of DLA onto the epoxy surface was neglected for the remaining experiments.

In actual field operations, a wide range of surface area to volume ratios are encountered. These values range from approximately 0.001 cm^{-1} for a 100 000-barrel fuel storage tank to 0.25 cm^{-1} for a 100-mile pipeline of approximately 6-in. diameter. In the laboratory, increasing surface area to volume ratios can be simulated by repetitive immersions of a material of interest into real or model jet fuel. Between each immersion, the material being studied is thoroughly cleaned to remove adsorbed additive.

The first material studied was 70:30 copper/nickel. Twenty strips, each measuring approximately 22.5 cm^2 , were suspended from wooden dowels by using size F, 4-ply polyester thread. The strips were thoroughly cleaned by using a modified ASTM procedure (ASTM Committee G1, 1981). The strips were first immersed in a 50% solution of concentrated HCl and water. After 5 min, the strips were removed and thoroughly rinsed with acetone and allowed to dry. The strips were subsequently immersed in a 0.2 M solution of NaOH for 5 min. After removal from the NaOH solution, the strips were thoroughly rinsed with distilled water followed by acetone and allowed to dry in a hood.

The volume of model fuel removed and analyzed for the container study was replenished to 2500 mL. A small amount of DLA was dissolved in the model fuel to readjust the concentration to approximately 3–4 ppm. A 100-mL aliquot was then removed and analyzed to determine the initial concentration. The 20 copper/nickel strips were immersed in the model fuel for 5 min. The strips were then removed from the model fuel and rinsed with acetone. They were subsequently cleaned by the same modified ASTM method described above.

A 100-mL aliquot of model fuel was removed after the 3rd, 6th, 14th, and 20th immersions for additive analysis. A linear decrease in concentration of DLA in the model fuel was observed as surface area increased.

The second material studied was zinc-plated steel. Twenty strips, each measuring approximately 22.5 cm^2 , were suspended from wooden dowels as before. These strips were cleaned by a similar method as the copper/nickel alloy. The acid rinse, however, was not used due to the reaction of concentrated HCl with zinc. The strips were rinsed thoroughly with acetone and allowed to dry. They were then immersed for 5 min in a 0.2 M solution of NaOH. After removal from the NaOH solution, the strips were thoroughly rinsed with distilled water followed by acetone and allowed to dry.

The volume of model fuel removed and analyzed for the copper/nickel alloy studies was replenished. The concentration of DLA was adjusted to approximately 4 ppm. A 100-mL aliquot was removed and analyzed to determine the initial concentration. The strips were immersed in the model fuel for 5 min. After the first immersion, a 100-mL aliquot was removed and analyzed for DLA concentration. Additional aliquots were removed and analyzed after the 7th, 14th, and 20th immersions.

For cold-rolled steel, the cleaning procedure was the same as for zinc-plated steel. Aliquots were removed for analysis before immersion of strips and after the 7th, 14th, and 20th immersions.

For borosilicate glass, the surface area for each slide was approximately 40.5 cm^2 . Twenty slides were cleaned by using the same modified ASTM method used for copper/nickel alloy. Aliquots were removed for analysis after the 3rd, 6th, and 10th immersions.

Results and Discussion

For each of the materials studied, there was a decrease in additive concentration with increasing surface area, as expected. The additive concentration in the model fuel was determined by comparison with a standard curve, where peak height was plotted against the concentration of a series of prepared standards. The concentration range of the DLA (97%) standards was between 0 and 10 ppm.

For each material studied, the concentration of depleted DLA was plotted against the corresponding surface area to volume ratio. Table II lists the R^2 correlation coefficient, slope, and intercept of linear least-squares analyses for each material. The concentrations of DLA listed in Table II were calculated from the least-squares linear fit for equations for each material. At a particular surface area to volume ratio for a given material, the concentration of DLA can be determined by the equation. The narrow range of differences in the initial concentration was neglected in the calculated relative adsorption constants listed in Table III.

Prior to immersion of a particular material in the model fuel, DLA is allowed to equilibrate with the epoxy surface of the container. After sufficient time for equilibration, approximately 5 min, a 100-mL aliquot of model fuel is removed and analyzed to determine its DLA content. This

Table II. HPLC Measurements of Dilinoleic Acid Depletion

material	slope	intercept	R^2	SA/vol	DLA concn*
70:30 Cu/Ni	-0.163	3.0	0.90	0.00	3.0
				0.61	2.9
				1.28	2.8
				2.02	2.7
cold-rolled steel	-0.118	2.6	0.89	4.72	2.2
				0.00	2.6
				1.31	2.4
				2.74	2.2
Zn-plated steel	-0.110	2.7	0.96	4.09	2.0
				0.00	2.7
				0.19	2.6
				1.37	2.5
glass	-0.088	2.9	0.51	2.86	2.3
				4.28	2.2
				0.00	2.9
				1.02	2.8
				2.12	2.7
				3.70	2.6

*Standard error = 0.08 = $\sigma/\bar{x}$.

Table III. Average and Relative Adsorption Constants for the Materials Studied

material	av K_{ad}	rel K_{ad}
cold-rolled steel	0.068 ± 0.005	2.00
70:30 Cu/Ni	0.061 ± 0.01	1.79
Zn-plated steel	0.057 ± 0.004	1.68
glass	0.034 ± 0.002	1.00

concentration is designated the initial DLA concentration, $[DLA]_{initial}$. After immersion of a particular test material in the model fuel, DLA begins to adsorb on the material's surfaces. This adsorption can be expressed as

$$[DLA]_{in} \rightarrow [DLA]_{ad} + [DLA]_{unad} \quad (1)$$

After a period of time, an equilibrium is reached between adsorbed and unadsorbed DLA in solution. This can be expressed as

$$[DLA]_{unad} = [DLA]_{ad} \quad (2)$$

The adsorption, K , can now be expressed as

$$K = [DLA]_{ad} / [DLA]_{unad} \quad (3)$$

$[DLA]_{ad}$ is not measured, but from eq 1, the mass balance, the following must be true:

$$[DLA]_{ad} = [DLA]_{in} - [DLA]_{unad} \quad (4)$$

Therefore, the adsorption, K , can be written as

$$K = \frac{[DLA]_{in} - [DLA]_{unad}}{[DLA]_{unad}} \quad (5)$$

The adsorption constant, K_{ad} , can be calculated by dividing K by the surface area to volume ratio at which K was calculated. K_{ad} can be expressed as

$$K_{ad} = \frac{([DLA]_{in} - [DLA]_{unad}) / [DLA]_{unad}}{SA/vol} \quad (6)$$

There were differences in the normalized K_{ad} for each of the four materials studied. This indicates that K_{ad} is material dependent. Relative adsorption constants for each of the materials are listed in Table III. It can be seen that the metal strips are considerably more effective in depleting DLA from solution than glass. The measured decrease in DLA concentration on glass surfaces is within the standard error for a single determination. This means that there is not a statistically significant loss. This is important, because glass is used extensively for laboratory analyses of DLA. For all of the metal surfaces, the loss

is statistically significant but quite low at the surface area to volume ratios investigated.

Application

The adsorption constants determined can be applied to current field problems and questions regarding quality assurance since care was taken to ensure a realistic surface area to volume ratio. Recently, a lubricity-related problem occurred at a U.S. military base. A low-lubricity fuel had had the minimum allowable concentration of lubricity enhancer, 9 ppm, added at the refinery. Since the active ingredient comprises approximately 50% of most commercial lubricity enhancer additives (Black et al., 1988), the actual initial concentration was 4.5 ppm. The fuel was pumped through a steel pipeline approximately 100 miles long before reaching the base. Lubricity-enhancer-free products also pass through this pipeline and, hence, may desorb previously adsorbed active ingredient from pipeline walls.

The calculated internal surface area to volume of jet fuel ratio of the pipeline was 0.39 cm^{-1} . The product of the average K_{ad} in Table III for steel and the surface area to volume ratio of the system yield a value of 0.026. This means that less than 3% of the active ingredient initially present could be lost from the fuel due to adsorption. This loss would be further decreased by adsorption of competing surface active material present in other fuel products which also pass through the line. These surface active materials may adsorb on pipeline surfaces and hence lower the loss by adsorption of the active ingredient in lubricity enhancer additives.

The calculated loss of active ingredient from the fuel is within the range of the standard error for a single determination. The loss is statistically insignificant and, therefore, the lubricity related problem is not a result of adsorptive loss of active ingredient. The fact that there was a lubricity-related problem in this particular case may be due to a number of factors. First, the lubricity enhancer additives are accepted and used, not for their ability to enhance lubricity but because they inhibit corrosion. Second, not all additives are based on dimers of linoleic acid or mixtures of carboxylic acids. Hence, not all additives are necessarily surface-active boundary lubricants. Third, and probably most important, there is no currently accepted test for measuring the lubricity of military jet fuel.

Conclusions

Adsorption constants, K_{ad} , were determined for a representative lubricity enhancer additive on four different materials. The K_{ad} values are valid over a wide range of useful surface area to volume ratios encountered in fuel-handling operations. The K_{ad} was quantitatively found to be material dependent. Adsorption was greater on metal surfaces and significantly lower on glass.

Loss of this typical active ingredient by adsorption was found to be insignificant within the allowable concentration range, even in the worst case example of a pipeline transfer (surface area to volume ratio approximately 0.4 cm^{-1}). Adsorptive loss in large fuel storage tanks, where the surface area to volume ratio is as low as 0.001 cm^{-1} , is also insignificant at all concentrations within the specified limits.

Acknowledgment

Parts of this work were funded by the Naval Air Propulsion Center and the U.S. Navy Energy Research and Development Office.

Registry No. DLA, 6144-28-1; SAE 1010, 12725-33-6; cupronickel 70-30, 11114-43-5; zinc, 7440-66-6.

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Received for review June 15, 1988

Accepted January 23, 1989

Preprints, Fuel Chemistry Division

American Chemical Society

Vol. 34, No. 2

THE LUBRICITY PROPERTIES OF JET FUEL
AS A FUNCTION OF COMPOSITION
PART 1: METHOD DEVELOPMENT

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ABSTRACT

In recent years, the quality of petroleum feedstocks used by refineries has decreased. This has necessitated the use of severe refinery processes in order to produce jet fuels of high thermal stability and cleanliness. Unfortunately, these processes remove naturally occurring polar material which impart a fuel's inherent lubricity. As a result, the lubricity properties of jet fuel products have decreased. This critical fuel property is essential for sustained high performance of fuel lubricated engine components. This paper describes a method that correlates naturally occurring and added carboxylic acids with fuel lubricity as measured by the Ball-on-Cylinder Lubricity Evaluator (BOCLE).

INTRODUCTION

In recent years, the quality of petroleum feedstocks has decreased. Thus, it has become necessary to employ severe refining processes in order to produce jet fuels of high thermal stability and cleanliness. Processes such as hydrotreating, hydrocracking, and clay filtering effectively remove the compounds which decrease thermal stability and hinder water removal by coalescence.¹⁻⁴ Unfortunately, some of these compounds are believed to impart a fuel's natural lubricity. Removal of these compounds, therefore, leads to a decrease in the operational lifetime of fuel lubricated engine components in some military and commercial aircraft. This in turn causes increased maintenance costs and down-time of aircraft. For the commercial airlines, this can cause a loss of revenue while an aircraft is grounded. For the military, this can lead to a decreased state of readiness.

Lubricity is a qualitative description of the relative abilities of two fluids, with the same viscosity, to limit wear and friction between moving metal surfaces.^{2,4} It may be the most critical fuel property degraded by refinery processes.^{5,6} There have been instances where the use of low lubricity fuel has caused loss of aircraft and human life.⁷

Considerable effort has been made in the development of a mechanical method which can be performed in the laboratory which will measure fuel lubricity. The current and most widely accepted method is the Ball-on-Cylinder Lubricity Evaluator (BOCLE). The lubricity of a fuel is determined by the measurement of a wear scar on a ball which has been in contact with a rotating cylinder partially immersed in a fuel sample. The reported value is the average of the major and the minor axes of the oval wear scar in millimeters. Typical values for jet fuels are between 0.45

and 0.95 mm.

This paper describes a method for estimating the lubricity properties of jet fuel by compositional analysis. The information developed by this technique is compared to measurements of the same fuels on the BOCLE. The method is based on a previously developed method for determining the concentration of corrosion inhibitor as a lubricity enhancer additive in fuel.⁸⁻¹⁰ The analysis procedure involves a base extraction of a fuel sample with subsequent analysis by high resolution size exclusion chromatography. The amount of naturally occurring organic acids extracted from the fuels correlate well with their respective BOCLE measurements.

EXPERIMENTAL

Reagents- HPLC grade uninhibited tetrahydrofuran (THF) and HPLC grade methylene chloride were obtained from Fisher Scientific. Six test fuels and a hydrocarbon standard used for BOCLE repeatability and reproducibility studies were obtained from the Naval Air Propulsion Center, Trenton, NJ. These samples included: two JP-4 fuels, one of which had been clay filtered; two Jet A fuels, one of which had been clay filtered; a JP-5 fuel; a JP-7 fuel; and ISOPAR M, an isoparaffinic fluid used as a low lubricity standard. A model JP-5 fuel was prepared using technical grade (99.7% purity) n-dodecane obtained from Phillips 66 Co. HPLC grade toluene was obtained from Burdick and Jackson Laboratories Inc. Other constituents of the model fuel were obtained from Fisher Scientific. These compounds included indan, decalin, t-butylbenzene, and cyclohexylbenzene. To investigate the effect of organic acid type on lubricity enhancement, the following acids were used: octanoic, decanoic, lauric, palmitic, stearic, cyclohexane carboxylic acid, and dodecylbenzene sulfonic acid.

Equipment and Materials- Samples were analyzed using a Beckman-Altex Microspherogel high resolution, size exclusion column, Model 255-80 (50A pore size, 30cm x 8.0mm I.D.). Uninhibited THF was used as the mobile phase. The THF was periodically sparged with dry nitrogen to inhibit formation of hazardous peroxides. The injector was a Rheodyne Model 7125. A Beckman Model 100-A HPLC pump was used for solvent delivery with a Waters Model 401 differential refractometer for detection. Peaks were identified using a Varian Model 9176 strip chart recorder. A Fisher Accumet pH Meter Model 610A and a Fisher Standard Combination Electrode Catalog Number 13-639-90 were used for pH adjustments. BOCLE measurements were performed at twenty different laboratories worldwide. The BOCLE used was an InterAv Model BOC 100. The cylinders used were Timken Rings Part Number F25061 obtained from the Falex Corp., Aurora, IL. The test balls used were 12.7mm diameter, SKF Swedish Steel, Part Number 310995A obtained from SKF Industries, Allentown, PA.

Method- Fuel samples were analyzed for organic acid concentration by a previously developed method.⁸ For each sample, 100 ml were extracted with 100 ml of 0.2M aqueous sodium hydroxide. The aqueous phase was drained into a clean beaker and acidified dropwise with concentrated hydrochloric acid. The pH of the aqueous solution was lowered to 2.0 ± 0.03 . The acidified aqueous phase was back-extracted with 100 ml HPLC

grade methylene chloride. The methylene chloride was drained into a clean beaker and allowed to evaporate. After evaporation, the residue was dissolved in 2.0 ml HPLC grade THF and transferred to a glass vial with a teflon-lined cap.

BOCLE measurements on the seven fuel samples were performed in duplicate at twenty laboratories in the United States and Europe. The BOCLE method used was according to appendix Y of the Aviation Fuel Lubricity Evaluation published by the Coordinating Research Council, Inc.¹¹ The lubricity of each sample was measured using both a 500 and a 1000 gram load for the ball on cylinder. The compositional analysis data is correlated with the 500 gram load BOCLE data.

To determine the effect of sulfonic acid on lubricity enhancement, six model fuel samples were prepared for BOCLE analysis. These samples are listed with their relative wear scar diameter measurements in Table 1.

RESULTS

Figures 1 and 2 are size exclusion chromatograms for the seven fuel samples. Figure 1 represents those fuels which were determined to have high lubricity. Figure 2 represents those fuels which were found to have low lubricity. The region of interest on the chromatogram is the area where retention volume is between 5.25 ml and 7.5 ml. The peaks which elute after 7.5 ml are artifacts and were not extracted from the fuel. In Figures 1a and 1b, the peaks with retention volumes less than 6.25 ml correspond to the presence of the lubricity enhancer additive. The peak which elutes at approximately 5.85 ml represents the major active ingredient in most commercial additives, dilinoleic acid (DLA). It has a molecular weight of 562 daltons. This material is prepared by a 1,4-cycloaddition (Diels-Alder) reaction of two linoleic acid molecules. The product is a monocyclic compound with a molecular weight twice that of linoleic acid. It possesses two carboxylic acid groups which are believed to be the points of adsorption to active surface sites.

The small peak which elutes at approximately 5.4 ml corresponds to the presence of trilinoleic acid (TLA). TLA, which is also a product of the Diels-Alder reaction, may possess either a partially unsaturated fused dicyclic ring structure or two isolated partially saturated cyclohexyl rings. It has a molecular weight approximately three times that of linoleic acid (840 daltons).

The fuels whose chromatograms are depicted in Figures 1c and, Figures 2a through 2d, do not possess the lubricity enhancer additive. Their lubricity properties are, for the most part, solely related to the presence of naturally occurring carboxylic acids. The correlation of acidic materials present which elute at 7.25 ml is made with the BOCLE measurements. This retention volume was arbitrarily chosen because it was representative of naturally occurring organic acids present in each of the samples.

Table 2 lists the BOCLE results of the seven fuel samples. Statistically, it can be seen that there are two distinct groups. Three

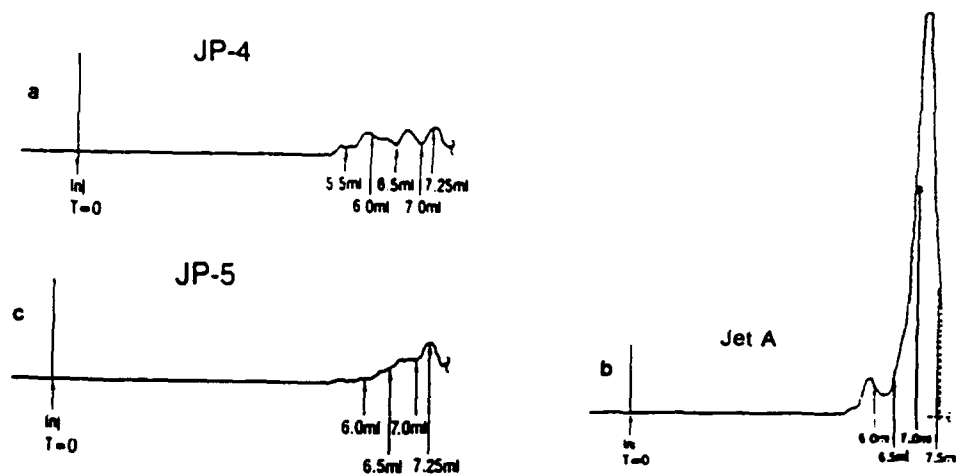


FIGURE 1: HPLC Chromatograms of High Lubricity Fuels as Determined by the Ball-on-Cylinder Lubricity Evaluator.

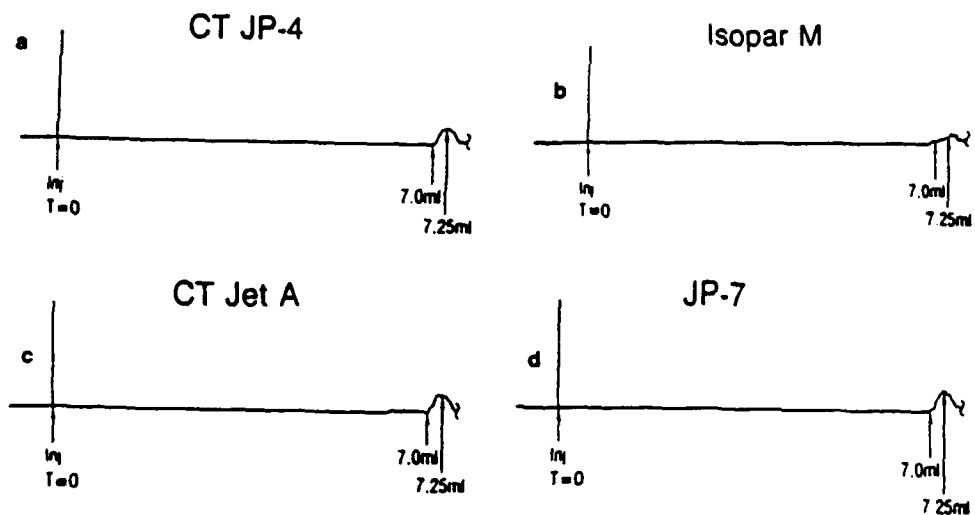


FIGURE 2: HPLC Chromatograms of Low Lubricity Fuels as Determined by the Ball-on-Cylinder Lubricity Evaluator.

fuels, JP-4, Jet A, and JP-5, were found to have high lubricity, and the four others, clay filtered JP-4, ISOPAR M, clay filtered Jet A, and JP-7, were found to have low lubricity. The results within each set are statistically the same. The average relative wear scar diameter for the high lubricity fuels is $0.64 \text{ mm} \pm 0.05 \text{ mm}$ (7.8%). The average relative wear scar diameter for the low lubricity fuels is $0.94 \pm 0.10 \text{ mm}$ (10.6%). This implies that the precision of the BOCLE is better for high lubricity rather than low lubricity fuels.

Table 3 compares the the peak height at 7.25 ml with the BOCLE measurements for each of the fuels. Both JP-4 and Jet A possess the lubricity enhancer additive. It is, therefore, not surprising that these were high lubricity fuels. It can be seen in Figure 1b and Table 3 that the Jet A sample had a significantly higher concentration of the naturally occurring carboxylic acids and lubricity enhancer additive than either the JP-4 or JP-5. The lubricity of the Jet A, however, was not significantly higher than the other high lubricity fuels. Previous work has shown that there is a minimum possible wear scar diameter. The addition of more lubricity enhancer additive or the presence of a greater amount of naturally occurring lubricity enhancing species will not decrease the wear scar diameter.¹¹ In each of the high lubricity fuels, the maximum lubricity has been achieved. Thus, the lubricity measurements for these fuels are the same.

There may be some question as to why the JP-5 sample had significantly higher lubricity than the four low lubricity fuels. In Table 3, it can be seen that the JP-5 sample has only twice the concentration of acidic species eluting at 7.25 ml than the low lubricity fuels, yet the lubricity properties are significantly better. By comparison of Figure 1c with Figures 2a through 2d, it can be seen that each of the fuels in Figure 2 possess a single peak which elutes at 7.25 ml. The JP-5 sample depicted in Figure 1c has, not only this peak, but higher molecular weight acidic species which elute between 6.25 and 7.0 ml. We propose that the presence of these naturally occurring components in addition to two to three times the concentration of material eluting at 7.25 ml, yields the higher lubricity characteristics.

Dodecylbenzene sulfonic acid (DBSA) was found to have no effect on lubricity at concentrations that are normally found in jet fuel. Table 1 shows that at DBSA concentrations up to 1.0 ppm, DBSA did not decrease wear scar diameter measurements for the model fuel. This is in agreement with work performed by Lazarenko, et al. They found that corrosion inhibitors, based on sulfonic acids did not increase jet fuel lubricity.¹⁴ Model fuel doped with 96.0 ppm of a carboxylic acid mixture had, however, significantly lower wear scar diameter measurements, i.e., lubricity had increased as expected.

DISCUSSION AND CONCLUSIONS

The effect of long chain carboxylic acids on boundary lubrication is well established. The presence of naturally occurring long chain carboxylic acids in jet fuel is believed to play a major role in lubricity enhancement. Any refinery procedure which removes these acids will have a

detrimental effect on the lubricity of jet fuel products. Thus, processes such as hydrotreatment, hydrocracking, and clay filtration will decrease jet fuel lubricity.

It is well known that clay filtration adversely affects jet fuel lubricity. It has long been believed that this is a result of the removal of naturally occurring polar materials in fuel which impart lubricity.^{2,3,7,12,13} The results of the BOCLE measurements confirm that lubricity does indeed decrease after clay filtration. The compositional changes can be seen by comparison of Figures 1b and 2c which represent Jet A fuel before and after clay filtration. The concentration of lubricity imparting organic acids has been drastically reduced. The lubricity enhancer additive has also been completely removed. The corresponding result is an extreme reduction in fuel lubricity. Comparison between clay filtered and non-clay filtered JP-4 cannot be made since these were two different fuels. It can be seen, however, that the mandatory corrosion inhibitor/lubricity enhancer additive is not present in the clay filtered sample.

This work has shown that a direct relationship between the presence of naturally occurring carboxylic acids and BOCLE measurements exists. Previous work by has also shown this relationship.⁸ They analyzed a series of additive-free JP-5 and Jet A samples for naturally organic acids and correlated their presence with the fuels' respective BOCLE measurements. Additional work, which will be published in a subsequent paper, has shown the relationship in Naval JP-5 field samples as well as Air Force JP-4 field samples.

Sulfonic acids, however, were not found to influence BOCLE measurements and, therefore, do not enhance lubricity. Other polar material in jet fuel may contribute to lubricity enhancement. The carboxylic acids, which are well known surface active and lubricity enhancing species, are likely to be the major contributor.

In the future, it appears as though the BOCLE will be accepted as the standard method for measuring lubricity in the laboratory. The compositional analysis method can be used as a supplementary method to the BOCLE for verification of lubricity measurements. There are, however, a few advantages to the compositional analysis method over the BOCLE. First, the BOCLE is operator sensitive. Second, the instrument is sensitive to contamination of the fuels and test materials. Third, the presence of dissolved oxygen and water in a sample will influence the wear scar generated. Fourth, the BOCLE is very sensitive to relative humidity.

The compositional analysis method is not sensitive to relative humidity or dissolved oxygen and water in a fuel sample. Trace contamination between samples does not occur as readily with the compositional analysis method and its influence is significantly less. The compositional analysis method is also able to distinguish between three types of high lubricity fuel which the BOCLE cannot. These include: a high lubricity fuel without corrosion inhibitor, a high lubricity fuel with corrosion inhibitor, and a low lubricity fuel with corrosion inhibitor.

Although the lubricity enhancer additive is mandatory in U.S. military

jet fuel, a number of Naval JP-5 fuel samples were indentified where the lubricity additive may not have been necessary. Addition of the lubricity enhancer additive to these fuels may have been an unnecessary expense. In addition, the lubricity enhancer additive has been shown to adversely effect the removal of water from fuel by coalescence. The use of the additive, therefore, may actually be detrimental rather than beneficial in some fuels.

Finally, for those fuels which have had the lubricity enhancer additive blended in at the refinery, the compositional analysis method can be used as a quality assurance and quality control procedure. Both the refiner and user can analyze a fuel for levels of both naturally occurring and added lubricity imparting organic acids.

TABLE 1

<u>SAMPLE</u>	<u>Conc. DBSA (ppm)</u>	<u>Conc. R-COOH (ppm)</u>	<u>Normalized WSD</u>
1	0.0	0.0	0.99
2	0.5	0.0	0.98
3	1.0	0.0	1.00
4	0.0	96.0	0.49
5	0.5	96.0	0.51
6	1.0	96.0	0.53

The Effect of Dodecylbenzene Sulfonic Acid on Lubricity as Measured by the BOCLE in the Presence and Absence of Carboxylic Acids.

TABLE 2

<u>SAMPLE</u>	<u>Normalized WSD</u>	<u>± 2σ</u>
JP-4	0.63	0.05
JET A	0.64	0.05
JP-5	0.65	0.05
CT JP-4	0.92	0.11
ISOPAR M	0.93	0.09
CT JET A	0.93	0.09
JP-7	1.00	0.11

The Lubricity of Fuel Samples as Measured by the Ball-on-Cylinder Lubricity Evaluator.

TABLE 3

<u>SAMPLE</u>	<u>Normalized WSD</u>	<u>Pk Hgt @ 7.25 mL</u>
JP-4	0.63	10.0 mm
JET A*	0.64	>165.0 mm
JP-5	0.65	** 15.5 mm
CT JP-4	0.92	6.5 mm
ISOPAR M	0.93	4.5 mm
CT JET A	0.93	6.0 mm
JP-7	1.00	7.5 mm

*Contained a lubricity enhancer additive

**Higher molecular weight acidic species were also present

The Comparison of Organic Acid Composition at 7.25 mL Retention Volume with Lubricity as Measured by the Ball-on-Cylinder Lubricity Evaluator.

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Preprints, Fuel Chemistry Division

American Chemical Society

Vol. 34, No. 2

THE LUBRICITY PROPERTIES OF JET FUEL
AS A FUNCTION OF COMPOSITION
PART 2: APPLICATION OF ANALYSIS METHOD

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ABSTRACT

In recent years, the quality of petroleum feedstocks used by refineries has decreased. This has necessitated the use of severe refinery processes in order to produce jet fuels of high thermal stability and cleanliness. These processes, however, tend to decrease the lubricity properties of jet fuel products. As a result, fuel lubricated engine components have been experiencing greater wear and mechanical failure. To alleviate this problem, a highly effective lubricity enhancer additive, based on mixtures of carboxylic acids, is mandatory in all U.S. military jet fuel. The additive, however, has been shown to interfere with the removal of water from jet fuel by coalescence. In addition, some fuels possess high levels of naturally occurring, lubricity enhancing carboxylic acids and, therefore, do not need the additive. This paper describes the application of an analysis method that distinguishes between fuels with and without the additive, and fuels that possess naturally occurring, lubricity enhancing carboxylic acids.

INTRODUCTION

In part 1 of this work, it was shown that a direct correlation exists between the presence of naturally occurring carboxylic acids and Ball-on-Cylinder Lubricity Evaluator (BOCLE) measurements.¹ This correlation was applied to a series of fuel samples that were used to determine the repeatability and reproducibility of the BOCLE instrument. Extensive BOCLE data had been generated to which the compositional analysis results could be compared. The compositional analysis method was found to be able to distinguish between naturally occurring and added lubricity enhancing carboxylic acids.

This paper applies the compositional analysis method to a series of Navy JP-5 jet fuel samples obtained from a worldwide survey of storage depots. BOCLE measurements were performed at the Naval Air Propulsion Center (NAPC), Trenton, NJ. As in the previous work, the presence of carboxylic acids in a fuel sample increased its inherent lubricity. The compositional analysis method also identified fuels which were deficient in the mandatory lubricity enhancer additive.

EXPERIMENTAL

Reagents- HPLC grade uninhibited tetrahydrofuran (THF) and HPLC grade methylene chloride were obtained from Fisher Scientific. Seven JP-5 fuel

samples, from the Navy's Second Worldwide Fuel Survey, were obtained from the Naval Air Propulsion Center.

Equipment and Materials- Samples were analyzed using a Beckman-Altex Microspherogel high resolution, size exclusion column, Model 255-80 (50A pore size, 30cm x 8.0mm I.D.). Uninhibited THF was used as the mobile phase. The THF was periodically sparged with dry nitrogen to inhibit formation of hazardous peroxides. The injector was a Rheodyne Model 7125. A Beckman Model 100-A HPLC pump was used for solvent delivery with a Waters Model 401 differential refractometer for detection. Peaks were identified using a Varian Model 9176 strip chart recorder. A Fisher Accumet pH meter Model 610A and a Fisher standard combination electrode Catalog Number 13-639-90 were used for pH adjustments. An Interav Model BOC 100 Ball-on-Cylinder Lubricity Evaluator was used for lubricity measurements. The cylinders were 100% spheroidized annealed bar stock, consumable vacuum melted AMS 6444 steel obtained from Jayna Enterprises, Inc., Vandalia, OH. The balls used were 12.7mm diameter, SKF Swedish Steel, Part Number 310995A obtained from SKF Industries, Allentown, PA.

Method- Fuel samples were analyzed for carboxylic acid concentration by a previously developed method.² For each sample, 100 ml were extracted with 100 ml of 0.2M aqueous sodium hydroxide. The aqueous phase was drained into a clean beaker and acidified dropwise with concentrated hydrochloric acid. The pH of the aqueous phase was lowered to $\text{pH } 2.0 \pm 0.03$. The acidified aqueous phase was back-extracted with 100 ml HPLC grade methylene chloride. The methylene chloride was drained into a clean beaker and allowed to evaporate. After evaporation, the residue remaining was dissolved in 2.0 ml HPLC grade THF and transferred to a glass vial with a teflon-lined cap.

BOCLE measurements were performed in triplicate on each of the fuel samples. The method used was according to appendix Q of the Aviation Fuel Lubricity Evaluation published by the Coordinating Research Council, Inc.³ The sum of the values obtained for each sample was averaged and the relative wear scar diameter measurements are reported in Table 1.

RESULTS AND DISCUSSION

As in previous work, the presence of carboxylic acids, both naturally occurring and added, correlates well with BOCLE measurements. The relative average wear scar diameter for each sample is listed in Table 1. The cylinders used for this work were somewhat softer than the Timken rings previously used in Part 1 of this work. As a result, the actual wear scar diameter measurements were somewhat lower with a narrower range.

It can be seen in Table 1 that five of the seven fuels analyzed possessed the lubricity enhancer additive. Four of these fuels had both the major constituent, dilinoleic acid (DLA), and a minor component present in some lubricity enhancer additives, trilinoleic acid (TLA). Two of the fuels analyzed, however, did not possess any appreciable amount of the mandatory lubricity enhancer additive.

In Figures 1 through 5, the major lubricity enhancer additive

component, DLA, elutes at approximately 5.85 ml. The DLA component has a molecular weight of about 560 daltons. This material is prepared by a 1,4-cycloaddition (Diels-Alder) reaction of two linoleic acid molecules. The product is a monocyclic compound with a molecular weight twice that of linoleic acid. It possesses two carboxylic acid moieties which are believed to be the points of attachment to active surface sites.

In Figures 1 through 4, the peak corresponding to the TLA component is also present. This component elutes at approximately 5.4 ml. The TLA component, which is also a product of the Diels-Alder reaction, has a molecular weight of approximately 840 daltons. It may possess either a partially unsaturated fused dicyclic ring structure or two isolated partially saturated cyclohexyl rings.

As expected, the fuels that possess the lubricity enhancer additive were found to have the highest lubricity. Those fuels that did not possess the lubricity enhancer additive, and were also deficient in naturally occurring carboxylic acids, were found to have the lowest lubricity. From what is known about carboxylic acids with respect to lubricity enhancement, continued use of these fuels could lead to lubricity related problems.

Table 2 lists the peak heights for the added and naturally occurring carboxylic acids extracted from the fuel samples. Fuel samples 1 through 3 each possessed similar amounts of the lubricity enhancer additive. Fuel sample 4 had slightly less than the first three fuel samples, while fuel 5 was devoid of the TLA component and had significantly less of the DLA component. Two sets of data for the naturally occurring carboxylic acids are listed. In previous work, it was found that some fuels possess two distinct molecular weight ranges of naturally occurring carboxylic acids.^{1,2} These two ranges are designated regions 3 and 4. These components have retention volumes of approximately 6.5 and 7.0ml respectively and can be clearly seen in Figure 3.

High resolution size exclusion chromatography separates components on the basis of molecular shape and size and, therefore, to an extent, molecular weight. In general, one would expect a normal distribution of straight chain alkanolic acids which parallels the distribution of normal alkanes present in a fuel. The presence of two separate peaks for the naturally occurring carboxylic acids indicates the presence of two distinct classes of constituents. Region 3 corresponds to the straight chain alkanolic acids, while region 4 corresponds to mono- and polycyclic carboxylic acids. The maxima for regions 3 and 4 correspond to the molecular weight of tetradecanoic acid (C_{14}), and octanoic acid (C_8) respectively. The condensed size of a cyclic compound, as opposed to a straight chain compound, yields a calculated molecular weight lower than its actual molecular weight. For this reason, region 4 is most likely comprised of not only monocyclic carboxylic acids, but polycyclic acids as well.

Maxima for regions 3 and 4 are not as well defined in other fuels examined. For these fuels, the height was measured at a retention volume that corresponds to the maxima in Figure 3. In Figures 1, 2, and 5, the concentration of carboxylic acids present in region 3 increased gradually as the molecular weight decreased. In each case, there is a very rapid

increase in carboxylic acid concentration in the region 4 molecular weight range. Similar results were found in earlier work.^{1,2}

In each fuel previously examined, there was some minimum amount of carboxylic acids present in region 4. Not all fuels, however, possessed the carboxylic acids which correspond to region 3. Some had very low concentrations, some had approximately equal concentrations. These differences may be a result of crude source, refinery operations, or storage conditions.

CONCLUSIONS

The compositional analysis method has been applied to a series of field samples to determine the presence of naturally occurring and added carboxylic acids are known to enhance jet fuel lubricity. The concentration present in a given fuel sample correlates well with its inherent lubricity as measured by the BOCLE.

A number of molecular weight ranges of carboxylic acids are present in most jet fuels. Two of these regions correspond to the presence of an added lubricity enhancer, and two or more correspond to naturally occurring lubricity enhancing carboxylic acids. The relative effectiveness of each region has not yet been determined. It is believed, however, that the dimer of linoleic acid is more effective than the trimer. This is a result of steric hindrance between trimer molecules when attached to surfaces.⁴⁻⁶

The relative effectiveness of the naturally occurring carboxylic acids is believed to increase as chain length increases. Daniel found that, in general, the ease of adsorption increases with increasing chain length. Boundary lubrication also increases as chain length increases.^{8,9} The lubricity properties of jet fuel, therefore, may increase as the presence of longer chain carboxylic acids increases. At some point, however, there is probably a limit to lubricity enhancement by increasing chain length. The relative effectiveness of region 3 over region 4, therefore, may be substantially different due to the differences in structure.

There may be some question as to why the mandatory lubricity enhancer additive is absent from two of the fuels examined. There are possible explanations for this. First, the lubricity enhancer additive was originally added to the fuel to inhibit corrosion to fuel handling and storage systems which resulted from dissolved oxygen and free-water present in fuel. The carboxylic acid based corrosion inhibitors were serendipitously found to enhance the lubricity properties of low lubricity fuels.¹⁰⁻¹³ As lubricity related problems became more prevalent, the primary purpose for the corrosion inhibitor was lubricity enhancement. Unfortunately, the military specification for jet fuel was not modified to include lubricity properities. Second, the additives are accepted and used, not for their ability to enhance lubricity, but to inhibit corrosion. Some of these additive are based on acylated glycols and acylated alkanolamines. the compositional analysis method described in this paper is not suitable for analysis of these materials. It should be noted that

these materials have been shown to be relatively ineffective lubricity enhancers. Third, the additive was not added at the refinery as it should have been. Additive loss due to adsorption in fuel handling has been found to be insignificant. Previous work has shown that as little as 3% is lost due to adsorption on the surfaces of a 100 mile pipeline.¹⁴

The compositional analysis method can be used as a supplement to the BOCLE. The BOCLE can determine if a fuel has sufficient lubricity characteristics. The compositional analysis method can determine if the lubricity is a result of naturally occurring or added carboxylic acids or both.

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TABLE 1

<u>SAMPLE</u>	<u>Relative WSD</u>	<u>TLA Present</u>	<u>DLA Present</u>
1. Roosevelt Roads, P.R.	0.67	YES	YES
2. Guantanamo, Cuba	0.70	YES	YES
3. Diego Garcia	0.71	YES	YES
4. Iorizaki, Japan	0.77	YES	YES
5. Gatun, Panama	0.79	NO	YES
6. Cartagena, Spain	0.86	NO	NO
7. Azores	1.00	NO	NO

The Relative Lubricity of Fuel Samples as Measured by the Ball-on-Cylinder Lubricity Evaluator.

TABLE 2

<u>SAMPLE</u>	<u>TLA Pk Hgt</u>	<u>DLA Pk Hgt</u>	<u>Reg. 3 Pk Hgt</u>	<u>Reg. 4 Pk Hgt</u>
1	4.0	15.5	14.5	126.0
2	4.0	15.0	11.0	25.0
3	4.0	16.0	20.0	22.0
4	1.5	11.0	4.0	3.5
5	0.0	7.5	12.0	74.0
6	0.0	0.0	5.0	8.5
7	0.0	0.0	7.5	6.5

The Results of the Compositional Analysis of Fuel Samples for Natural and Added Carboxylic Acids.

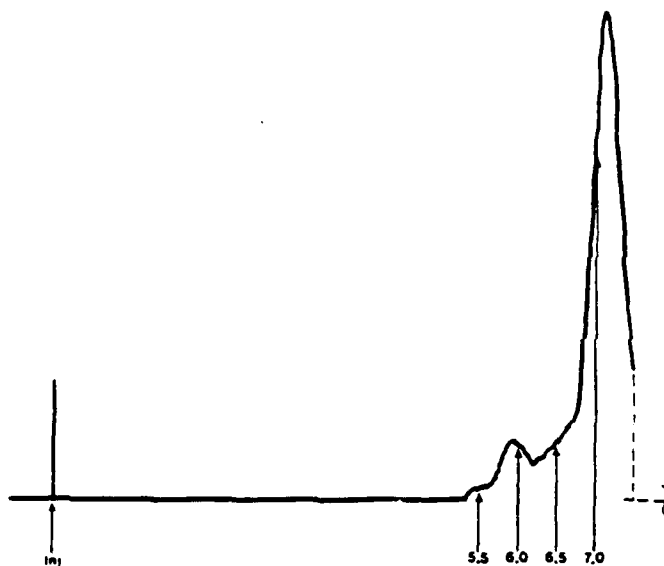


FIGURE 1: EPLC Chromatogram of Base Extracted JP-5 Jet Fuel from Roosevelt Roads, Puerto Rico.



FIGURE 2: HPLC Chromatogram of Base Extracted JP-5 Jet Fuel from Guantanamo, Cuba.



FIGURE 3: HPLC Chromatogram of Base Extracted JP-5 Jet Fuel from Diego Garcia.



FIGURE 4: HPLC Chromatogram of Base Extracted JP-5 Jet Fuel from Iorizaki, Japan.

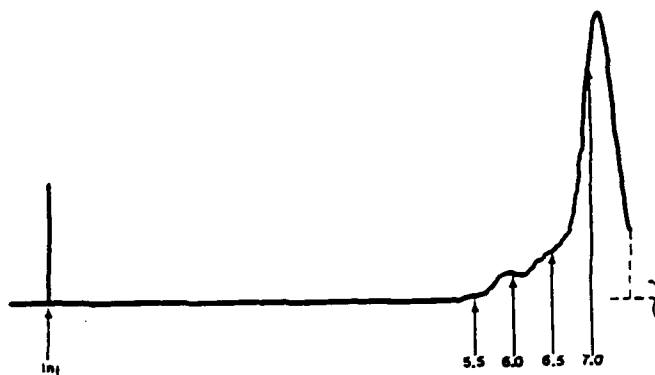


FIGURE 5: HPLC Chromatogram of Base Extracted JP-5 Jet Fuel from Gatun, Panama.



FIGURE 6: HPLC Chromatogram of Base Extracted JP-5 Jet Fuel From Cartagena, Spain.



FIGURE 7: HPLC Chromatogram of Base Extracted JP-5 Jet Fuel from the Azores.

Preprints, Fuel Chemistry Division

American Chemical Society

Vol. 35, No. 2

THE LUBRICITY PROPERTIES OF JET FUEL
AS MEASURED BY THE BALL-ON-CYLINDER LUBRICITY EVALUATOR

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KEYWORDS: Lubricity, Jet Fuel, BOCLE

ABSTRACT

In recent years the quality of petroleum feedstocks used by refineries has decreased. This has necessitated the use of severe refinery processes in order to produce jet fuels of high thermal stability and cleanliness. Unfortunately these processes remove the compounds that are responsible for a fuel's inherent lubricity. As a result, fuel lubricated engine components are experiencing greater wear and mechanical failure. The Ball-on-Cylinder Lubricity Evaluator (BOCLE) was developed to predict a fuel's tendency to cause lubricity related problems. This paper discusses the influence of trace polar species on lubricity, the use of additives to increase lubricity, changes in a fuel's lubricity during storage, and inadequacies of the BOCLE. Finally, a suggested long term solution to lubricity problems by hardware modifications will be discussed.

INTRODUCTION

The incidence of lubricity related problems in commercial and military jet aircraft has increased over the past twenty years. This is a result of the need for more severe refinery processes to remove trace fuel species that adversely affect thermal stability and water removal by coalescence.¹⁻⁴ These processes also remove trace polar species that are responsible for a fuel's inherent lubricity properties.

Lubricity is a qualitative description of the relative abilities of two fluids, with the same viscosity, to limit wear and friction between moving metal surfaces.^{2,4} It may be the most critical fuel property degraded by refinery processes.^{5,6} The continued use of low lubricity fuel can lead to a decrease in the operational lifetime of fuel lubricated engine components. This leads to increased maintenance costs and down-time of aircraft. Furthermore, the use of low lubricity fuel has been implicated in the loss of certain military aircraft.

In the late 1960s, it was serendipitously found that a pipeline corrosion inhibitor had a significant effect on lubricity enhancement. The additive's original intended purpose was to decrease corrosion to fuel handling systems and transfer lines.⁴ The additive is effective as a corrosion inhibitor due to its surface-active nature. The active

ingredient in most corrosion inhibitors is a dimeric organic acid, usually dilinoleic acid (DLA). It is the surface-active nature of the dimeric acid that causes the corrosion inhibitor to be an effective lubricity enhancer.

The use of a corrosion inhibitor as a lubricity enhancer is now required in all military JP-4 and JP-5 jet fuel.⁷ Unfortunately the additive can hinder water removal by coalescence. In other cases a fuel may have adequate lubricity initially and would preclude the use of the additive. Currently there is no lubricity specification for either commercial or military jet fuel. This has been due primarily to the lack of a test method; hence, the mandatory addition of the additive to assure adequate lubricity.

During the past fifteen years considerable effort has been made to develop a mechanical method to measure fuel lubricity. The current and most widely accepted method is the Ball-on-Cylinder Lubricity Evaluator (BOCLE). The lubricity of a fuel is determined by the measurement of an oval wear scar on a ball that has been in contact with a rotating cylinder partially immersed in a fuel sample under controlled conditions.⁸ The reported value is the average of the major and minor axes of the oval wear scar in millimeters. Two limitations to this method are: First, the BOCLE is run at 25°C, a temperature that is not characteristic in aircraft environments. Second, the test is limited to a measurement of boundary lubrication, a lubrication regime not characteristic of currently used aircraft fuel pumps.^{9,10}

In the United Kingdom a second method is being used. This method, developed and used exclusively by Shell Research, Ltd., is known as the Thornton Aviation Fuel Lubricity Evaluator (TAFLE). This consists of a stationary cylinder loaded onto a rotating cylinder both of which are completely immersed in the fuel sample. Measurements can be obtained at both ambient and elevated temperatures. This test also measures scuffing load which is generally characteristic of fuel system failures.^{9,10}

EXPERIMENTAL

Reagents- HPLC grade uninhibited tetrahydrofuran (THF) and HPLC grade methylene chloride were obtained from Fisher Scientific. JP-5 and Jet A jet fuel samples were obtained from the Naval Air Propulsion Center (NAPC). JP-4 jet fuel samples were obtained from Wright-Patterson Air Force Base (WPAFB). Carboxylic acid standards were obtained from a variety of sources including; Aldrich Chemical Company, Inc., LaChat Chemicals, Inc., and PolyScience, Inc. Trimethylsilyl ester derivatives of the carboxylic acids and jet fuel base extracts were prepared using Power Sil-Prep obtained from Alltech Associates, Inc.

Equipment and Materials- For HPLC analyses, samples were analyzed using a Beckman-Altex Microspherogel high resolution, size exclusion column, Model 255-80 (50A pore size, 30 cm x 8.0 mm i.d.). Uninhibited THF was used as a mobile phase. The THF was periodically purged with dry nitrogen to inhibit the formation of hazardous peroxides. The injector was a Rheodyne loop/valve Model 7125. A Beckman Model 100-A HPLC pump was used for solvent delivery with a Waters Model 401 differential refractometer

for detection. A Varian Model 9176 strip chart was used to record peaks. A Fisher Accumet pH Meter Model 610A and a Fisher Standard Combination Electrode Catalog Number 13-639-90 were used for pH adjustments.

Gas Chromatography/Mass Spectrometry (GC/MS) analyses were performed using a Hewlett-Packard Model 5890 GC coupled to a Finnigan MAT ion trap detector. An all glass GC inlet was used in combination with a 0.2 mm x 50 m OV-101 fused silica capillary column. Data were collected using an IBM AT Personal Computer with ITDS software (version 3.0).

BOCLE analyses were performed using an InterAv Model BOC 100. The cylinders used were Timken Rings Part Number F25061 obtained from the Falex Corp., Aurora, IL. The test balls used were 12.7 mm diameter, Swedish Steel, Part Number 310995A obtained from SKF Industries, Allentown, PA.

Methods- HPLC analyses of fuel extracts were performed using a previously developed method.¹¹⁻¹³ This involved the extraction of 100 mL of jet fuel with an equal volume of 0.2 M NaOH. The aqueous phase was drained and acidified with concentrated HCl. The acidified aqueous phase was subsequently back-extracted with 100 mL of HPLC methylene chloride which was then drained and allowed to evaporate. The residue was dissolved in 2.0 mL HPLC THF for analysis.

BOCLE measurements were performed according to the method described in appendix Y of the Aviation Fuel Lubricity Evaluation published by the Coordinating Research Council, Inc.⁸

RESULTS

Figure 1 is an HPLC chromatogram of a base extract from a typical JP-5 jet fuel. The active ingredient of the lubricity enhancer additive, DLA, has an elution volume of 5.85 mL. The DLA component has a molecular weight of 562. This material is prepared by a 1,4- cycloaddition (Diels-Alder) reaction of two linoleic acid molecules. The product is a monocyclic compound with a molecular weight twice that of linoleic acid. It possesses two carboxylic acid moieties which are the points of attachment to the active surface sites.

The peak that elutes at approximately 5.4 mL corresponds to trilinoleic acid (TLA). The TLA component, which is also a product of the Diels-Alder reaction, has a molecular weight of approximately 840. It may possess either a partially unsaturated fused dicyclic ring structure or two isolated partially saturated cyclohexyl rings.

The components with elution volumes of approximately 6.5 mL and 7.0 mL correspond to naturally occurring base extractable materials. These peaks are designated regions 3 and 4 respectively. These peaks can be clearly seen in Figure 2. The components that elute in what are designated regions 3 and 4 are believed to play a significant role in the inherent lubricity of jet fuel as measured by the BOCLE. Earlier work has shown a relation between the presence of these components and BOCLE measured lubricity.¹⁴⁻¹⁵ In general, as the concentration of components that

elute in regions 3 and 4 increase, the lubricity of a fuel sample measured by the BOCLE increases.

While performing routine analyses of jet fuel samples, an interesting change in the fuel samples was noted. A series of JP-5 field samples were analyzed for base extractable material. After nine months of ambient storage, these same samples were analyzed a second time. It was found that the amount of base extractable material that elutes in regions 3 and 4 had increased. Table 1 lists the peak heights of regions 3 and 4 before and after nine months of ambient storage.

BOCLE analyses were run to determine if there had been a concomitant change in lubricity. Since these were actual field samples of JP-5 jet fuels and, therefore, contained the mandatory lubricity enhancer additive, these fuel samples were all considered to be high lubricity fuels originally. It was found, however, that lubricity had increased. Previous work with an early version of the BOCLE yielded similar results. The lubricity of eight additive-free JP-5 and Jet A fuel samples were measured before and after 18 months of ambient storage. The change in wear scar diameter measurements for these fuels are listed in Table 2. It can be seen that the lubricity had increased in most cases. The wear scar diameters measured are smaller than those that would be measured on the current version of the BOCLE. This is a result of a metallurgical change in the cylinders to increase repeatability and reproducibility.

The increase in base extractable material with a concomitant increase in BOCLE measured lubricity is probably a result of oxidative changes in the fuel. Free radical autoxidation mechanisms are well known and readily occur in some fuels. These mechanisms can lead to the formation of trace levels of carboxylic acids that are known to enhance BOCLE measured lubricity.

The relation between lubricity and fuel composition is of great interest. Attempts have been made to correlate a number of fuel properties to lubricity measurements with little or no success. Early work performed by Grabel showed that straight chain carboxylic acids were among the most effective lubricity enhancers at very low concentrations.¹⁶ The effect of straight chain carboxylic acids on boundary lubrication is well known and well documented. It's not surprising that an corrosion inhibitor based on carboxylic acids is also an effective lubricity enhancer. Grabel attempted to correlate the total acid number of a fuel to its lubricity as measured by the BOCLE. It was found that there was a relation, however, it would not serve as a adequate prediction of a fuel's lubricity. The conclusion is that there are acids that contribute substantially to the total acid number that are not involved in lubricity.

Combined gas chromatography/mass spectrometry (GC/MS) was used to identify components present in regions 3 and 4. With the knowledge of the effect of carboxylic acids on BOCLE measurements, comparison between fuel extracts and carboxylic acid standards were made. Both the fuel extracts and standards were derivatized to form their trimethylsilyl analogs to facilitate GC/MS analysis. After analysis of a standard mixture of derivatized carboxylic acids, a variety of fuel extracts were analyzed. Carboxylic acids were found to be present at low concentrations. These

were identified by both GC retention time and by their mass spectra. To aid in identification, multiple ion detection was also used for samples with overlapping peaks. The specific alkanolic acids found ranged from heptanoic acid (C_7) to undecanoic acid (C_{11}). The total concentration of the alkanolic acids varied with different samples. In most cases the total concentration was on the order of a few parts per million. Previous work has shown that as little as 2 ppm of added alkanolic acids can significantly improve BOCLE measured lubricity.

In addition to the acids, the majority of the species present in the fuel extracts were substituted alkyl phenols. Earlier work by Grabel has shown that these materials are not effective lubricity enhancers at low concentrations. At higher concentrations they may, however, contribute to BOCLE measured lubricity.

SUMMARY

The BOCLE is a useful tool in the laboratory for jet fuel lubricity measurements. Its limitations, however, must be recognized. The test is performed at 25°C, well below the operating temperature of aircraft fuel systems. Compounds that exhibit a beneficial influence on lubricity in the BOCLE test may fail at higher temperatures. The BOCLE analysis is performed in a different lubrication regime than is found in current aircraft fuel systems. This may lead to erroneous conclusions about a fuel's ability to impart lubricity in actual fuel systems. For instance, the BOCLE measured lubricity of a fuel is not influenced by the presence of sulfur compounds. Jet fuel lubricity as measured by the TAFLE, indicates that sulfur compounds increase the load limit of a fuel before scuffing occurs. This means that the BOCLE may fail a fuel that is capable of high loads in an actual fuel pump.

Lubricity related problems have been associated with only certain specific aircraft. The use of the lubricity enhancer additive has been found to adequately alleviate these problems. Other aircraft have not been found to exhibit any lubricity related problems. One may ask why there is a concern about lubricity. In the past the Navy has had problems with lubricity as a result of shipboard fuel handling practices. As JP-5 fuel is depleted from shipboard storage tanks, seawater is pumped in for ballasting. Seawater has been shown to effectively remove the lubricity enhancer additive by forming dicationic salts of the DLA.^{12,13} This results in jet fuel with inadequate lubricity.

Another cause for recent lubricity problems is the lack of a lubricity specification. Additives used for lubricity enhancement are used, not for their ability to enhance lubricity, but their ability to inhibit corrosion. Of the additives qualified for use in jet fuel¹⁷, some are not effective surface active lubricity enhancers.

Two recommendations as an approach to short term and long term lubricity concerns are as follows: First, delete the additives from the Qualified Products List that are not found to enhance lubricity. Of the additives remaining, select those additives that are most effective for lubricity enhancement, are most cost effective, and are readily available.

Second, design aircraft components that are not affected by the continued use of low lubricity fuel. Long term problems with jet fuel lubricity should be approached by hardware modification not by the continued use of additives.

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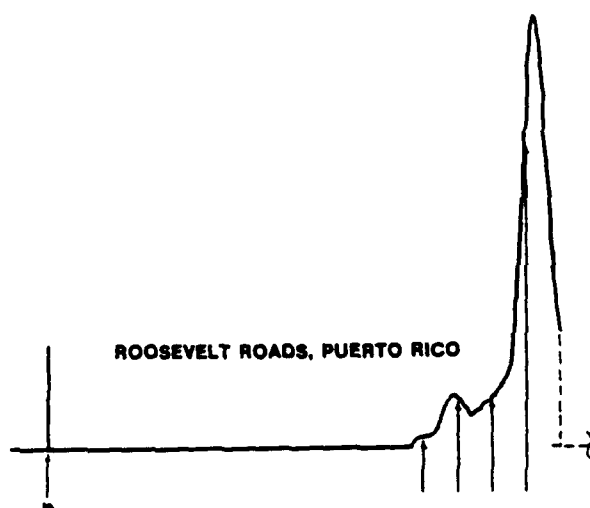


FIGURE 1



FIGURE 2

HPLC CHROMATOGRAMS OF JP-5 FIELD SAMPLES

TABLE 1

SAMPLE	Reg. 3 Pk Hgt		Reg. 4 Pk Hgt	
	Before	After	Before	After
Roosevelt Roads	14.5	28.0	128.0	55.0
Guantanamo Bay	11.0	28.0	25.0	200
Diego Garcia	20.0	22.0	22.0	85.0
Ioraki, Japan	4.0	4.0	3.5	11.0
Gatun, Panama	12.0	15.0	24.0	250
Cartagena, Spain	5.0	12.0	8.5	29.0
Azores	7.5	7.0	6.5	13.0

CHANGE IN CONCENTRATION OF BASE EXTRACTABLE MATERIAL AFTER
NINE MONTHS OF STORAGE

TABLE 2

SAMPLE	ORIGINAL WSD	REMEASURED WSD
1	0.28 mm	0.23 mm
2	0.32 mm	0.26 mm
3	0.28 mm	0.27 mm
4	0.43 mm	0.28 mm
5	0.31 mm	0.34 mm
6	0.62 mm	0.75 mm
7	0.53 mm	0.36 mm
8	0.52 mm	0.41 mm

CHANGE IN WEAR SCAR DIAMETER MEASUREMENT FOR ADDITIVE-FREE
JET FUELS AFTER 18 MONTHS OF STORAGE

GC-TR-87-1628

REFERENCE FILTERS FOR
ELECTROSTATIC CHARGING TENDENCY
MEASUREMENTS OF FUELS

PREPARED FOR
NAVAL RESEARCH LABORATORY
4555 OVERLOOK DRIVE, S.W.
WASHINGTON, D.C. 20375-5000
UNDER CONTRACT N00014-86-C-2288

PREPARED BY
GEO-CENTERS, INC.
7 WELLS AVENUE
NEWTON CENTRE, MA 02159

SEPTEMBER 1987

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) GC-TR-87-		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
3a. NAME OF PERFORMING ORGANIZATION GEO-CENTERS, INC.	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION	
7c. ADDRESS (City, State, and ZIP Code) 7 Wells Avenue Newton Center, MA 02159		7b. ADDRESS (City, State, and ZIP Code)	
3a. NAME OF FUNDING/SPONSORING ORGANIZATION Naval Research Laboratory	8b. OFFICE SYMBOL (If applicable) Code 6180	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
7c. ADDRESS (City, State, and ZIP Code) 4555 Overlook Avenue, S. W. Washington, DC 20375-5000		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO. 62233N
		TASK NO. 70838	WORK UNIT ACCESSION NO. 61-0085
11. TITLE (Include Security Classification) REFERENCE FILTERS FOR ELECTROSTATIC CHARGING TENDENCY MEASUREMENTS OF FUELS (U)			
12. PERSONAL AUTHOR(S) Wilbur A. Affens			
3a. TYPE OF REPORT	13b. TIME COVERED FROM 7/86 TO 6/87	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION Final Report on one phase of NRL Contract #N000 14-86-C-2288			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		Electrical conductivity, charging tendency, charge density, electrostatics, static electricity, electrostatic ignition, jet fuels	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
A study has been made to determine whether laboratory filter papers might be suitable as reference filters for the determination of charging tendencies of jet fuels as measured in the EXXON Mini-Static Tester (MST). From the filter papers which were investigated it was concluded that, compared to commerical fuel filters, these filters do not generate enough charge to afford repeatable and reliable measurements. Some correlation was observed between the polarity of the generated charges and the nature of the filter paper surfaces. However, attempts to repeat these experiments (continued)			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL Robert N. Hazlett		22b. TELEPHONE (Include Area Code) 202-767-3559	22c. OFFICE SYMBOL 6180-659:RNH:cak

19. Abstract (continued)

after a time period of about six to eight months were unsuccessful because of variations in the data, particularly that of polarity of the charge. It is suggested that the variations may have been due to relative humidity and temperature changes in the laboratory over the time period. Another possible explanation might be that there were changes in fuel composition due to degradation.

A few studies of some ion exchange resin coated filter papers suggest some tentative generalizations regarding these papers.

It was observed that the flow rate of fuel through each type of filter was not constant for any given run. Since it was necessary to have accurate flow rate data for each filter in order to be able to calculate charging tendency from the measured streaming current, a method was devised to make this measurement.

Some suggestions are made for modifying the MST method and proposals for future research are presented.

2nd INTERNATIONAL CONFERENCE ON LONG-TERM
STORAGE STABILITIES OF LIQUID FUELS
San Antonio, Texas, USA
July 29 - August 1, 1986

FUEL-SOLUBLE BIOCIDES FOR CONTROL OF FUNGAL CONTAMINANTS
IN HYDROCARBON FUELS [2]

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ABSTRACT

Water is frequently present in both military and commercial fuel systems and this occurrence may allow a select group of microorganisms to proliferate sufficiently to produce troublesome accumulations of particulate matter. A possible method of dealing with this problem is to add a biocide to the fuel which has the dual property of being soluble in the fuel and of partitioning sufficiently into any water phases present to inhibit microbial growth. Five such biocides were evaluated for effectiveness in controlling growth of major fungal contaminants, retention of effectiveness with storage time in fuel/water systems, and susceptibility to inactivation by fuel tank sludge. A mixture of isothiazolin compounds proved effective in controlling fungal growth at an exceptionally low concentration of less than one part per million and, in contrast to other compounds tested, showed no tendency to be inactivated by sludge.

INTRODUCTION

Microbial contamination of naval hydrocarbon fuels has caused serious problems in the past ranging from filter and coalescer blockages to corrosion from dissolved sulfur compounds (1,2,3). The use of gas turbines to power ships has accentuated the need for high quality fuel essentially free of particulate matter and constituents which contribute to corrosion of turbine blades or other engine components. Recently acute problems appear to have been avoided by good housekeeping procedures although the cost of dealing with contamination in terms of time and expense for upkeep of purification equipment may sometimes be considerable. There is a latent danger of unusual development of microbial growth should a set of especially favorable conditions

occur since recent surveys show that water and viable microorganisms are always likely to exist in fuel storage tanks on ships (3). It thus has appeared advisable to have effective methods on hand for coping with microbial contamination exceeding the capacity of normal purification equipment and procedures.

The use of biocides offers an obvious method of preventing microbial growth. Biocides for treating fuel must have the special property of being at least slightly soluble in fuel and of partitioning sufficiently into any water phase present to inhibit microbial growth there. In earlier work in this laboratory, biocides were evaluated which could be added directly to the water phase because it appeared unlikely that any fuel-soluble biocide could partition sufficiently into the relatively large volumes of water existing in many ship tanks to establish biocidal concentrations. However, fuel biocides are now available which are inhibitory at very low concentrations and it appeared worthwhile to evaluate certain of these in systems relevant to the situation in ship storage tanks. An important practical advantage would be that fuel could be pretreated with biocide at the necessary concentration and the handling and injection of toxic materials on ships avoided. An important disadvantage is that any new fuel additive would have to be examined for possible deleterious effects to engines and fuel handling equipment.

Biocides were chosen for evaluation on the basis of favorable results by other investigators (4), earlier studies in this laboratory (5,6), and preliminary experiments. It was of particular interest to determine the storage stability of the biocides and their susceptibility to inactivation by fuel tank sludge because the potential naval application may require that the biocide retain anti-microbial activity over prolonged periods and treatment of tanks containing accumulations of microbiological debris and fuel and water-derived particulate matter may be necessary.

MATERIALS AND METHODS

Biocides

Table 1 shows the chemical names of the active ingredient of the biocides tested along with the form in which they were added to the fuel, their sources and the designations used in this report.

Microbial Inoculum

A strain of the "kercene fungus", Cladosporium resinae DK, originally isolated from a contaminated ship tank was the test organism. It was grown on Potato Dextrose Agar (Difco) supplemented with 0.5% yeast extract. Inocula were prepared by washing the surface of actively growing one-week old slant cultures with a small amount of 0.05% Tween 80 in Bushnell-Haas mineral salts medium. The resulting suspension was diluted with additional medium to give a viable count of about 10^7 colony forming units per ml.

Storage Effects

The general procedure was to challenge biocide-treated fuel/water test units which had been stored for periods up to six months with inoculations of fungi and then to make observations of growth at intervals up to 15 weeks.

For this 4.0 ml of sterile Bushnell-Haas mineral salts medium were added to 25 x 145 mm test tubes followed by an overlayer of sterile naval distillate fuel with or without dissolved biocide. At zero time and after 2, 4, 8, 16 and 24 weeks of storage at 26°C, the water bottoms of duplicate test units in each treatment category were inoculated with 10^6 colony forming units of C. resinae (in 0.1 ml. aqueous medium) and returned to the 26°C incubator.

Effects of Sludge

These tests were carried out at the same time in similar test units and on the same time schedule as the storage experiments. Three ml of aqueous medium and one ml of sludge prepared by pooling 15 different sludge samples from storage tanks of four ships were used. Volume estimations made after high speed centrifugation showed that the sludge consisted of

about 33% fuel, 46% water and 21% solid sediment. The aqueous phase had a refractive index corresponding to a sea salt concentration of 25 ppt. The sludge was sterilized by autoclaving. In the test units the sludge distributed itself partly at the bottom of the tubes and partly at the fuel/water interface leaving a clear intermediate aqueous layer.

Monitoring Fungal Growth

Visual estimates of fungal growth were made at weekly intervals. In the presence of sludge such estimates were sometimes difficult when only small amounts of growth were present. Heavier growth was readily detected at the sludge/water interface and in a water film between the fuel and the container wall just above the interface. In doubtful cases, small samples of the aqueous phase were examined by phase microscopy.

The rating system used was as follows:

- 0 = no growth
- 1 = slight mycelial sediment
- 2 = formation of substantial mycelial floc
- 3 = floc plus some interfacial growth
- 4 = substantial interfacial growth
- 5 = fungal mat around the interface
- 6 = thick mat that forms a plug

RESULTS AND DISCUSSION

The two concentrations of each biocide used were selected on the basis of preliminary tests and other information available to give border-line control of microbial growth at the lower concentration and complete control at the higher concentration.

Figures 1-3 show the combined results of experiments to evaluate the effects on biocides of both storage and sludge. In the control test units without biocide, growth of C. resinae was rapid and prolific whether sludge was present or not (Fig. 1). At the lower concentration levels, only biocides A and C showed complete control of fungal growth during the 15 weeks observation. Biocide B allowed retarded growth while D showed only a slight inhibition. Biocide E was inhibitory in clean

systems but completely inactivated by sludge. At the higher concentration, fungal growth was completely controlled by all biocides except D in clean systems.

After one month of storage (Fig. 2) biocide A allowed growth in the presence of sludge while uninhibited growth occurred with biocides D and E. Biocide B allowed growth in clean systems but, in contrast with unstored systems, completely inhibited growth with sludge. At the higher concentration levels, results in all cases were the same as for no storage.

After six months storage (Fig. 3) at the lower concentration levels, biocide C alone retained complete control of fungal growth. Biocide A was uninhibitory with sludge but allowed only slow growth without sludge. The loss of anti-fungal activity of Biocide B in clean systems seen after one month storage was accentuated after six months, but control with sludge was retained. With biocide D there was also an indication of better control in systems with sludge. Biocide E was no longer inhibitory after six months.

After six months at the higher concentrations, biocides A and E showed the same inactivation by sludge seen at the lower concentration but inhibition in clean systems was complete. Biocide D continued to show better control with sludge than without as seen at the shorter storage times. The tapered bar graph in this case is meant to show that only one of the duplicate test units showed growth.

Our results with biocides A and E generally agreed with those of Smith and Crook using a different test method (9). They also found biocide E to be easily inactivated by exposure to sludge and soil. However biocide A appeared more resistant to inactivation by sludge in their experiments than in ours. These authors also observed that low concentrations of mixtures of these two biocides was very effective against microbial fuel contaminants.

Considerable differences exist in the response of the different biocides to storage and sludge. Biocides A and E were inactivated by sludge and E, especially, did not retain activity

on storage. Biocides B and D, on the other hand, appeared more active with sludge than in clean systems. A number of possible factors may be responsible for these differences. Most of the biocides are subject to hydrolysis or oxidation and so become inactive with time (6,7,8,9,10,11). The oil/water partition ratios of the biocides differ and the rates at which partition equilibrium is reached may also differ. Sludge provides particulate surfaces on which adsorption of biocides can occur. As an interfacial barrier, sludge may retard the rate at which biocides diffuse from the oil to the aqueous phase and thus prolong a biocidal concentration especially at the interface where fungal growth tends to occur. It should also be pointed out that in this investigation those test units to which sludge was added had about 12% less water than those without. While all of the observed effects could be explained on the basis of these factors, other unidentified interactions no doubt exist. There are insufficient data available to warrant speculative explanations concerning specific biocides.

Biocide C completely inhibited fungal growth at the lowest concentration (1 ppm) of any biocide evaluated; effectiveness at this low concentration was maintained with storage and in the presence of sludge. There is evidence that this biocide undergoes slow hydrolysis (7,8) which would reduce anti-microbial activity. Evidently it would be necessary to use still lower concentrations than used here to detect any loss in activity with storage time from this effect. The favorable results observed here with this biocide justify further evaluations of its application limits. Its effectiveness at lower concentrations and in the presence of thick deposits of sludge would be of particular interest.

ACKNOWLEDGEMENTS

Financial support for this study was provided by the David Taylor Naval Ship Research and Development Center, Annapolis, MD, Richard Strucko, project engineer. We thank the following companies for biocide samples: E.I. duPont de Nemours & Co.; Bull and Roberts, Inc.; Rohm & Haas Co.; Olin Research Center.

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TABLE 1

<u>Biocide Designation</u>	<u>Active Ingredients</u>	<u>Stock Solution</u>	<u>Source</u>
A	1-(BUTYLAMINO)CARBONYL-1H-BENZIMIDAZOL- 2-YL CARBAMIC ACID METHYL ESTER	5% IN DIMETHYL FORMAMIDE + 2.5% BUTYL ISOCYANATE	duPont
B	MIXTURE: 2,2' OXYBIS(4,4,6-TRIMETHYL 1,3,2-DIOXABORINANE) (27.4%) AND 2,2'-(1-METHYL-TRIMETHYLENE DIOXY)BIS- (4-METHYL-1,3,2-DIOXABORINANE) (67.6%)	95% IN PETROLEUM NAPHTHA	U.S. BORAX
C	MIXTURE: 5-CHLORO-2-METHYL-4- ISOTHIAZOLIN-3-ONE AND 2-METHYL-4-ISOTHIAZOLIN-3-ONE	1.5% IN DIPROPYLENE GLYCOL	ROHM & HAAS
D	2-N-OCTYL-4-ISOTHIAZOLIN-3-ONE	45% IN PROPYLENE GLYCOL	ROHM & HAAS
E	TERTIARY BUTYLAMINE PYRIDINETHIONE	1.69% IN PROPYLENE GLYCOL	OLIN

FIGURE 1. GROWTH OF *C. resiniae* IN BIOCIDES TREATED FUEL/WATER SYSTEMS

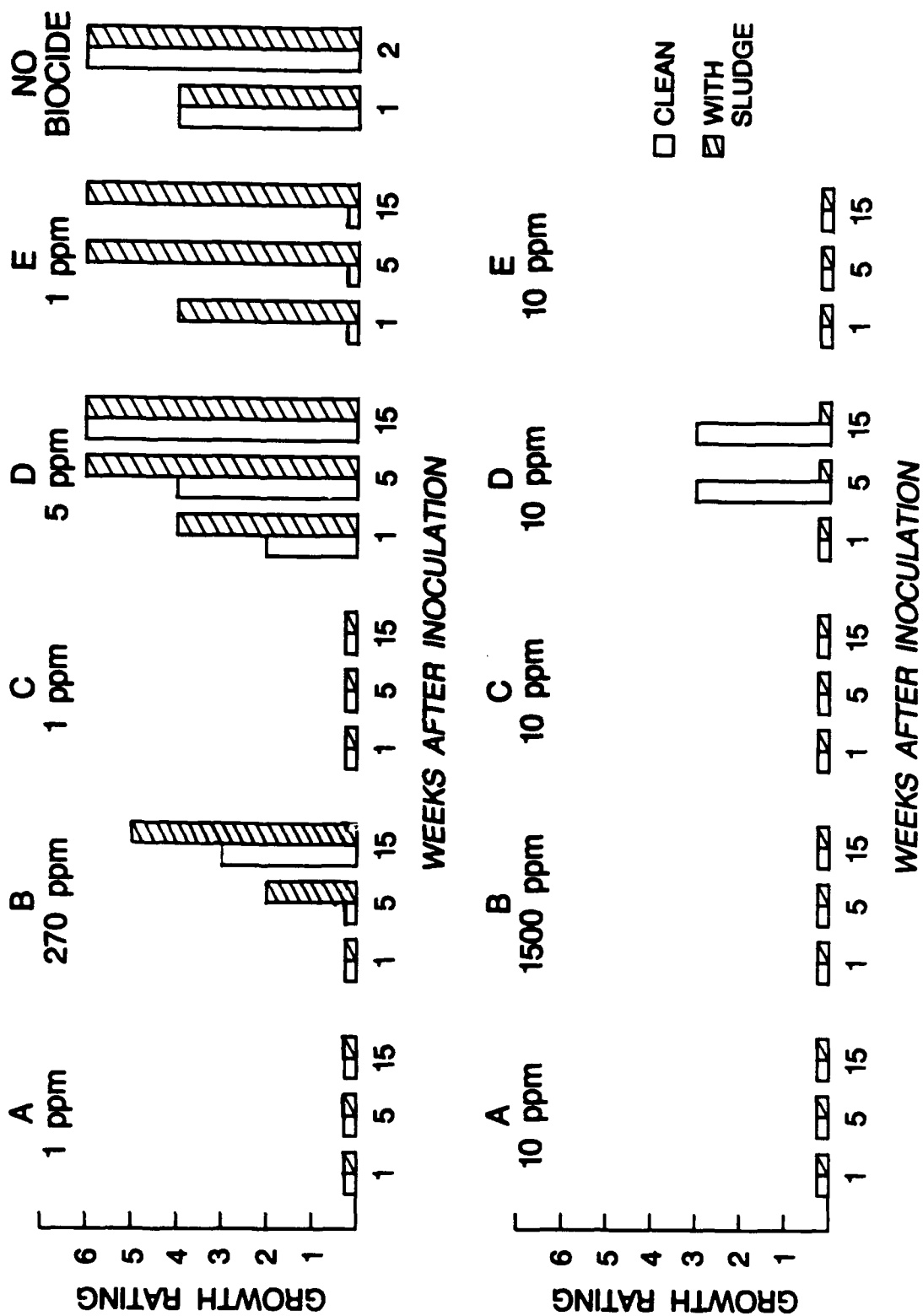


FIGURE 2. GROWTH OF *C. resinæ* IN FUEL/WATER STORED WITH BIOCIDES FOR ONE MONTH

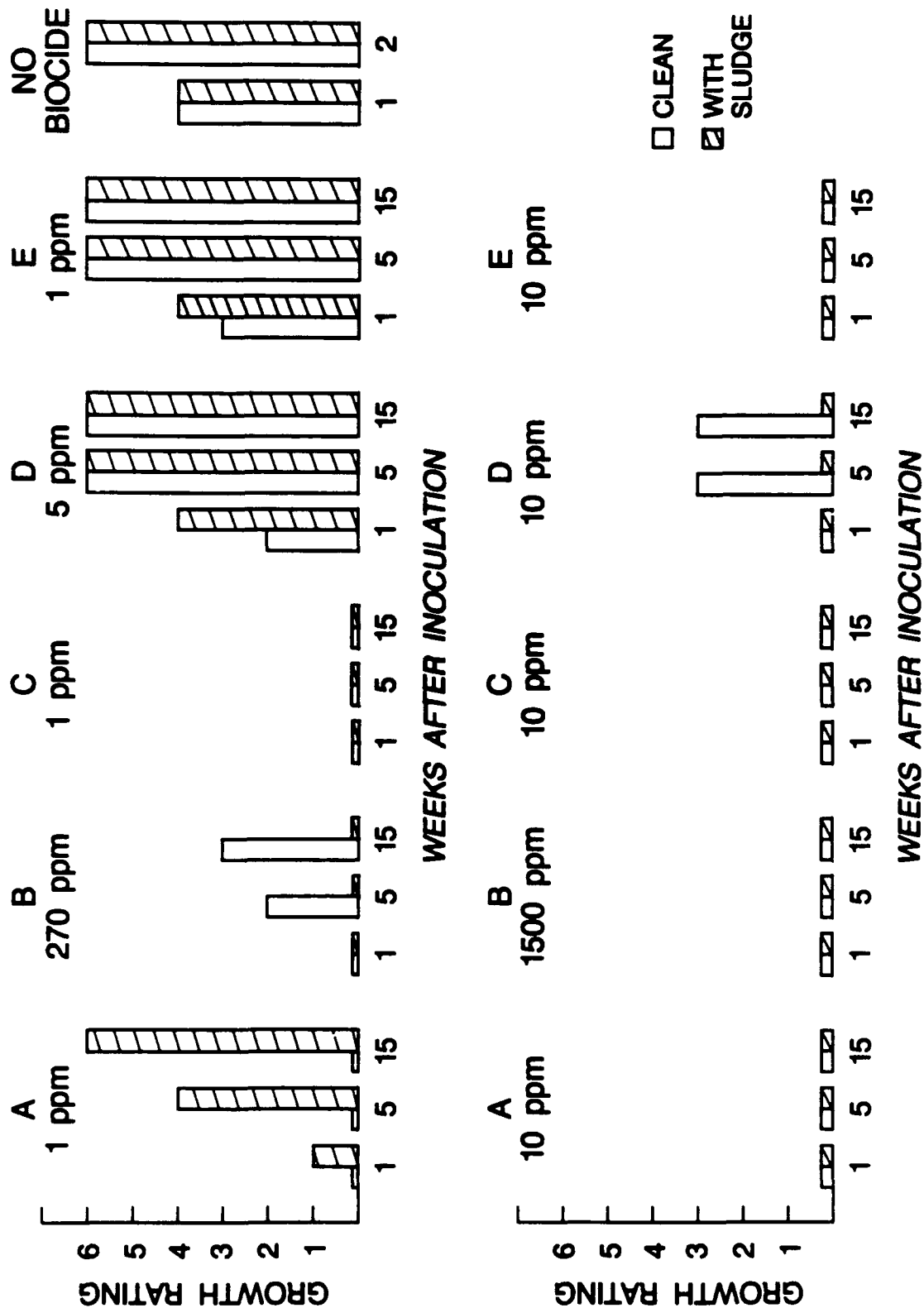
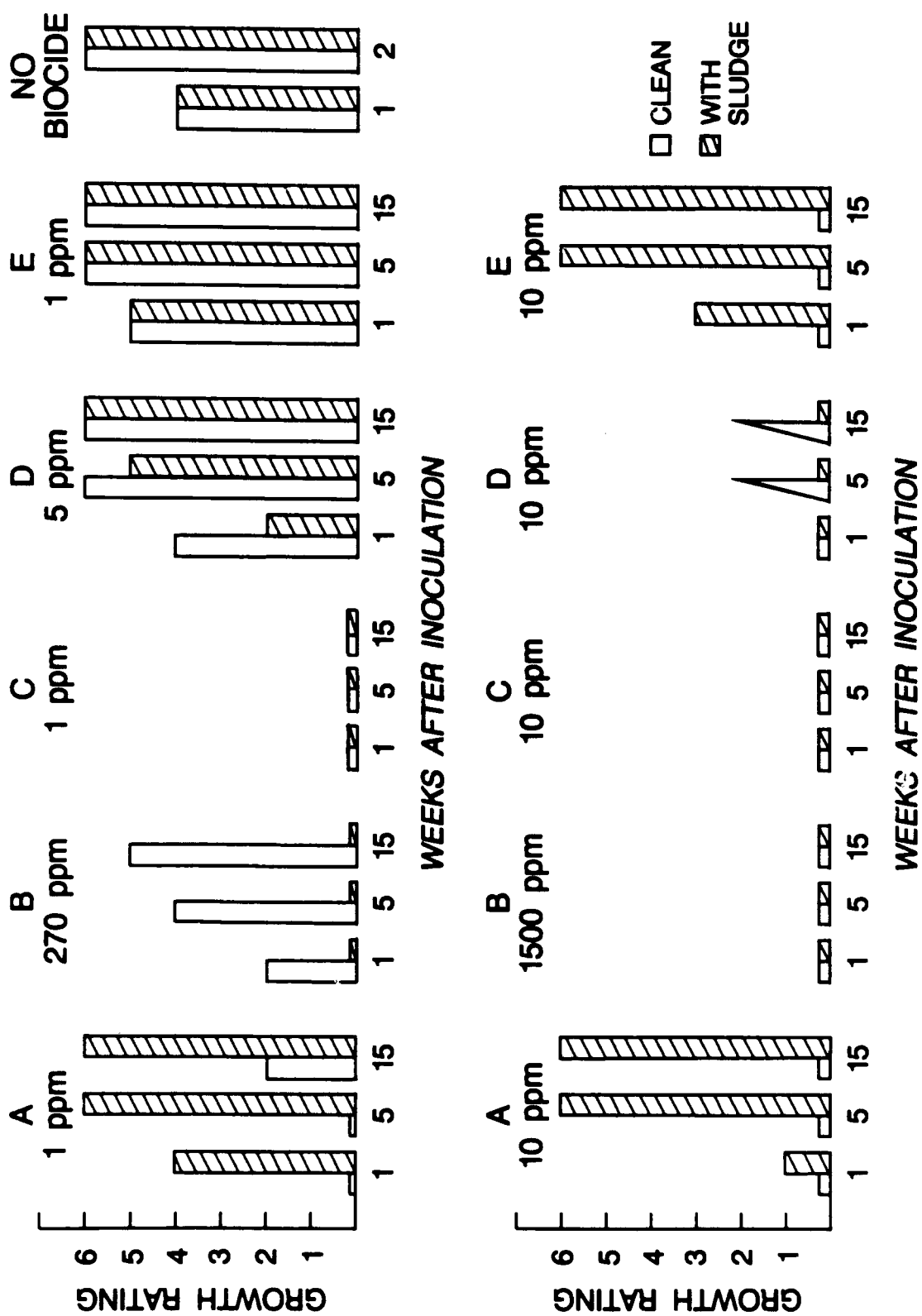


FIGURE 3. GROWTH OF *C. resinae* IN FUEL/WATER STORED WITH BIOCIDES FOR SIX MONTH



Fuel-soluble biocides for control of *Cladosporium resinae* in hydrocarbon fuels

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Received 27 August 1986

Revised 6 February 1987

Accepted 6 February 1987

Key words: Biocide; *Cladosporium resinae*; Fuel; Fungi; Isothiazolone

SUMMARY

Five fuel-soluble biocides – a benzimidazole fungicide, an organoboron, a pyridinethione and two isothiazolone products – were evaluated for inhibition of a typical hydrocarbon fuel contaminant, *Cladosporium resinae*, in fuel water systems. The biocides exhibited marked differences in anti-fungal activity with storage and in the presence of sludge. A methylchloro methyl-isothiazolone mixture prevented growth of the fungus at a concentration of one part per million and, in contrast to other biocides tested, showed no tendency to be inactivated by storage or the presence of sludge.

INTRODUCTION

Microbial contamination of hydrocarbon fuels can cause operational problems ranging from corrosion to filter plugging wherever the presence of water offers the opportunity for growth [3]. On naval ships, water is invariably present in fuel storage tanks as a result of condensation or deliberate addition as ballast [5,14]. Because microbial contamination occasionally causes problems which are time-consuming and expensive to correct, it has been considered advisable to have effective methods on hand for coping with acute situations which may arise in the future.

Biocides offer an obvious method of preventing microbial growth. Earlier work in this laboratory emphasized biocides which could be added directly to the water phase, because it appeared unlikely that fuel-soluble biocides at acceptable concentrations could partition sufficiently into a relatively large volume of water to reach a biocidal concentration there [6–8]. The present study was undertaken because fuel-soluble biocides which are inhibitory at very low concentrations are now available, and it appeared worthwhile to evaluate certain of these in systems relevant to the situation in ship storage tanks. An important practical advantage in the use of fuel-soluble biocides would be that fuel could be pretreated with biocide at the necessary concentration, and the handling and injection of toxic materials on ships could be avoided.

Choices of biocides for this study were made on the basis of the work of other investigators

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[2,3,11,15,17,18], previous studies in this laboratory [6-8] and preliminary experiments. For comparison, a widely used fuel biocide was included. The anticipated applications required that emphasis be placed on determining the stability of the biocides with storage in fuel/water systems and their susceptibility to inactivation by fuel tank sludge. The fungus, *Cladosporium resinae*, was chosen as the test organism because it is ubiquitous in fuel systems and is recognized as a significant source of particulate contamination [3,14]. Additional screening studies are in progress with mixed bacterial inocula containing sulfate-reducers, a well-known cause of sulfur contamination in stored fuels.

MATERIALS AND METHODS

Biocides

Table 1 shows the sources, letter designations, and active ingredients of the biocides used; Fig. 1 shows the chemical structures. In the test systems described below, biocides were added to autoclave-sterilized naval distillate fuel. Two different concentrations of each biocide were selected to give border-line control of microbial growth at the lower concentration and complete control at the higher

concentration. These concentrations were calculated on a weight basis (w/w).

Test organism

Cladosporium resinae DK, originally isolated from a contaminated ship tank, was grown on Potato Dextrose Agar (Difco, Detroit, MI) supplemented with 0.5% yeast extract (Difco). Inocula were prepared by washing the surface of actively growing 1-week-old slant cultures with a small amount of 0.05% Tween 80 in Bushnell-Haas mineral salts medium [1]. The resulting suspension was diluted with additional medium to give viable counts of about 10^7 colony-forming units per ml.

Test systems

The general procedure was to challenge biocide-treated fuel/water test units which had been stored for periods of up to 6 months in the presence and absence of sludge with inoculations of fungi and to monitor growth thereafter.

To test the effect of storage, 4 ml of sterile Bushnell-Haas mineral salts medium [1] were added to 25×145 mm test tubes and overlaid with 40 ml of sterile naval distillate fuel with or without dissolved biocide. At zero time and after 2, 4, 8, 16 and 24 weeks of storage at 26°C, the water bottoms of du-

Table 1
Biocides tested

Biocide designation	Active ingredients	Stock solution	Source
A	1-(Butylamino)carbonyl-1H-benzimidazol-2-yl carbamic acid methyl ester	5% in dimethyl formamide + 2.5% butyl isocyanate	DuPont
B	Mixture: 2,2'-oxybis-(4,4,6-trimethyl-1,3,2-dioxaborinane) (27.4%) and 2,2'-(1-methyltrimethylene dioxy)bis-(4-methyl-1,3,2-dioxaborinane) (67.6%)	95% in petroleum naphtha	U.S. Borax
C	Mixture: 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one	1.5% in dipropylene glycol	Rohm and Haas
D	2-N-octyl-4-isothiazolin-3-one	45% in propylene glycol	Rohm and Haas
E	Tertiary butylamine pyridinethione	1.69% in propylene glycol	Olin

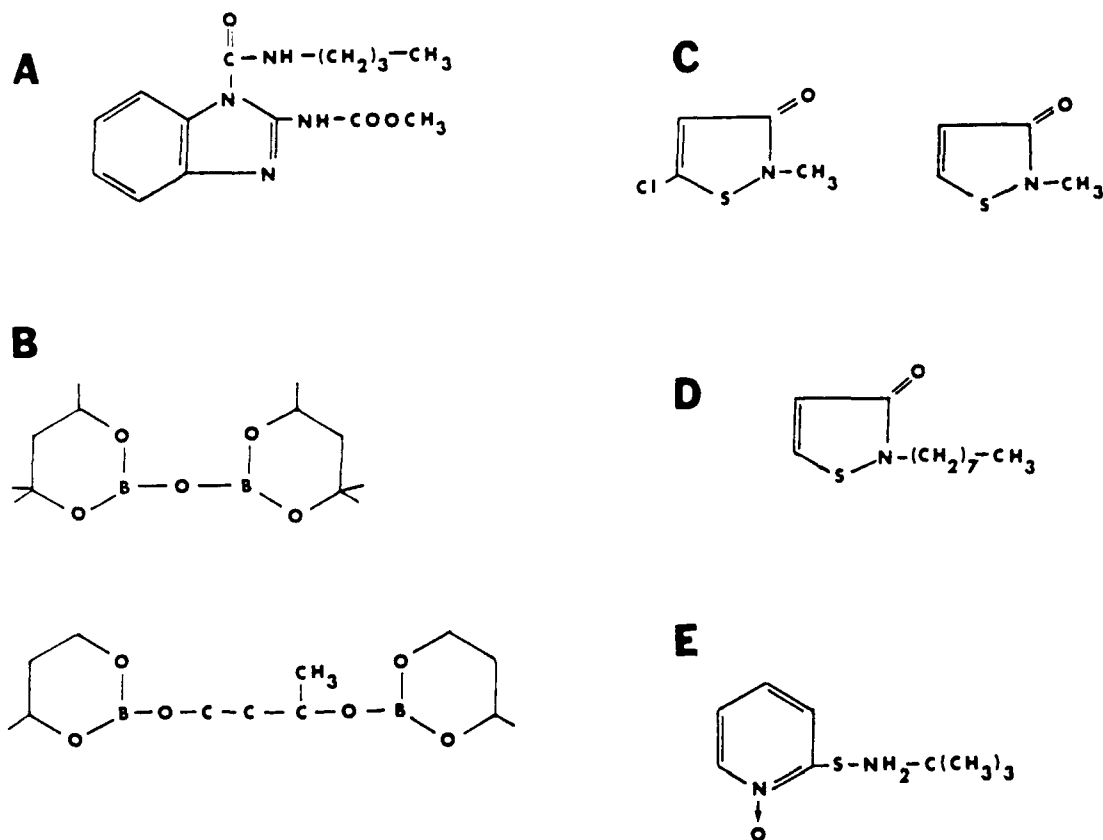


Fig. 1. Structural formulae of biocides tested.

plicate test units in each treatment category were inoculated with 10^7 colony-forming units of *C. resiniae*.

Tests to determine the effects of sludge were carried out at the same time in similar test units and on the same time schedule. Forty milliliters of fuel were dispensed over 3 ml of mineral salts medium and 1 ml of sludge containing solid matter which distributed itself partly at the bottom of the test units and partly at the fuel water interface, leaving a clear intermediate aqueous layer. The sludge was prepared by pooling 15 different sludge samples from storage tanks of four ships, and consisted of 33% oil, 46% water (estimated from refractive index to contain 25 ppt sea salt) and 21% sediment. It was sterilized by autoclaving prior to use. Inoculation, duplication, incubation and storage were as described above for non-sludge-containing units.

The test units were examined each week and es-

timates of fungal growth were made visually using a numerical rating from one to six as given in Fig. 2. In previous investigations using a similar system, it was shown that reproducible results could be obtained when ratings were made in a consistent manner by the same person; biomass approximately doubled for each unit increase in rating [12]. Occasionally, to confirm doubtful cases, small samples of aqueous phase were removed and examined by phase contrast microscopy.

RESULTS AND DISCUSSION

Growth of *C. resiniae* was rapid and prolific in control test units without biocide whether sludge was present or not (Fig. 2). When biocide-containing test units were inoculated without prior storage, only biocides A and C showed complete control of

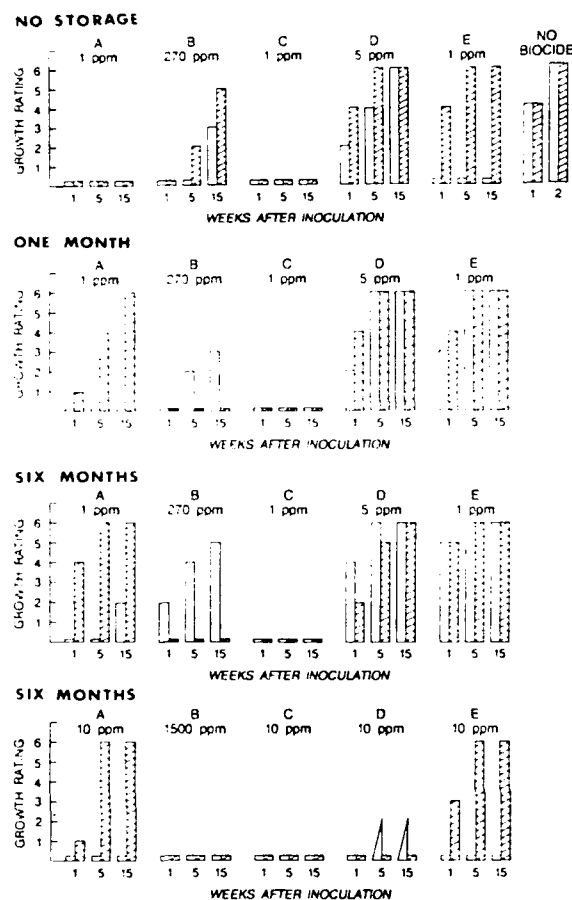


Fig. 2. Growth of *C. resinae* inoculated at zero time and after 1-month and 6-month storage of fuel water systems treated with biocides A-E. $\square$, without sludge; ▨ , with sludge. Growth ratings: 0 = no growth, 1 = slight mycelial sediment, 2 = formation of substantial mycelial floc, 3 = floc plus some interfacial growth, 4 = substantial interfacial growth, 5 = fungal mat at interface, 6 = thick mat at interface.

fungal growth at the lower concentration levels. Biocide B allowed retarded growth, which is not unexpected since it is not intended for situations where the water fuel ratio is so high. Biocide D showed only a slight inhibition. Biocide E was inhibitory in clean systems, but completely inactivated in systems containing sludge. At the higher concentrations with no storage (data not shown in Fig. 2), fungal growth was completely controlled by all biocides except D which allowed a growth rating of three in clean systems only 5 weeks after inoculation.

After 1 month of storage, biocide A allowed growth in the presence of sludge, while uninhibited growth occurred with biocides D and E. Biocide B allowed growth in clean systems but, in contrast with unstored systems, completely inhibited growth with sludge. At the higher concentration levels (data not shown in Fig. 2), no growth occurred with any biocide with the exception of D which allowed the same growth rating of three in 5 weeks' time after inoculation as in the case with no storage.

After 6 months of storage at the lower concentration levels, biocide C alone retained complete control of fungal growth. Biocide A was uninhibitory with sludge but allowed only slow growth without sludge. The loss of anti-fungal activity of biocide B in clean systems seen after 1 month of storage was accentuated after 6 months, but control with sludge was retained. With biocide D there was also an indication of better control in systems with sludge. Biocide E was no longer inhibitory after 6 months.

After 6 months at the higher concentrations, biocides A and E showed the same inactivation by sludge seen at the lower concentration but inhibition in clean systems was complete. Biocide D continued to show better control with sludge than without, as seen at the shorter storage times. The tapered bar graph (Fig. 2) in this case is meant to show that only one of the duplicate test units showed growth, an exception to the otherwise general agreement of duplicates.

Considerable differences clearly exist in the responses of the different biocides to storage and sludge. A number of factors may be responsible. Most biocides are subject to hydrolysis or oxidation and therefore become inactive with time [4,9,10,13,17,19]. The oil water partition ratios of the biocides differ and the rates at which partition equilibrium is reached may also differ. Sludge provides particulate surfaces on which adsorption and/or inactivation of biocides can occur. As an interfacial barrier, sludge may retard the rate of biocide diffusion from the oil to the aqueous phase and thus, as may be the case with biocides B and D, prolong a biocidal concentration at the interface where fungal growth is most likely to occur. It

should also be pointed out that those test units to which sludge had been added contained about 12% less water than those without. Other explanations for our observations are likely to exist as well, but there are insufficient data to speculate more specifically.

Our results with biocides A and E generally agree with those of Smith and Crook [17] using a different test method. However, biocide A appeared to be more resistant to sludge inactivation in their experiments. These authors also observed that low concentrations of mixtures of biocides A and E were very effective against microbial fuel contaminants.

A major finding of this study is that biocide C, the methylchloro methyl-isothiazalone mixture, completely inhibited fungal growth at a concentration of 1 ppm; effectiveness at this low concentration was retained with storage and in the presence of sludge. There are few reports of the use of this biocide to treat distillate fuels [11,18], and none that detail the effects of storage and sludge stress on its efficacy. While the results of laboratory investigations should only be extrapolated to 'real world' systems with great caution, we feel that the favorable results observed here with biocide C justify further evaluations of its application limits.

These screening evaluations were intended to select those biocides which were effective against a major fungal biodeteriogen under conditions generally favorable to the growth of fungi (nutrients, pH and temperature) and unfavorable to the biocides (aging and sludge presence). Similar screening evaluations are being carried out with mixed bacterial cultures containing sulfate-reducing bacteria. These combined results should serve to define conditions for further work using more realistic test systems.

ACKNOWLEDGEMENTS

We thank the companies listed in Table 1 for providing generous biocide samples, and the David Taylor Naval Ship Research and Development Center, Annapolis, MD for financial support.

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CONTROL OF SULFATE-REDUCING BACTERIA IN HYDROCARBON FUEL TANKS

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INTRODUCTION

Most of the problems originating with microbial detteriogens of fuels stored on naval ships or in land based tanks have arisen from fungi or sulfate-reducing bacteria. Fuel degrading fungi contribute to particulate matter and sludge and sulfate reducers produce fuel soluble sulfides and sulfur. Both groups of microorganisms contribute to corrosion.

Although the effects of microbial fuel contamination can be satisfactorily controlled by minimizing the presence of water and maintaining the purification equipment, other measures may occasionally be needed. The use of biocides provides one obvious solution and a number of studies have been published concerning their effectiveness especially with fungi (Neihof et al., 1982; Smith and Crook, 1986; Morchat et al., 1986). In earlier work, we have evaluated several promising biocides for control of fungi: the effect of seawater and sludge on biocidal activity was also examined (Andrykovitch and Neihof, (1987a). In this paper we report on the results of studies using three of the same biocides to control sulfate-reducing bacteria.

The disadvantages of using biocides are their expense and the potential hazards to personnel and to the environment. We have explored a possible alternative which would be less objectionable, namely, alkanization of the aqueous phase in contact with the fuel (Andrykovitch and Neihof, 1987b). This approach has already been explored for controlling the growth of the fuel fungus, Amorphotheca (Cladosporium) resinae, with some success (May and Neihof, 1981). In test systems consisting of equal volumes of fuel and buffered aqueous media, fungal growth could be completely controlled if a pH of 9 or more was maintained. The present study extends this approach to the control of sulfate-reducing bacteria.

MATERIALS AND METHODS

Biocides

The biocides were all widely used commercial products and included a mixture of dioxaborinanes [2,2'-methyl-trimethylenedioxy-bis-(4-methyl-1,3,2-dioxaborinane and 2,2'-oxy-bis-(4,4,6-trimethyl-1,3,2-dioxyborinane]; a mixture of 5-chloro-2-methyl-isothiazolin-3-one and 2-methyl-4-thiazolin-3-one; and tertiary butylamine pyridinethione. The manufacturers' data were used to calculate the amount of biocide needed to attain the desired concentration in the fuel. Concentrations were expressed as parts per million (ppm) of active ingredient by weight in the fuel.

Bacterial Cultures

A mixed culture of anaerobes and aerobes including sulfate reducing bacteria was obtained from a sample of fuel tank sludge by inoculation into Sisler's triple strength medium (Sisler and Zobell, 1950). The culture was maintained by periodic transfer to the same medium. A sulfate-reducing bacterium, designated NRL-9 and tentatively identified as a strain of Desulfovibrio desulfuricans was isolated from the same sludge using the roll tube technique (Hungate, 1969).

Suspensions for inoculation of test units were prepared by growing the organisms at 26°C in Postgate's Medium B (Postgate, 1963) which contained 0.01 percent each of sodium thioglycollate and ascorbic acid as reducing agents. The actively motile cells were harvested by centrifugation at 5000 rpm and washed in sterile seawater (SWR) containing the same concentrations of reducing agents as the growth medium. The washed cells were resuspended in SWR to a density of 10^7 - 10^8 per ml.

Test Units

Duplicate 50 ml tubes with screw caps gasketed with Teflon were used for each test condition. An equal volume of autoclaved marine diesel fuel with or without biocide was layered over 25 ml of Medium B buffered to the required pH by addition of 0.1M 2-(N-cyclohexylamino) ethanesulfonic acid (CHES, Sigma). The pH of the medium was readjusted to the desired value after autoclaving. Test units were inoculated with 0.5 ml of washed cell suspension, incubated at 26°C, and observed for turbidity and the appearance of the black iron sulfide precipitate indicative of sulfate reduction.

The test units were monitored for up to 3 months, although no changes were generally noted after two weeks of incubation. Invariably test units that showed no blackening were found to be devoid of viable sulfate reducing bacteria when a portion of the aqueous phase was transferred to

fresh Medium B or Sisler's medium. Duplicate test units agreed in all cases.

RESULTS AND DISCUSSION

Biocide Evaluation

Table 1 summarizes the results with biocides. Clearly the mixture of isothiazolones was effective at the lowest concentrations. The minimum inhibitory concentration was different for the dioxaborinanes depending on whether the pure culture or the mixed culture was used. The reasons for this are not known but the complex interactions possible in mixed cultures could be readily responsible.

Evaluations made several years ago in this laboratory (Klemme and Neihof, 1969) of the dioxaborinanes and the pyridinethione in controlling the growth of a mixed culture containing sulfate reducers are difficult to compare with the results here because biocides at that time were added directly to the aqueous phase; the culture was also different and the media were less favorable for sulfate reducer growth. Assuming that most of the biocide initially in the fuel phase in the present work eventually partitioned into the water phase where microbial growth takes place, it appears that the concentration of the dioxaborinanes necessary for control was similar to that found for the earlier work, namely 10,000 to 15,000 ppm. However, the pyridinethione failed to show any control at concentrations that were effective in the earlier studies. This may be due to the more favorable growth medium used here and possibly to the susceptibility of this biocide to inactivation by the reducing conditions imposed by Medium B.

It can be seen from a recent study (Andrykovitch and Neihof, 1987a) that all of the biocides used here were effective at lower concentrations in controlling the fuel fungus, A. resinae, than they were in inhibiting sulfate reducers. The mineral salts medium used with fungi was probably relatively poor compared to the medium used here for sulfate reducers. Also, given the tendency of A. resinae to grow at the water/oil interface, it may be that the diffusion of biocide from oil to water may keep the interfacial concentration of biocide sufficiently high to be lethal or inhibitory to fungi there. Sulfate reducer cultures do not show this preference for the interface.

Any recommendation for a choice of biocides for use in fuel storage tanks will have to await more realistic tests, but the low effective concentration of the isothiazolones against both fungi and sulfate reducers and their resistance to inactivation by sludges as shown by Andrykovitch and Neihof (1987a) makes this biocide look very promising.

Table 1. Comparison of the Effects of Biocides on Sulfate-reducing Bacteria and A. resinae in Test Tube Systems.

Biocide	Concentration (ppm)	Organism		
		NRL-9	Mixed Culture	<u>A. resinae</u> ^a
Mixture of Dioxaborinanes	1500	+	+	0
	3000	+	+	0
	10000	0	+	0
	15000	0	0	0
Mixture of Isothiazolones	1	+	+	0
	25	+	+	0
	50	0	0	0
	100	0	0	0
Tertiary Butylamine	10	+	+	0
	50	+	+	0
Pyridinethione	100	+	+	0
	200	+	+	0

+ = growth; 0 = no growth

^aData from Andrykovitch and Neihof, 1987a.

Table 2. Comparison of the Effect of High pH on Sulfate-reducing Bacteria and A. resinae in Test Tube Systems.

pH of Aqueous Phase	Organism		
	NRL-9	Mixed Culture	<u>A. resinae</u> ^b
7.6	+	+	+
8.1	+	+	+
8.6	+	+	+
9.1	0	0	0
9.6	0	0	0

+ = growth; 0 = no growth

^bData from Andrykovitch and Neihof, 1987b.

Alkanization

Table 2 shows the results of the experiments to determine the pH level necessary to prevent sulfate reducer growth. The initial pH values are shown. Decreases of as much as 0.8 to 0.9 unit at pH 8.6 were noted in the early weeks of incubation with added bacteria. These decreases were less (0.0 to 0.4 unit) at higher and lower initial pH values. Uninoculated controls underwent no reduction in pH greater than 0.2 unit.

No growth of NRL-9 or the mixed culture occurred at pH 9.0. In numerous trials with both cultures, the critical pH at which growth was controlled lay consistently between pH 8.6 and 9.1. This low value is not in agreement with other reports that a pH of 10 failed to stop the growth of sulfate reducers (Klemme and Neihof, 1969). The explanation for this discrepancy may lie in the different culture used here and the peculiarities of Medium B which contains a heavy precipitate.

In view of the fact that a pH of 9.0 appears to control the growth of fungi (Andrykovitch and Neihof, 1987b) it may be that a rather modest increase in aqueous pH would be sufficient to control the biodeteriogens of fuel. Other aspects of the approach which need to be examined are the effects of alkanization on the emulsification of water in contact with diesel and other fuels which may contain emulsifying constituents. The most suitable basic compound for increasing the pH with the least likelihood of creating particulate matter or promoting corrosion would also need to be determined.

SUMMARY

Three fuel-soluble commercial biocides (a mixture of dioxaborinanes, a mixture of isothiazolones and a pyridinethione) were evaluated for their effectiveness in controlling growth of a pure culture of sulfate-reducing bacteria and of a mixed culture containing sulfate-reducers in fuel/water test tube systems. The mixture of isothiazolones was effective at the lowest concentration.

An investigation was also made of the inhibiting effects of raising the pH of the aqueous phase on sulfate reducer growth. Growth of both the pure and mixed cultures was inhibited as the aqueous pH approached 9.0. Because the major fungal contaminant of fuels was found in earlier studies to be completely inhibited by the biocide concentrations and alkaline pH which stopped growth of sulfate reducers, it appears that either of the treatment methods would be promising for control of the major biodeteriogens of hydrocarbon fuels.

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Acknowledgment

We thank Bull and Roberts, Rohm and Haas, and Olin Co's. for biocide samples.

Presented at the 1986 CRDEC Conference on Chemical Defense, Aberdeen Proving Ground, MD, November, 1986, proceeding published 1987.

E. SHIPBOARD ATMOSPHERIC MONITORING FOR COLLECTIVE PROTECTION APPLICATIONS

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ABSTRACT

The U.S. Navy supports a shipboard atmospheric characterization task to identify potential challenges to shipboard Collective Protection Systems (CPS). Surface ships with special tasks or missions are being examined as a part of this task. To assist in meeting the task objectives, external locations on-board an aircraft carrier were selected for monitoring ambient atmospheric particulate and vapor levels under a variety of operational conditions. Charcoal packed sorbent tubes and small pore membrane filters were used to trap vapors and particulates, respectively. Particulates were analyzed using optical microscopy and vapors were identified by GC and GC/MS. Small, solid particles detected include carbon, sea salt and corrosion remnants. Vapors detected include Freons, hydrocarbons associated with jet fuel and chlorinated hydrocarbons.

INTRODUCTION

Collective Protection Systems (CPS) used by the Navy are designed to protect internal ship spaces from the introduction of toxic and lethal chemical compounds. The use of CPS allows Naval personnel to work/operate during periods of attack that could include the use of toxic materials such as chemical and/or biological agents. In order to properly assess the efficiency of performance of CPS, it is important to know the particulate and vapor challenges these systems will encounter. Thus, the U.S. Navy supports a "Shipboard Atmospheric Characterization Task" that seeks to identify the potential challenges (routine and non-routine) faced by the CPS, as well as the potential sources of these challenges. Surface ships (i.e., platforms) that perform special tasks or missions are candidates for sampling and/or monitoring within this characterization task.

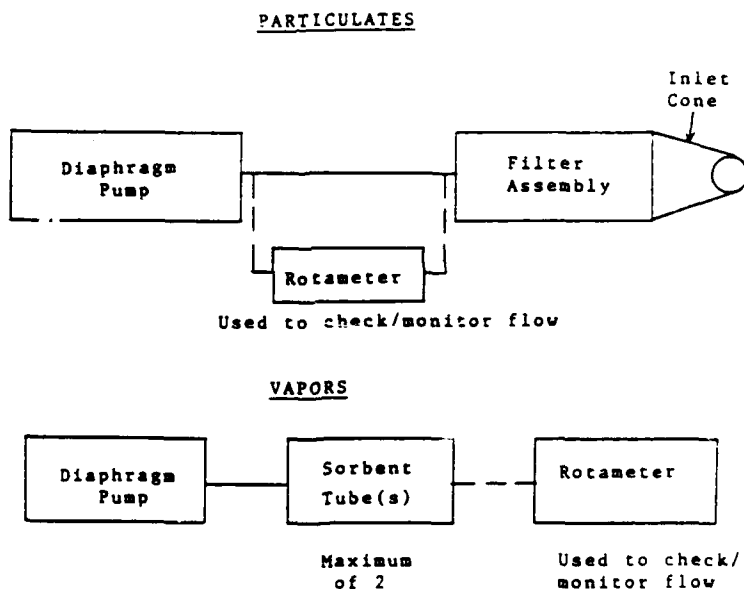
This paper outlines the results obtained from particulate and vapor monitoring performed aboard an aircraft carrier. In

addition, the analytical results for the vapors collected from this shipboard monitoring are compared with analytical results from filter media used in longer-term CPS applications.

EXPERIMENTAL AND ANALYTICAL METHODS

Figure 1 is a schematic of the sampling system used to collect both vapors and particulates. Because of shipboard space limitations, the sampling system was kept as simple and compact as possible.

Figure 1: Schematic of the Particulate and Vapor Sampling System



Particulate Collection

For particulate collection, the sampling train consisted of a filter assembly and a rubber diaphragm pump. The filter assembly consisted of a filter holder designed to support standard 47 mm diameter cellulose acetate membrane filters and a Teflon cone to control sample introduction. Two filters of differing pore size were employed back-to-back in each holder to effect two stage particle separation. The pore size of the front filter was 0.8 μm and the rear filter was 0.45 μm .

A Nikon phase contrast microscope, with magnification between 25 and 400, was used to examine the captured particulates. A calibrated reticle eyepiece was used to determine particle size.

Vapor Collection

For vapor collection, the sampling train consisted of a sorbent packed sampling tube(s) and a diaphragm pump. Each individual sorbent sampling tube contained two sections (i.e., front and rear). Coconut charcoal served as the adsorption medium. A maximum of two sorbent tubes in series was used.

Each section of an individual sampling tube was separately prepared for analysis. Preparation consisted of extracting the adsorbed chemicals from the sorbent with carbon disulfide (CS₂). A Varian gas chromatograph was used to initially screen and identify compounds in the extracts and a Hewlett-Packard gas chromatograph/mass spectrometer was used to confirm a compound's presence. Table 1 lists the conditions used for the two instruments.

TABLE 1
Conditions For The Two Analytical Instruments

INSTRUMENT:	<u>Varian</u>	<u>Hewlett-Packard</u>
MODEL	3700	5710A/5980A
COLUMN	0.21 mm, 50 m, OV-101, capillary	0.31 mm, 50 m, SP-2100, capillary
OVEN TEMPERATURE	Programmable, 4 min @45C, 5 deg/ min to 260C	Programmable, 11 min @50C, 4 deg/ min to 220C
DETECTOR	FID	MS
CARRIER GAS	Helium	Helium
FLOW (through column)	60 ml/min, 60 to 1 split, 1 ml/min	60 ml/min, 60 to 1 split, 1 ml/min

RESULTS AND DISCUSSION

Particulates

The particulates observed were carbon particles, sea salt crystals, metal fragments, yellow crystals and rust colored particles. The majority of the particles were carbon, less than 0.25 μ m in size and were deposited on the 0.8 μ m filter. Some carbon particles in the 0.25 to 0.75 μ m size range were also observed. Carbon particles greater than 1 μ m were not observed on any of the samples.

Varying sizes and shapes of sea salt crystals were also observed. The largest sea salt crystal was $9\text{ }\mu\text{m} \times 16.5\text{ }\mu\text{m}$. The metal fragments were all less than $5\text{ }\mu\text{m}$.

Individual particles were observed on filters from the majority of sampling locations. Mixing between different types of particles was evidenced in samples from a minority of locations. For example, in these minority of samples, sea salt crystals overlain with carbon particles were observed. These samples were representative of sites located away from direct aircraft exhaust. High volume sampler data is needed to validate and extend the measurements obtained to date.

Vapors

Figures 2 to 4 reproduce some of the chromatograms obtained from the CS₂ extracts. Movement of adsorbed chemical species through the sorbent tube is illustrated by Figures 2 and 3. Figure 2 is the chromatogram of the CS₂ extract from the front section and Figure 3 is from the rear section of the same sorbent tube. Notice that the rear section of the sorbent tube contains chemical species (see Table 2) not contained in the front portion. This is a good illustration of movement of adsorbed species through the sampling tube during the sampling period.



Fig. 2: GC of CS₂ Extract
From Front Section of
Carbon Sorbent Tube
(Sample A7-7-1F)



Fig. 3: GC of CS₂ Extract
From Rear Section of
Carbon Sorbent Tube
(Sample A7-7-1R)

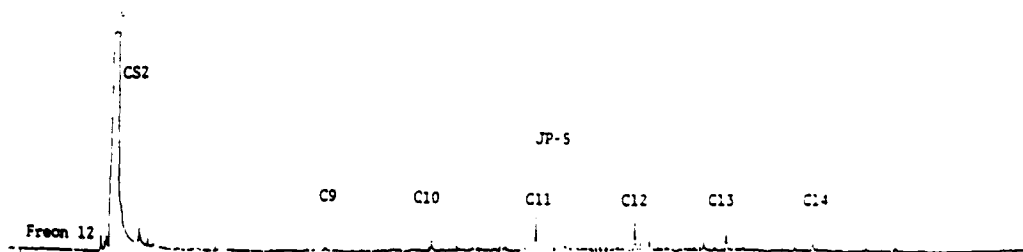


Fig. 4: GC of CS₂ Extract
From Carbon Sorbent Tube
(Sample A5-7-F)

Table 2 lists the compounds preliminarily identified from the sorbent tube sampling (e.g., Figures 2 to 4, as examples). Also given are the elution times and potential sources. These compounds can be associated with jet-fuel (JP-5); cleaning, aircraft repair and maintenance (Freon and chlorinated hydrocarbons) and aerosol can propellants (Freons). These compounds and the observed particulates represent some of the potential challenges to collective protection systems.

TABLE 2
Preliminary Compound Identification And Potential Sources

<u>Compound</u>	<u>Elution Time (min)</u>	<u>Potential Source</u>
CF ₂ Cl ₂ (Freon 12)	3.0 - 3.1	ACP
Freon (?)	3.16	
Freon (?)	3.2 - 3.25	
C ₂ F ₃ Cl ₃ (Freon 113)	3.25 - 3.35	CRM
CS ₂	3.4 - 3.5	(EXTRACTANT)
C ₂ Cl ₃ H ₃ (1,1,1)	3.98	CRM
?	4.3	
C ₂ Cl ₃ H	4.76	CRM
Aliphatic Hydrocarbons (C ₉ to C ₁₄)	10.45 - 26.4 (10.45, 13.95, 17.4, 20.63, 23.6, 26.4)	JP-5 FUEL

ACP = Aerosol Can Propellant

CRM = Cleaning, Aircraft Repair and Maintenance

Comparison of the carrier sampling results with analytical results from filters in-service for extended periods (i.e., however, not the same type of platform) do indicate differences. Particularly noteworthy is the absence of the most volatile compounds (Freon 12, 113, etc.) from the in-service filter results. The chlorinated hydrocarbon 1,1,1 trichloroethane is present in both environments, but appears greatly diminished in the filter environment. In the filter environment, xylene and JP-5 hydrocarbon components are the most prevalent compounds identified. To resolve the differences observed, it is recommended that both short-term atmospheric sampling and long-term atmospheric filtration be accomplished on the same platform.

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NRL Memorandum Report 6052

A System for Evaluating Sorbent Lifetimes

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September 17, 1987

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT (See page ii)	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) NRL Memorandum Report 6052		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Naval Research Laboratory	6b. OFFICE SYMBOL (If applicable) Code 6180	7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) Washington, DC 20375-5000		7b. ADDRESS (City, State, and ZIP Code)	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Naval Sea Systems Command	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) Washington, DC 20362-5101		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO. 64506N	PROJECT NO. S0410-SL
		TASK NO.	WORK UNIT ACCESSION NO. DN080-124
11. TITLE (Include Security Classification) A System for Evaluating Sorbent Lifetimes			
12. PERSONAL AUTHOR(S) Mamezko*, Richard A. and Little, Ralph C.			
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 10/84 TO 9/85	14. DATE OF REPORT (Year, Month, Day) 1987 September 17	15. PAGE COUNT 28
16. SUPPLEMENTARY NOTATION *GEO-CENTERS, Inc., Newton Centre, MA 02159			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		Adsorbent Dynamic adsorption	
		Test system	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
A modular laboratory test system has been assembled that has the flexibility to evaluate 1. Adsorbent materials—present and/or proposed, newly developed adsorbents. 2. Detectors—MOS, piezoelectric, chemiresistors, etc. 3. Vapor challenges—the effects on adsorption from both single and multiple challenges. Initial efforts have focused on using the system to determine effective residual service lifetime of a laboratory analog of a Collective Protection System carbon filter. A carbon bed was subjected to two different challenges and the concentration wave front was observed by strategic sampling of the flow at a location within the bed. The in-bed sampling was achieved by embedding a hypodermic needle which diverted a small flow through a MOS sensor external to the bed.			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL Ralph C. Little		22b. TELEPHONE (Include Area Code) (202) 767-2312	22c. OFFICE SYMBOL Code 6180

3. DISTRIBUTION/AVAILABILITY OF REPORT

Distribution authorized to U.S. government agencies only; test and evaluation; September 1987. Other requests shall be referred to the Commanding Officer, Naval Research Laboratory, Washington, DC 20375-5000.

Naval Research Laboratory

Washington, DC 20375-5000



NRL Memorandum Report 6282

Decontamination/Contamination Avoidance Solutions and Materials

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Chemistry Division*

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August 17, 1988

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
4. PERFORMING ORGANIZATION REPORT NUMBER(S) NRL Memorandum Report 6282			7a. NAME OF MONITORING ORGANIZATION		
6a. NAME OF PERFORMING ORGANIZATION Naval Research Laboratory	6b. OFFICE SYMBOL (If applicable) Code 6182	7b. ADDRESS (City, State, and ZIP Code)			
6c. ADDRESS (City, State, and ZIP Code) Washington, DC 20375-5000		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Naval Sea Systems Command	8b. OFFICE SYMBOL (If applicable)	10. SOURCE OF FUNDING NUMBERS			
8c. ADDRESS (City, State, and ZIP Code) Washington, DC 20362-5101		PROGRAM ELEMENT NO	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Decontamination/Contamination Avoidance Solutions and Materials					
12. PERSONAL AUTHOR(S) Taylor, R.G., Smidt, S., Matuszko,* R., Shirley, J. and Little, R.C.					
13a. TYPE OF REPORT Interim	13b. TIME COVERED FROM 8/86 to 8/87	14. DATE OF REPORT (Year, Month, Day) 1988 August 17		15. PAGE COUNT 214	
16. SUPPLEMENTARY NOTATION *GEO Centers, IHc.					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Decontamination Chemical agent defense		
			Sodium dichloroisocyanurate Navy decon formulation		
			C/W agent		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
Laboratory and literature investigations were conducted on the properties of oxidizers, surfactants and simulants in order to determine their suitability for use in a chemical agent decontamination formulation. Properties such as stability, compatibility, reactivity, pH and safety were examined. Sodium Dichloroisocyanurate in combination with the water soluble shipboard deck cleaner is recommended for further live agent testing.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL Randv Taylor			22b. TELEPHONE (Include Area Code) (202) 767-3556		22c. OFFICE SYMBOL Code 6182

Presented at the 1988 CRDEC Conference on Chemical Defense, Aberdeen Proving Ground, MD, November, 1988, proceeding published 1989, p. 285.

CHARACTERIZATION OF CONTAMINATED AIR PURIFICATION CARBONS

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and Richard A. Matuszko (2)

ABSTRACT

This study had two objectives; namely, identification of analytical methods for and characterization of air purification carbons exposed to contaminated environments. The two carbons examined were in an oceanic environment for periods of 7 and 31 months. Each exposed carbon filter was separated into three fractions perpendicular to the air flow. The analytical methods selected for characterizing the carbons include weight loss/density, pH, GC, GC/MS, DSC, TGA, and DMMP vapor challenge. Significant differences are observed both among the three fractions (intrasample) and between different in-service carbons (intersample). The changes observed as functions of time and location within the filter have important implications for shipboard air purification applications.

INTRODUCTION

The US Navy is planning and designing for increased use of Collective Protection Systems (CPS) onboard surface ships. These systems will be used to provide purified (filtered) air to internal ship spaces to maintain operations during attacks that could utilize CB agents. Prototype CPS use impregnated activated carbon and HEPA filters to remove vapors and particulates from influent air streams before passage to the inner ship spaces. However, the air in a shipboard environment can also contain potential filter contaminants from sources such as cleaning and maintenance operations, power plant operations, aircraft operations, missile firings, gunnery rounds, fires, etc. The impact of/from these challenges must also be identified if the Navy is to correctly predict the lifetimes and limitations of the HEPA and charcoal filters.

This study had two objectives: 1) selection of methods for carbon analysis, and 2) characterization of in-service air purification carbons. The initial group of analytical methods selected for carbon

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characterization were pH, gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), weight loss, and single/multiple vapor challenge tests. These tests have been used to characterize selected weathered and reference carbons.

The characterization of the two weathered TEDA impregnated ASC Whetlerite carbons (N-117 and # 9079) reported in this paper are from the USS BELLEAU WOOD prototype CPS. These carbons were removed from their containers in three layers perpendicular to the direction of air flow through the carbon bed. These layers have been designated as inlet (I), center (C) and outlet (O). The layered removal allows for examination of the filter medium for differences (i.e., contaminant distribution, adsorbent changes, etc.) within the filter.

EXPERIMENTAL PROCEDURES

WEIGHT LOSS: Fifteen gram samples of the selected carbons were placed in a Blue M box type muffle furnace at 150 deg.C for three hours. The samples were removed, cooled in a desiccator and reweighed. The difference in weight reflects primarily the loss of water from the sample.

GAS CHROMATOGRAPHY (GC) AND/OR MASS SPECTROMETRY (GC/MS): The atmospheric species adsorbed on the carbon during service were determined using GC and/or GC/MS. The GC utilized was a Varian Model 3700 with a flame ionization detector (FID). The GC/MS was an HP 5710A GC interfaced with an HP 5980A MS. The GCs, which were temperature programmed, utilized either a 50 m OV-101 or a 50 m SP-2100 capillary column. Sample preparation consisted of adding 0.6 gm of carbon to 3 ml of carbon disulfide. One microliter of the sample was injected into the GCs which were set with a 60 to 1 split ratio.

VAPOR CHALLENGE: The laboratory generated vapor challenges were controlled using an IBM PC-AT interfaced with an ISAAC I2000 data acquisition unit (Ref.3). The vapor challenge system was composed of air sources, bubblers, mass flow controllers and a Perkin Elmer Sigma 2000 capillary GC with FID. The adsorbent weight/volume was standardized by employing a 5.1 cm carbon bed depth in the sample module. Dimethyl-methyl phosphonate (DMMP) was employed as the vapor challenge.

THERMAL ANALYSIS (TA): TGA measures the weight loss of a sample as a function of temperature. DSC measurements determine the quantity of heat that carbons are able to absorb as a function of temperature. The DSC and TGA analyses were performed on a Perkin-Elmer System 7 Thermal Analysis (TA) system. A sample size of approximately 20 mg was used.

pH MEASUREMENTS: For pH determination, a 1 gram sample of carbon was added to 25 ml. of low megohm distilled water and the pH determined using an Orion Model 401 IONALYZER with a Fisher Pencil Combination 0-14 pH electrode. Stirring of the sample was accomplished with a Fisher Thermix Stirrer.

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RESULTS AND DISCUSSIONS

The two carbons that have been characterized were in an oceanic environment for periods of 7 (N-117) and 31 (# 9079) months. Both samples are TEDA impregnated ASC Whetlerite carbons. As seen in Table 1, there is a noticeable difference in the weight loss between the layers of each sample as well as between the samples. These two carbons were removed from the USS BELLEAU WOOD CPS at the same time so they experienced the same conditions over the last seven months (lifetime of N-117). The major weight loss is presently attributed to water found on the carbon. A portion of that weight loss is also due to the low molecular weight materials which can volatilize under the conditions of the weight loss experiments. The interesting feature to note is that there appears to be less water loss from the inlets of both samples and also a smaller weight loss for # 9079 in general. This is consistent with the fact that those portions of the carbon samples having a higher loading of adsorbed hydrocarbon materials should have less remaining capacity to adsorb water.

The GC measurements of the carbon disulfide extracts of N-117 and # 9079 clearly indicate that the identified adsorbed species (confirmed using GC/MS) are not homogeneously distributed within the filter. These adsorbed species can be classified into four chemical classes; namely, aliphatic hydrocarbons, aromatic hydrocarbons, halogenated alkanes/alkenes and substituted cyclohexanes/cyclohexenes. The chromatograms in figure 1 illustrate the differing chemical species on the three N-117 fractions. The least volatile compounds, including aliphatic C9 to C16 hydrocarbons (nonane to hexadecane), xylene and substituted aromatics, etc. are contained in the inlet fraction. The more volatile toluene, chlorinated alkanes and some aliphatic and aromatic hydrocarbons found in the outlet fraction are ready to be swept out of the filter.

Figure 2 illustrates essentially the same results for carbon # 9079 as for N-117 except that the adsorbed materials have migrated further into the carbon bed. Many of the heavier hydrocarbons found on the inlet portion of N-117 are now found in the center portion of # 9079. The same is true for the comparison between the center and outlet portions.

Differential Scanning Calorimetry (DSC) has been found to yield information about changes that have occurred on weathered carbons compared with unweathered reference carbon samples. All weathered carbons have dramatically increased endotherms compared with the unweathered reference carbons. Figure 3 illustrates the difference in heat absorption between weathered # 9087 and unweathered # 9039. Carbon 9087 is representative of a mixed 9000 series weathered carbon. The endotherm between 75 and 115 deg.C in # 9087 is probably associated with the 15 to 20% water content in the sample, while # 9039 contains 2 to 5% water. Between the two samples there are also differences due to the amount of adsorbed hydrocarbons. Other changes accounting for the steep heat absorption behavior above 125 deg.C warrant further investigation. To aid in this investigation, an analysis of the effluent from the TGA or DSC should be analyzed with FTIR, GC or GC/MS.

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The pHs of aqueous extracts of carbon samples N-117, # 9079 and their respective unweathered carbons are summarized in Table 2. One of the most interesting pH changes observed is associated with carbon N-117. Note that the inlet fraction is considerably more acidic (5.0) than the center and outlet fractions (7.8 and 7.9). This indicates that the center and outlet portions still resemble unweathered carbons. For the 9000 series, the inlet portion is similar to the N-117 inlet. However, the pHs of the center and outlet portions are very different from unweathered carbon.

The interesting questions of how acidic can the pH become and what causes the change in pH remain unanswered and need to be investigated further. The addition of organic acids (not found) or atmospheric acids (i.e., H_2SO_4) absorbing on/in the water adsorbed on the carbon is a possibility.

DMMP challenges were used to generate breakthrough curves and monitor the displacement of species previously adsorbed on the carbons. Since DMMP is a strong adsorber, it was anticipated that materials that were adsorbed less strongly could be displaced. As can be seen in figure 4, the inlet portion has only a hint of material being displaced. The large peak eluted is the DMMP challenge. The outlet and center portions are similar with the outlet portion having higher peak intensities. There is a peak present in the center portion chromatogram which is not present in the outlet portion. There is also the possibility that there are some peaks present under the DMMP peak. The second largest single peak has been preliminarily identified as n-decane. The use of multiple columns or different polarity columns should lead to the identification of these unknowns.

DMMP breakthrough curves were also generated for the fractions of N-117 and # 9079 and their reference carbons N-152 and # 9039 respectively. Figure 5 compares the breakthrough behavior for # 9039 and the fractions of # 9079. Note that # 9079 (I) exhibits a DMMP breakthrough time approximately one-half that of # 9039. The # 9079 (C) and # 9079 (O) breakthrough times are approximately three quarters that of # 9039 with the # 9079 (C) time shorter than the # 9070 (O) time.

CONCLUSIONS

A variety of characterization tests; namely, weight loss, pH, thermal analysis (TGA & DSC), GC, GC/MS, and single vapor challenge, have been employed to identify and determine the differences that exist among three fractions of two weathered carbons. It has been shown that a non-homogeneous distribution of materials is observed on the carbon bed and that this distribution changes with the weathering time. pH measurements of the water extracts of the carbons show increased acidity with weathering and also show variations within the bed. GC and GC/MS analysis of CS2 extracts of the carbons indicate that organic contaminants migrate non-uniformly within the carbon bed and influence carbon bed adsorption behavior and residual filter life.

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These results indicate that the carbon bed must be viewed as a dynamic system. The single vapor challenge has shown that weakly adsorbed materials can be displaced by strong adsorbers. This has important implications when considering the use of strong and/or weak adsorbers for compromising carbon beds. Characterizing the type, amount and distribution of the contaminants on weathered carbons is critical in evaluating and predicting residual filter life, carbon effectiveness and protection ability.

ACKNOWLEDGEMENT

The work reported in this paper was supported under Navy project element 63514N.

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TABLE 1
WEIGHT LOSS/DENSITY

	ORIGINAL	FINAL	WEIGHT LOSS
	gm/cc	gm/cc	%
N100 SERIES			
INLET	.832	.668	19.7
CENTER	.822	.635	22.7
OUTLET	.821	.627	23.6
VIRGIN	.644	.625	3.0
9000 SERIES			
INLET	.849	.717	15.6
CENTER	.821	.664	19.1
OUTLET	.811	.646	20.3
VIRGIN	.648	.615	5.1

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TABLE 2
pH OF WATER EXTRACTIONS

	N100 SERIES	9000 SERIES
INLET	4.9	4.9
CENTER	7.8	6.6
OUTLET	7.9	6.9
VIRGIN	8.1	7.9

FIGURE 1
CHROMATOGRAMS OF N117

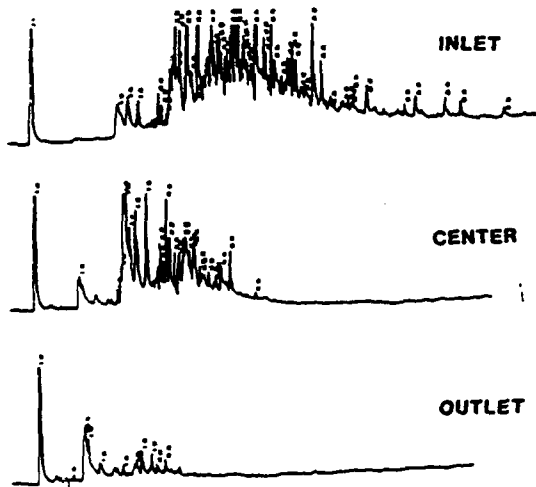
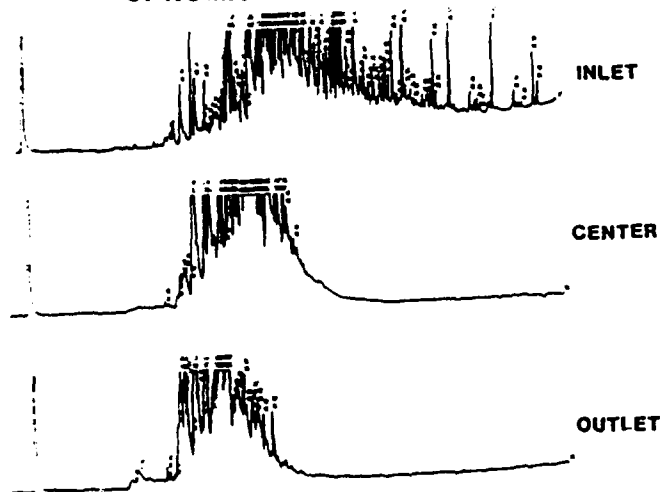


FIGURE 2
CHROMATOGRAMS OF 9079



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FIGURE 3

THERMAL ANALYSIS OF CPS CARBON #9087 AND 9039

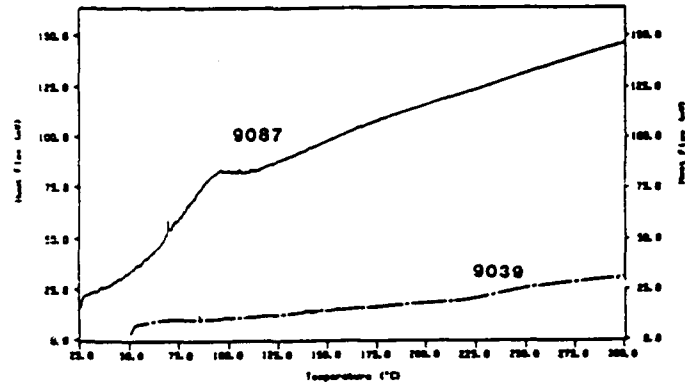


FIGURE 4

DMMP FLUSH OF 9079 CARBON

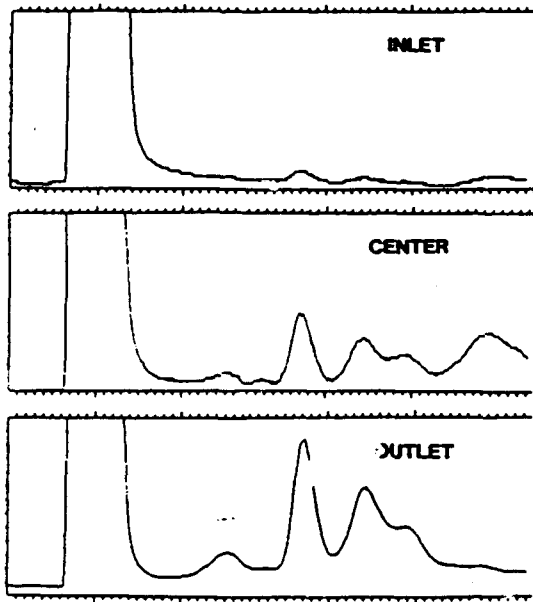
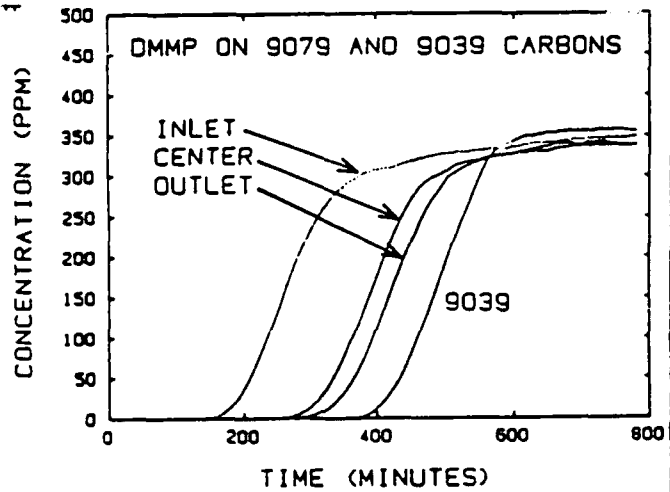


FIGURE 5



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Presented at the 1988 CRDEC Conference on Chemical Defense, Aberdeen Proving Ground, MD, November, 1988, proceeding published 1989, p. 293.

DYNAMIC ADSORPTION BEHAVIOR OF COLLECTIVE PROTECTION AIR FILTRATION CARBONS VERSUS A BINARY VAPOR CHALLENGE

Richard A. Matuszko (1), Louis Isaacson (1), and Robert A. Lamontagne (2)

ABSTRACT

The objective of this continuing study is the determination of the effects of binary vapor challenges on air purification carbons. The results reported here are for the vapors n-nonane and dimethyl methylphosphonate challenging TEDA impregnated carbon. The vapor pair was studied in a test matrix that included initial single vapor fractional pre-treatment of the carbon followed by single or binary vapor challenges. The temporal behavior of the effluent was continuously monitored using gas chromatography. Thus, breakthrough curves (adsorption/desorption information) were obtained simultaneously for both components.

The data indicates that the vapors tested compete for the same adsorption sites on the carbon. In the competition for adsorption sites, the stronger adsorber displaces the weaker adsorber. In selected cases, this displacement effect leads to concentrations in the effluent exceeding those in the influent (roll-up). The importance and implications of roll-up, partial bed contamination, and competitive adsorption of dissimilar compounds will be discussed.

INTRODUCTION

Air purification by vapor adsorption on activated carbon has been studied for many years. Most of the work, however, has centered around single component breakthrough studies because of the ease of measuring/determining vapor concentrations in the bed effluent. The bulk of the multi-component breakthrough research has been restricted to theoretical work. The actual laboratory work that has been done on multi-component, dynamic adsorption has focused on binary adsorption of compounds in a homologous series (Ref. 3,4). Since these challenge compounds demonstrate similar physical properties (i.e. polarity, diffusivity, structure, and volatility), it is expected that they will behave similarly in an adsorptive system.

To better understand competitive, multi-component, physical adsorption on activated carbon, it is necessary to study compounds that have different physical properties. If it is determined that two compounds are competing for the same adsorption sites, then any differences in the compounds' physical properties, can, if wisely selected, reveal information about adsorption and the adsorbent. For example, differences in adsorbate structure can be used to elucidate pore size effects by observing whether the adsorbent's micropore

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structure does/does not prevent the challenge vapors from reaching the common adsorption sites and displacing the vapor already adsorbed. In addition, differences in volatility and/or polarity of the adsorbates can yield insight into the specific adsorption equilibria associated with the adsorbate challenge.

Some past work has investigated binary vapor adsorption of dissimilar compounds on activated carbon in a flow system (Ref. 5-7). The work reported here expands on previous studies by examining the adsorption of the dissimilar compounds dimethyl methylphosphonate (DMMP), and n-nonane. DMMP represents a polar, low volatility molecule with a somewhat spherical shape, while n-nonane is a non-polar, higher volatility substance with a linear molecular form. From breakthrough curves generated for challenges of these two compounds, insight into the adsorption process and the carbon structure is sought.

EXPERIMENTAL

A computer controlled vapor mixing system was used to generate challenges to a carbon bed. The system used is described in reference (8). A 12-30 mesh TEDA impregnated ASC Whetlerized carbon was used for the studies. To obtain consistent packing of the bed, the carbon was added via a two foot free fall into a cylindrical glass tube. The glass tube had an inside diameter of 1.6 cm. The amount of carbon added was standardized at a bed depth of 5.1 cm which yielded a total bulk volume of 10.2 cc. Prior to use, the carbon was dried at 150 deg C for 3 hours. The total flow through the carbon was 2.5 l/min which yields a linear face velocity of 1250 cm/min.

For reference, single vapor challenges for both n-nonane and DMMP were performed to generate breakthrough/desorption curves and determine equilibrium capacities. A series of binary challenges were then investigated. The vapor pair was studied in a test matrix that included initial single vapor saturation of the carbon followed by single or binary vapor challenges. In addition, each carbon was 10% and 50% saturated with nonane and subsequently challenged by DMMP. Vapor challenges in all cases were generated at 350 ppm (v/v).

RESULTS AND DISCUSSION

Figures 1-7 show the plots of the effluent concentrations for the investigated vapor challenges on the TEDA impregnated carbon. Results for a series of analogous tests on a 12-30 mesh unimpregnated BPL carbon were reported in reference (9). The plots are labeled so that a "+" indicates that the two components were combined in the feed, and a "/" represents a change in feed conditions. For example, the figure 4 heading of "n-NONANE/n-NONANE+DMMP ON TEDA" indicates an experiment where the TEDA carbon is originally challenged with nonane followed by a combined nonane and DMMP challenge.

Baseline data for DMMP and n-nonane were established by challenging the carbon with 350 ppm(v/v) until saturation of the bed was achieved. Once equilibrium was established, the challenge vapor was turned off (7 hours for

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the nonane and 12 hours for the DMMP) and the bed was swept with clean dry air. The subsequent breakthrough/desorption curves for nonane and DMMP are figures 1 and 2, respectively. In both cases, it appears that the clean air is unable to effectively remove the adsorbate. Indeed, a mass balance shows that 85% nonane and 79% DMMP of the equilibrium adsorbate mass remains on the carbon after the clean air sweep.

The first multiple challenge experiment involved equilibrating the carbon with a nonane feed for 7 hours followed by a DMMP single challenge for 13 hours. The results, given in figure 3, indicate that the nonane desorption behavior is different than in the comparable clean air sweep of figure 1. It would appear that the DMMP is effectively removing the nonane from the carbon. A mass balance shows that 8% of the equilibrium nonane mass remains after 8 hours of DMMP sweeping in comparison to the 85% remaining mass for the analogous 8 hour clean air sweep of figure 1. In fact, at the end of the figure 3 experiment, less than 5% of the equilibrium mass of nonane remains adsorbed on the carbon. This nearly complete displacement of the nonane by DMMP implies that DMMP adsorbs on the same sites as nonane.

Figure 4 gives the results of a second binary challenge experiment where the carbon was equilibrated with a nonane feed for 7 hours followed by a combined nonane and DMMP challenge for 13 hours. As in the figure 3 experiment, the DMMP appears to be displacing the nonane from the carbon. This displacement, coupled with the nonane already present in the feed, creates a "roll-up" effect where the nonane effluent concentration exceeds its maximum feed concentration. In effect, the figure 4 system works to concentrate the nonane vapors in the air stream. A mass balance for the nonane shows that after 8 hours of combined DMMP and nonane sweep, 31% of the equilibrium nonane mass remains on the carbon. At the end of 13 hours, the nonane mass remaining on the carbon has been reduced to 21% of its equilibrium value.

In another series of experiments, the carbon was partially saturated with a nonane feed and subsequently challenged by DMMP. Figures 5 and 6 give the results of a 50% and 10% nonane saturation respectively. In figure 5, the nonane feed was removed and replaced by a DMMP feed at 2.5 hours. In figure 6, the feed switch was performed at 0.5 hours. In both experiments, a mass balance shows that less than 15% of the total nonane challenge remained adsorbed on the carbon by the end of the DMMP sweep.

Figure 7 gives the results of an experiment where the carbon was subjected to a combined nonane and DMMP feed. As in the figure 4 experiment, the nonane concentration in the effluent exceeds the feed concentration. The carbon is once again acting to concentrate the weaker adsorbing vapor in the effluent. The nonane is able to adsorb on the section of the carbon bed that the DMMP wave front has not reached. When the DMMP wave approaches, the nonane is displaced and is forced to readorb downstream. At the end of the bed, there is no carbon to readorb the nonane, so it is eluted. The nonane therefore travels at the leading edge of the DMMP wave front. This is evidenced in the two compounds having comparable breakthrough times at low concentrations.

One of the most interesting aspects of this binary challenge study is the difference observed in DMMP breakthrough behavior as a function of carbon.

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contamination and feed composition. Table 1 compares DMMP breakthrough times (i.e. time to reach 15 ppm DMMP in the bed effluent). At equilibrium, DMMP displaces nonane from the carbon quite effectively. However, during breakthrough experiments various rate effects become evident. The decrease in DMMP breakthrough times noted in Table 1 can be attributed to nonane reducing the DMMP adsorption rate.

TABLE 1

Comparison Of DMMP Breakthrough Times

Challenge	Breakthrough Time
DMMP	341 MIN
NONANE+DMMP	146 MIN
NONANE/DMMP	169 MIN
NONANE/NONANE+DMMP	104 MIN

CONCLUSIONS

The competitive adsorption between n-nonane and DMMP provides insight into the entire adsorption process. The displacement of nonane by DMMP indicates that the DMMP is adsorbed at the same sites where nonane adsorbs. This implies that the micropores in the carbon do not prohibit the flow of DMMP to sites available to the nonane.

The breakthrough curves for both components reveal dynamics of the nonane-DMMP adsorption system. When the challenges are combined, both components demonstrate similar breakthrough times, indicating that they travel as a combined concentration wave. Since DMMP displaces nonane, the nonane travels at the front of the DMMP concentration wave. In selected cases, the DMMP wave causes the nonane to "roll-up", resulting in effluent concentrations exceeding those of the feed. Additionally, nonane contamination of the carbon leads to a decrease in the DMMP adsorption rate and thus a reduction in the DMMP breakthrough time.

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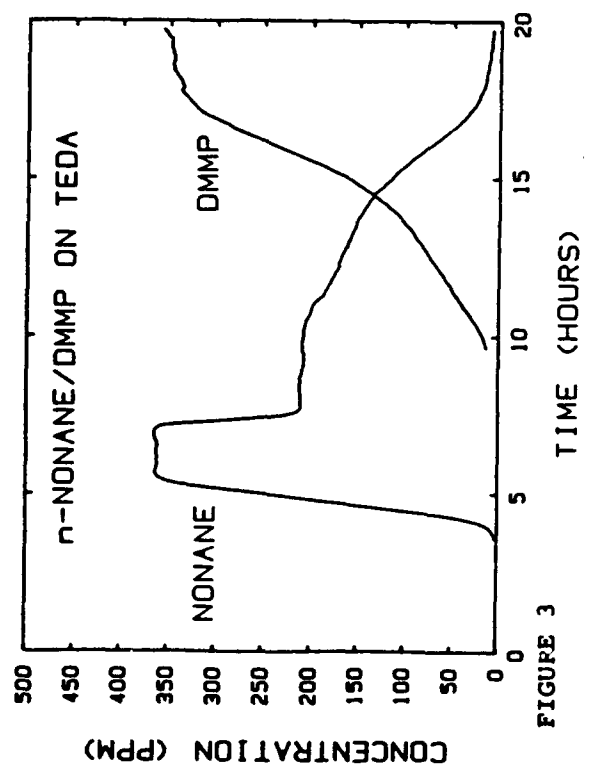
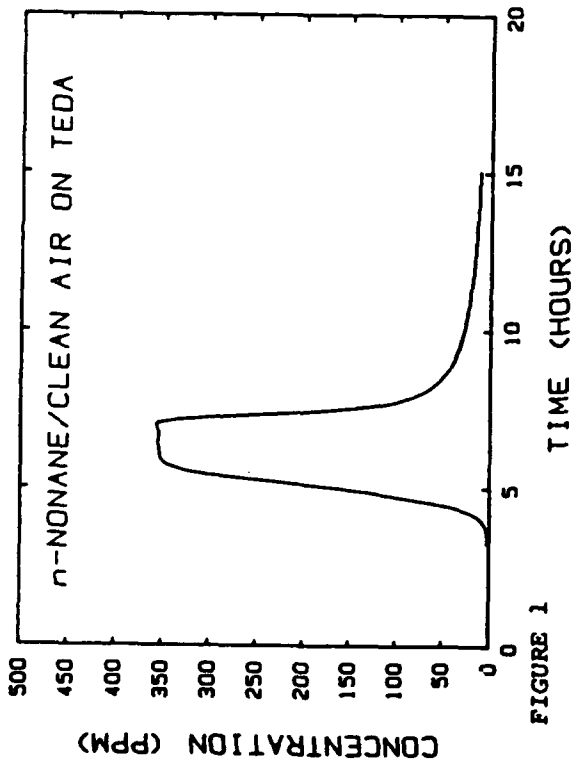
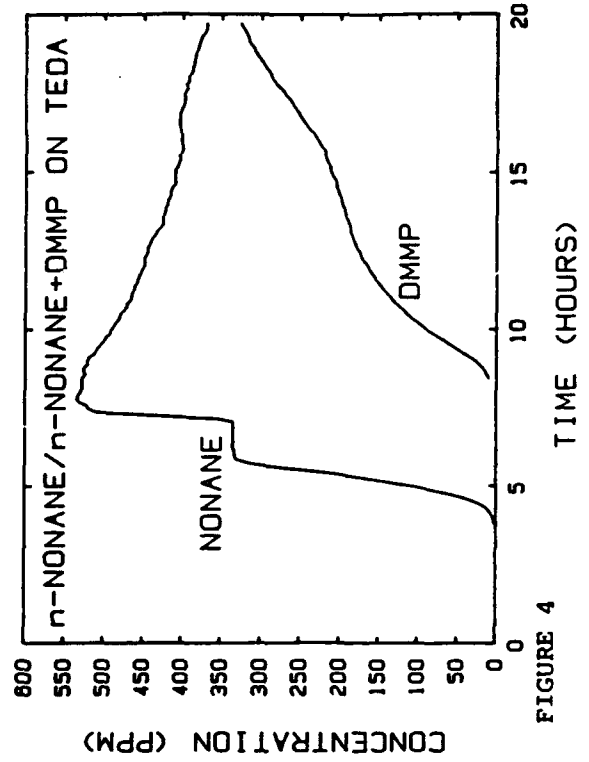
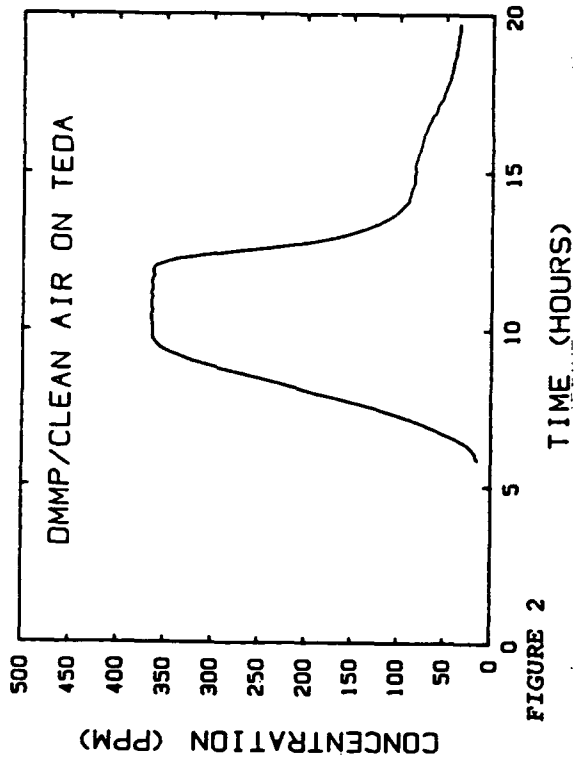
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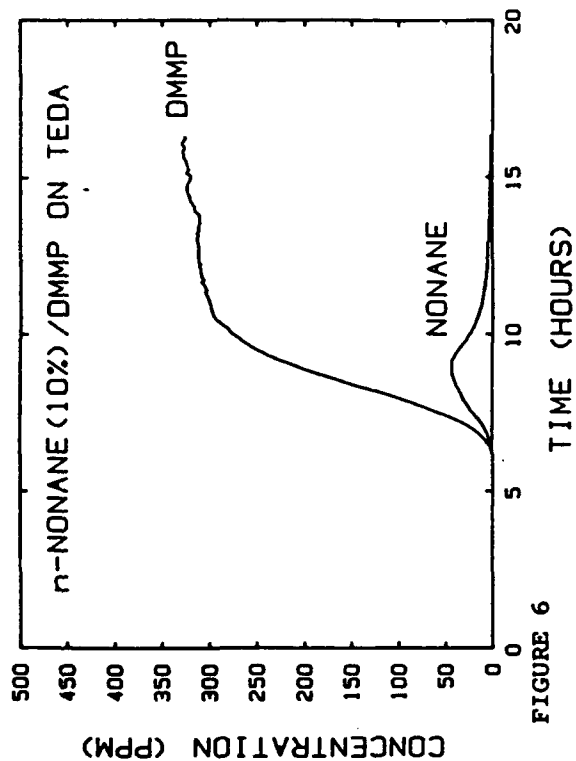


FIGURE 6

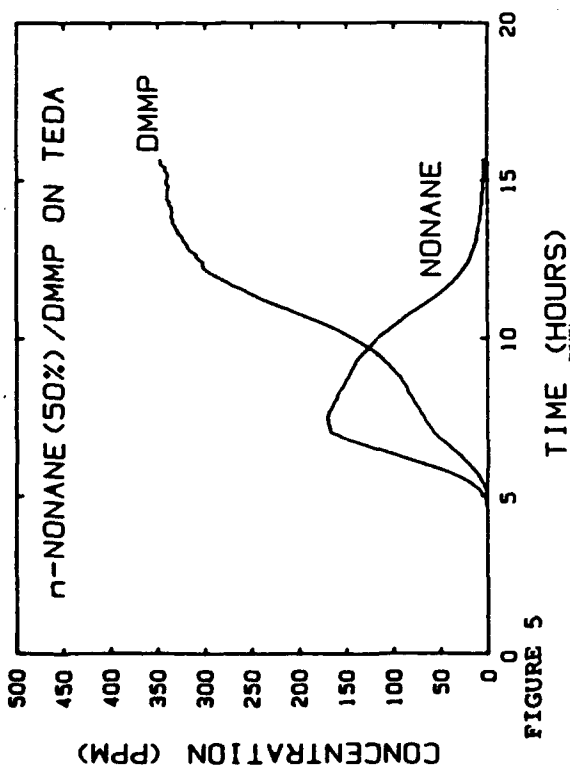


FIGURE 5

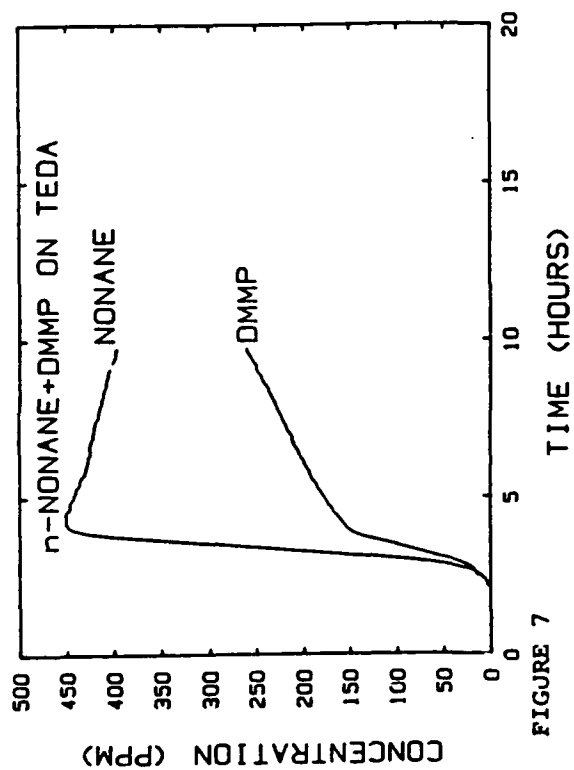


FIGURE 7

UNCLASSIFIED

Presented at the 1989 CRDEC Conference on Chemical Defense, Aberdeen Proving Ground, MD, November, 1989, to be published in proceedings.

CHARACTERIZATION OF A WEATHERED CARBON DISPLAYING AGGLOMERATION TENDENCIES

Robert A. Lamontagne (1), Richard J. Colton (1), Henry A. Hoff (1), Richard A. Matuszko (2), Louis Isaacson (2), and Joseph Rössin (3)

ABSTRACT

An air purification carbon weathered in a marine environment for a period of 21 months has been characterized. This weathered carbon was divided into four fractions and analyzed for moisture, pH, DMMP capacity, organic loading and impregnated metal speciation (XPS, EDX, SEM). The physical and chemical character of the agglomerated portion will be compared with the character of the other fractions.

INTRODUCTION

At the present time, activated carbon is the medium of choice for use in single pass air filtration systems. This carbon can be used in the natural state or impregnated with a variety of materials to enhance its filtration efficiency or reactivity. Depending upon the weathering profile that the carbon experiences, its filtration efficiency will vary. --

One environment that is extremely harsh is the marine environment. The presence of high relative humidities and associated marine atmospheric products presents unique problems not found in other air filtration environments and applications. To our knowledge, the effect of high relative humidities and environmentally produced marine materials on the impregnated metal species on the carbon has not been documented.

Impregnated carbons are presently being used in the Collective Protection Systems (CPS) onboard some Naval vessels. In addition to the marine environment, these carbons experience varied weathering regimes depending upon the mission of the ship. These in-service air purification carbons are routinely analyzed using a suite of analytical methods (4).

Upon retrieval of some of these carbons and subsequent downloading for analysis, it was noted that the carbon in the inlet portion of the carbon filter bed nearest to the metal retaining mesh had formed clumps. These clumps were easily broken with light pressure but still resistant to breaking with gentle handling. The present procedure for downloading the carbon filters is to apportion the carbon into three sections perpendicular

to the direction of air flow. These three fractions have been labeled inlet, center and outlet. In the situation where clumps were noticed, a fourth fraction was created and labeled "clump".

Upon drying the carbon for moisture content, it was noticed that the carbons from the filters which exhibited clumping displayed a whitish or grayish coating on the clumps and on a percentage of the loose carbon particles. This whitish coating had been observed previously on carbons which did not show/produce clumps. The percentage of non-clumped carbon particles which were coated was very small, usually less than 1% of the carbon present.

It was decided to view these clumps and some of the individual carbon particles that exhibited the whitish coating under a low power microscope. It was clear that some form of crystalline structure was present on the surface of the carbon particles. A decision was made to examine the carbon fractions with scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX) and x-ray photoelectron spectroscopy (XPS) in addition to the standard characterization analyses normally performed.

This paper addresses the characterization results of one air purification carbon that has been weathered in a marine environment. It should be noted that a number of other carbon filters also show clumps or exhibit a tendency to produce clumps. This is deduced from carbon particles which produce a whitish coating upon drying. Isaacson et. al.(5) in a companion paper in the proceedings, will discuss the changes in metal impregnation in more detail.

EXPERIMENTAL

The characterization analyses usually performed on the carbon samples have been reported previously (4), but will be briefly reviewed:

WEIGHT LOSS: Samples are weighed, heated in a box type muffle furnace for three hours, cooled in a desiccator and reweighed.

pH MEASUREMENTS: Weighed carbon samples are placed in a known volume of doubled distilled water and the pH determined with a pencil combination 0-14 pH electrode.

ORGANIC LOADING: The atmospheric organic species adsorbed on the carbon during service were determined by extracting a weighed sample of carbon in a measured volume of carbon disulfide then analyzed using a capillary gas chromatograph with a flame ionization detector.

DMMP CHALLENGE: Carbon samples are subjected to a DMMP vapor challenge and the effluent profile analyzed. The complete vapor generation system is detailed in the report by Matuszko and Little (6).

The surface analyses performed to characterize the surface of the carbons were:

- 1) The EDX experiments were performed with a Princeton-Gamma Tech (PGT) System 4 Plus windowless detector mounted on a Hitachi S 800 scanning electron micrograph. The SEM electron accelerating voltage was 10 kV. The carbon samples were placed on stainless steel mounts for analysis.
- 2) The XPS experiment was performed with a Surface Science Laboratory SSX 100-03 spectrometer using a monochromatized Al K α x-ray source (1486.6 eV). The carbon clump was placed onto a piece of indium foil.

RESULTS AND DISCUSSION

The carbon being discussed has been weathered in a marine environment for a period of 21 months. Table 1 shows the weight loss for the inlet, center and outlet portions of the weathered carbon as well as for a reference carbon. Note that major weight loss occurs in all portions of the sample, with the center and outlet sections slightly exceeding the inlet section. This behavior is typical of most weathered carbons we have examined. The major weight loss is presently attributed to water with a portion also due to the low molecular weight organics present.

TABLE 1

WEIGHT LOSS

INLET	18 %
CENTER	21 %
OUTLET	23 %
REFERENCE	3 %

Figure 1 shows the degree of whitish coating appearing on the surface of the carbon particles in the inlet portion. The outlet portion does not exhibit carbon particles with the whitish coating. The center portion contains a few whitish particles which are probably due to contamination from the inlet portion during downloading from the filter. Other carbon filter samples in which a very small percentage of coated carbon particles was evident in inlet fraction after heating did not exhibit any evidence that there was intermixing between the fractions. This may very well be a case where the percentage of coated particles is too small to become identifiable in the center section. In no samples have any coated particles been found in the outlet portion.

Table 2 gives the results for pH, color of the water solution of the carbon and the surface area for each fraction of carbon (5). The several reference carbons (unweathered carbon from the same lots) used in the filters have pH's in the range 7.9 to 8.1. The reference carbon for this sample has a pH of 8.1. The clump carbon water extract is much more acidic than the other fractions. Note the progression from an acidic nature in the clump to a neutral condition or slightly alkaline condition in the outlet.

TABLE 2
pH ANALYSIS

SAMPLE	pH	COLOR	AREA (M2/GM)
CLUMP	3.9	BLUE/GREEN	37
INLET	4.7	CLEAR	241
CENTER	6.9	CLEAR	~~492~~
OUTLET	7.6	CLEAR	611
REFERENCE	8.1	YELLOW/GREEN	712

There is also a very dramatic color change for the water solutions of these carbon extracts. The reference carbon (unweathered) has the characteristic yellow/green color while the weathered carbons produce a clear solution which is consistent with the results from other weathered carbons. It has been found that a weathering time of four to six months produces a clear solution. Weathering times of less than four months produce degrees of the yellow/green color. The clump sample produces a blue/green color. This color is consistent with the preliminary XPS and EDX analysis.

The surface area results are given as additional evidence that there are very dramatic differences within the filter bed. The reference carbon exhibits an acceptable surface area for a TEDA impregnated carbon. The surface area decreases as the bed is traversed from the outlet to the inlet. There is approximately a 75 % decrease in the surface area between the inlet and outlet. The clump sample represents a special case. It can be stated that this portion of the filter has little or no filtration capacity with a surface area of only 37 square meters per gram.

Figure 2 presents the gas chromatographic results from the organic loading analysis. The adsorbed species can normally be classified into four major chemical classes; namely, aliphatic hydrocarbons, aromatic hydrocarbons, halogenated alkanes/alkenes and substituted cyclohexanes/cyclohexenes. Previously published results (4) for other carbon samples show the same type of hydrocarbon distribution with the higher boiling materials located on the inlet portion of the bed such as aliphatic C10 to C16 hydrocarbons, and substituted aromatics. The outlet sample contains the more volatile materials such as toluene, xylene, chlorinated alkanes and some aliphatic (C9-C11) hydrocarbons. The center fraction represents a transition between the inlet and outlet in regard to the type of organic loadings identified.

Figure 3 compares the chromatogram of the inlet sample with the clump sample. There is a distinct difference in the hydrocarbon distributions on the two samples. The clump sample has predominately higher boiling compounds with much greater intensities than the inlet sample. The clump sample also exhibits a step series of hydrocarbon peaks starting with C10 and progressing to C16 (n-hexadecane). The inlet sample has C11 and C12 as its two most intense peaks. This distribution of hydrocarbons gives some indication of the types of changes that have taken place on the surface of

the carbon. The more volatile species (xylene, toluene, nonane) are not able to adsorb on to the inlet carbon surface because of the high boilers strongly adsorbed onto this portion of the carbon filter. This analysis is consistent with the smaller weight loss in the inlet portion with the assumption that those portions of the bed having a higher loading of adsorbed hydrocarbons should have less capacity to adsorb water vapor.

DMMP challenges are used to generate the breakthrough curves of figure 4. The reference carbon exhibits a breakthrough time of approximately 8 hours for the DMMP challenge used. The ~~inlet sample~~ has a much reduced capacity for DMMP as evident in the breakthrough time of approximately 3 hours. This is consistent with the organic loading results which indicate a high level of high boiling, strongly adsorbed organic materials on the carbon. The center and outlet samples have intermediate times consistent with the characterization results obtained. The center breakthrough time occurs slightly earlier than the outlet one.

Upon observing the clump samples under a low power microscope, small crystals were observed on the surface. These crystals appeared to dehydrate under the optic light of the microscope in about two hours and produced the whitish coating observed when the samples were dried in the oven. Preliminary XPS analysis indicated that the crystals on the surface were copper sulfate with five waters of hydration (Fig.5). SEM photographs coupled with (EDX) analysis are consistent with the presence of copper sulfate on the surface. The preliminary EDX analysis indicates that most of the surface of the carbon in the clump sample is covered with copper sulfate. No copper sulfate was found in the other portions of the bed. As expected, individual carbon particles with the whitish coating also had copper sulfate present on the surface.

The XPS and EDX analysis presents clear evidence that copper sulfate is present on the surface of the carbon in the clump samples. This is consistent when the clump samples are placed in water since the characteristic blue/green color of copper sulfate is observed. Surface area analysis indicates that there is minimum surface area available for adsorption to take place. The gas chromatograph results indicate a variable, but predictable organic distribution adsorbed onto the surface of the carbon. The organic species identified on the clumps and inlet portions represent high boiling, strongly adsorbing hydrocarbons. The clump sample is different from the rest of the carbon in the bed. Weight loss and DMMP challenge have not been performed on the clumps because of the difficulty in obtaining a large enough quantity to perform the analysis. However, we believe that the results from these analyses would support the general consensus that the clump samples and those carbon samples that exhibit a whitish coating upon drying would be uniquely different from the bulk carbon.

How copper sulfate is produced on the surface of the carbon is speculative at the present time. Exposure to a marine environment with high relative humidities must be taken into consideration as well as the presence of acid rain as a source of sulfate for the clumping phenomena. Remote marine aerosol particles consist primarily of sulfates and sea salts (7). It is generally assumed that the sub-micron fraction of the sulfate particles are formed in a gas-to-particle conversion process by oxidation

of marine sulfur dioxide (8). There is sulfur present in the carbon, but the amount present is insufficient to produce the amount of copper sulfate present on the surface. The mechanism(s) which produce copper sulfate on the surface of the carbon is being investigated.

CONCLUSIONS

The results of the analyses for this carbon show: 1) copper sulfate is formed on the clump and inlet portion of the bed with subsequent loss of adsorption capacity and reactivity; 2) higher boiling, strongly adsorbing hydrocarbons keep water from adsorbing in the inlet region of the bed; 3) organic contaminants migrate non-uniformly within the carbon bed; 4) pH measurements show the inlet portion of the bed to be acidic while the outlet portion is in the neutral range.

The differences documented for the various fractions of the bed indicate that these changes can have a profound effect on the filter bed. The cumulative results effectively decrease the bed depth and overall efficiency of the filter. Characterizing the type, amount and distribution of the contaminants on weathered carbons is critical in evaluating and predicting residual filter life, carbon effectiveness and protection ability.

ACKNOWLEDGEMENT

This work was supported under Navy project element 63514N.

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FIGURE 1

SAMPLE AFTER DRYING

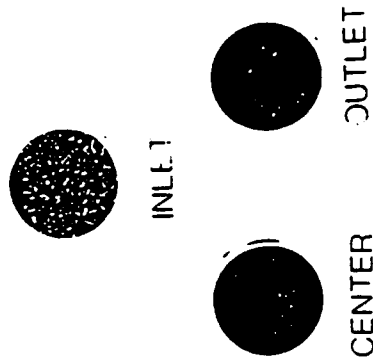


FIGURE 2

CHROMATOGRAM OF CARBON DISULFIDE
EXTRACT OF CARBON SAMPLE

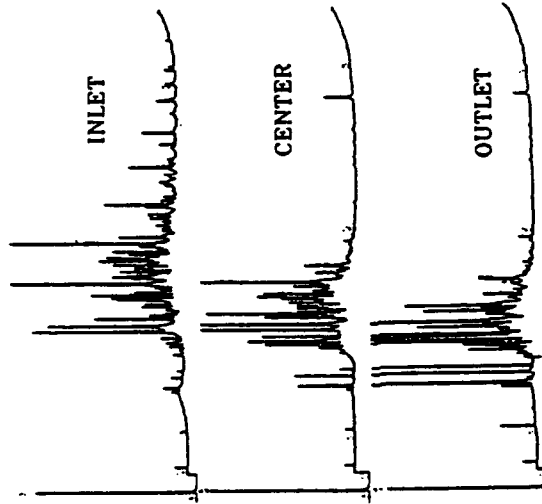


FIGURE 3

CHROMATOGRAM OF CARBON DISULFIDE
EXTRACT OF CARBON SAMPLE

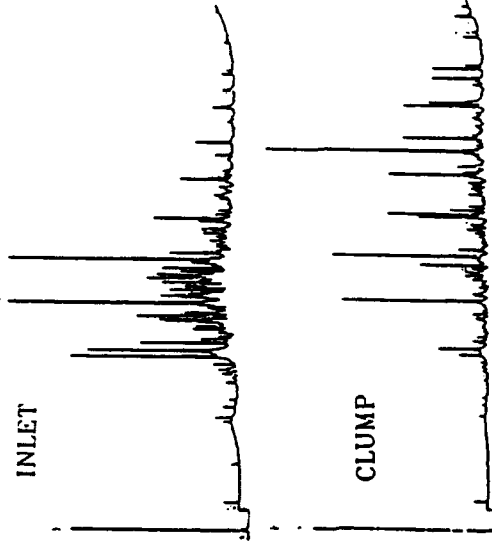


FIGURE 4

DMMP ON N-100 SERIES CARBON
350-370 PPM CHALLENGE

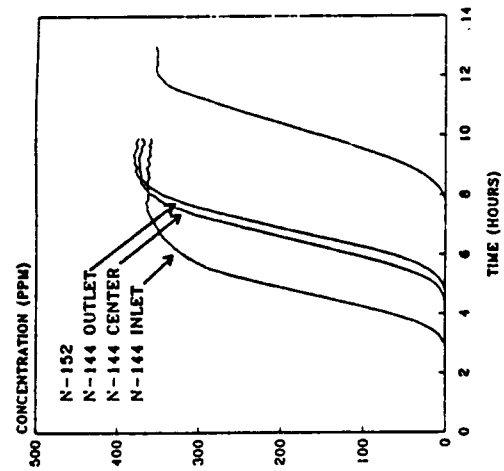
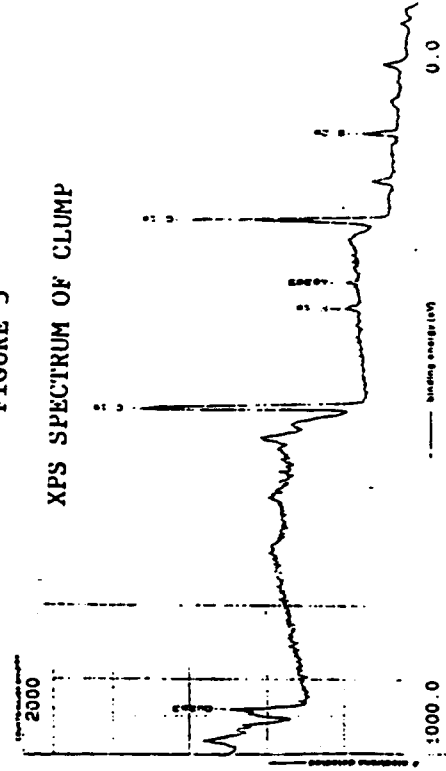


FIGURE 5

XPS SPECTRUM OF CLUMP



Presented at the 1989 CRDEC Conference on Chemical Defense, Aberdeen Proving Ground, MD, November, 1989, to be published in proceedings.

SINGLE AND BINARY ADSORPTION OF n-NONANE AND XYLENE ON BPL CARBON

Richard A. Matuszko¹, David K. Friday¹, Louis Isaacson¹,
and Robert A. Lamontagne²

ABSTRACT

Single component isotherms are measured for n-nonane and xylene on BPL carbon using an automated, static adsorption apparatus. The isotherm data are correlated using a modified Antoine equation. A Binary adsorption isotherm relationship is produced from the single component correlations using the Ideal Adsorbed Solution Theory (IAST). Breakthrough curves are measured for single vapor and selected binary mixture feeds. A computer stage model, integrating the correlated single isotherms and IAST binary isotherm, is used to predict both the single and binary component breakthrough curves. The model predictions are compared with the measured breakthrough data.

Single component breakthrough data show that xylene breaks through later than nonane under identical test conditions. However, measured binary breakthrough data with equimolar feeds show a roll-up of xylene. The stage model predicts this xylene roll-up. The phenomenon of roll-up and the concept of selectivity reversal for a binary system is investigated.

INTRODUCTION

For many years, researchers have sought to unlock the secrets of multi-component equilibria. Because of the difficulties involved with measuring multi-component data, research has centered on creating adequate predictive models using information obtained from single component data. Langmuir's extended isotherm³ was the first of the multi-component, predictive isotherm models. It suffered, however, from its very limited applicability due to its poor fit of even the single component data.

In 1965, Myers and Prausnitz⁴ developed the Ideal Adsorbed Solution Theory (IAST) which allowed the use of any single component isotherm equation to predict multi-component isotherms. In 1980, Suwanayuen and Danner⁵ introduced the Vacancy Solution Theory (VST) which correlated single component data into their single component isotherm model and extended it to a multi-component isotherm. Both theories were effective in predicting isotherms for selected multi-component systems, but began to lose appeal when their limitations were investigated. The VST was not thermodynamically consistent, and forced the user to use a specific single component isotherm

model. The IAST was thermodynamically consistent and allowed any single component isotherm equation to be used, but suffered from its inability to predict systems where the adsorbed phase was non-ideal.

To address the imperfections of the IAST, modifications were performed using binary data to calculate mixing parameters such as activity coefficients. Although these modifications improved the accuracy of the multi-component isotherm fits, and have great utility in many applications, they stray from the original purpose of the predictive model. The IAST was originally proposed to avoid the tedious task of measuring multi-component data and provide an adequate engineering approximation of the multi-component adsorption isotherm.

Some attempts to modify IAST have, in fact, led to erroneous applications of mixing parameters. Assumptions that non-idealities of mixing are the answer to imperfect multi-component fits of the IAST have led to the incorrect calculation of activity coefficients. Myers⁶ shows that failure of the IAST to accurately predict multi-component isotherms in a number of systems is not due to non-unity activity coefficients, but due to the inadequacy of the single component isotherm model employed.

It has been further claimed that IAST does not, and in fact can not, predict irregular isotherm behavior such as the formation of azeotropes. Hyun and Danner⁷ and Coroyannakis⁸ each state that IAST can not predict an adsorption azeotrope and selectivity reversal. Myers, with his Heterogenous IAST⁹, shows that a selectivity reversal can be predicted with the IAST if the correct single component isotherm model is employed.

This paper proposes that using the modified Antoine equation first proposed by Hacskaylo and LeVan¹⁰ to correlate single component isotherm data, IAST can and will predict a selectivity reversal for a binary system. The adsorbate pair of xylene and n-nonane on BPL carbon is investigated and shown to yield a selectivity reversal. IAST is applied and yields a qualitative prediction of the selectivity reversal.

THEORY

First, isotherm data are correlated using a modified Antoine equation first proposed by Hacskaylo and LeVan¹⁰. The equation has the form:

$$\ln(P_i) = A_i + \ln(\theta_i) - \frac{B_i + b_i(1 - \theta_i)}{C_i + T} \quad (1)$$

The Antoine coefficients are readily found in the literature. The parameters b and the normalizing factor for θ_i ($n_{0,i}$) are fit using a Newton-Raphson routine to minimize the function:

$$\text{Error} = \sum (|\ln(P_{\text{calculated}}) - \ln(P_{\text{experimental}})|) \quad (2)$$

Binary isotherms are generated using the Ideal Adsorbed Solution Theory (IAST) with the LeVan isotherm equations for each component. It should be noted that the IAST can be readily extended to more than two

components. However, for this paper, we are confining the analysis to two components. Details of the IAST are given in reference 4.

The LeVan isotherm is particularly well suited for adaptation into the IAST because it reduces to Henry's law at low coverage. In addition, for computer programs that use values of n_1 to calculate values of P_1 , the IAST-LeVan isotherm system reduces to easily calculable explicit functions. The IAST spreading pressure integral,

$$f_1(\tau) = \int_0^{n^*_1} \frac{d \ln P}{d \ln n} dn \quad (3)$$

when combined with equation (1), reduces to the form:

$$f_1(\tau) = n^*_1 + \frac{b_1 n^*_1{}^2}{2n_{0,1}(C_1 + T)} \quad (4)$$

The spreading pressure functions of equation (4) are then set equal for each component yielding:

$$n^*_1 + \frac{b_1 n^*_1{}^2}{2n_{0,1}(C_1 + T)} = n^*_2 + \frac{b_2 n^*_2{}^2}{2n_{0,2}(C_2 + T)} \quad (5)$$

Equation (5) is solved simultaneously with the IAST requirement that there is no change in the area/molecule on mixing:

$$\frac{1}{n_1 + n_2} = \frac{x_1}{n^*_1} + \frac{x_2}{n^*_2} \quad (6)$$

to yield explicit solutions for n^*_1 and n^*_2 as functions of n_1 and n_2 . Corresponding values of P^*_1 and P^*_2 are readily obtained using equation (1) substituting n^*_1 and n^*_2 for n_1 for each single component isotherm. Finally, using the IAST vapor phase - adsorbed phase equilibrium expression:

$$P_i = x_i P^*_i \quad (7)$$

the vapor phase concentrations P_1 and P_2 are obtained.

Breakthrough curve predictions are generated using a stage model similar to that employed by Friday and LeVan¹¹. It is assumed that the system is isothermal with no axial dispersion and negligible vapor phase accumulation. An external film resistance is employed using a linear driving force approximation.

SELECTIVITY REVERSAL

The spreading pressure integral in equation (3) is equivalent to the area under an isotherm curve from 0 to P^*_1 plotted as n vs $\ln P$ as shown in Figure 1. An equilibrium requirement of the IAST is that the spreading pressures, and thus the areas under the isotherm curves bounded by 0 and

P^*_1 , be equal. Since the isotherm equations are fixed for each system, areas under the curves are varied by selecting values of P^*_1 such that the spreading pressure integrals for each component are equal.

In certain binary adsorption systems, the Henry's law slope for component 1 is greater than that of component 2 while the molar saturation capacity, $n_{0,1}$, is greater for component 2 than for component 1. In these situations, the single component isotherms cross. In selected cases, to achieve equal areas under the n vs $\ln(P)$ curve as required by the IAST, the relative values of P^*_1 and P^*_2 must reverse. Myers and Prausnitz define a selectivity⁴, $s_{1,2}$:

$$s_{1,2} = \frac{x_1/y_1}{x_2/y_2} = \frac{P^*_2}{P^*_1} \quad (8)$$

From this definition, it follows that a reversal in the relative magnitudes of P^*_1 and P^*_2 results in a reversal of the selectivity $s_{1,2}$ (i.e. $s_{1,2} > 1$ to $s_{1,2} < 1$).

EXPERIMENTAL

MATERIALS

The adsorbent used for these experiments was a 12-30 mesh BPL carbon obtained from Calgon corp. The carbon was prepared prior to use by heating in a drying oven for 3 hours at 150 degrees C. The adsorbates selected for the experiments were n-nonane (Phillips 66, 99% purity) and a xylene mixture containing meta, para, and ortho isomers (Fisher Scientific, A.C.S. certified grade). These adsorbates were used without further purification.

DATA COLLECTION

The experimental apparatus for collecting isotherm data consisted of a Cahn micro-balance integrated with a vacuum pump and a computerized data acquisition and control system. Details of the system and operating procedure can be found in reference 12.

A computer controlled system was employed to generate and test vapor challenges to a fixed bed of the BPL adsorbent. The amount of carbon added was standardized at a bed depth of 1 cm. Details of the system and operating procedure can be found in reference 13.

RESULTS AND DISCUSSION

A prediction of the isotherm behavior for the xylene/nonane system was generated using the IAST-LeVan binary isotherm model. Figure 2 is a plot of the prediction which shows that the IAST predicts a selectivity reversal for the binary pair. The line in Figure 6 represents the concentrations of xylene and nonane where the selectivity is one. According to this prediction, if a breakthrough experiment was performed using feed concentrations on the left side of the unity selectivity line, xylene should roll-up. If, however, the feed concentrations were to the right of the unity selectivity line, nonane should roll-up.

In an attempt to confirm the predicted selectivity reversal, breakthrough experiments were run using feed conditions on either side of the line of equal selectivity. Figure 3 gives the results of the first of the binary challenge experiments. The stage model prediction using the IAST is also shown on the plot. Xylene and nonane at 200 ppm each were fed simultaneously to a clean bed of BPL carbon. According to the IAST isotherm prediction, the data should exhibit a roll-up of xylene. It can be seen that both the data and the stage model show a roll-up of xylene. Important features such as time of initial breakthrough of the toe of each wave as well as the qualitative features of the roll-up phenomenon are predicted by the stage model.

Breakthrough experiments were then run with very high feed concentrations to confirm that a selectivity reversal would indeed occur. Figure 4 gives the results of a breakthrough experiment with an equimolar feed of xylene and nonane of 3000 ppm. As the IAST isotherm predicts, the selectivity has reversed and the nonane is rolled-up by the xylene.

The failure of the IAST-LeVan isotherm to predict exact breakthrough behavior of a binary pair that demonstrates the non-idealities found in the nonane/xylene system does not in any way reflect poorly on the theory as a whole. Considering that the isotherm prediction uses no fitted binary parameters, is considered ideal, and uses no low coverage isotherm data, the ability to qualitatively predict binary breakthrough behavior when combined with the stage model is quite remarkable.

CONCLUSIONS

1. The IAST can predict selectivity reversals if the proper single component isotherm model is used.
2. For a selectivity reversal to occur in the IAST, the single component isotherms must cross in a plot of moles/mass carbon versus partial pressure.
3. Engineering predictions of binary component breakthrough behavior can be performed using single component isotherm data.

NOTATION

A_i, B_i, C_i	-	Appropriate Antoine coefficients for component i
b_i	-	LeVan equation fitting parameter for component i
$f_i(\tau)$	-	spreading pressure function for component i
n_i	-	number of moles of component i in adsorbed phase per unit mass of adsorbent in equilibrium with P_i
$n_{0,i}$	-	saturation capacity of adsorbent for component i per unit mass of adsorbent
n^*_i	-	number of moles of component i in adsorbed phase per unit mass of adsorbent in equilibrium with P^*_i
P_i	-	partial pressure of component i

P^*_1	-	pressure of pure component 1 corresponding to spreading pressure τ in equilibrium with n^*_1
$s_{1,2}$	-	selectivity coefficient for component 1 relative to component 2
x_1	-	mole fraction of component 1 in adsorbed phase
y_1	-	mole fraction of component 1 in gas phase
τ	-	spreading pressure
θ_1	-	$n_1/n_{0,1}$ - fractional surface coverage

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EVALUATION OF SPREADING PRESSURE
MOLES/Kg CARBON vs LOG PARTIAL PRESSURE

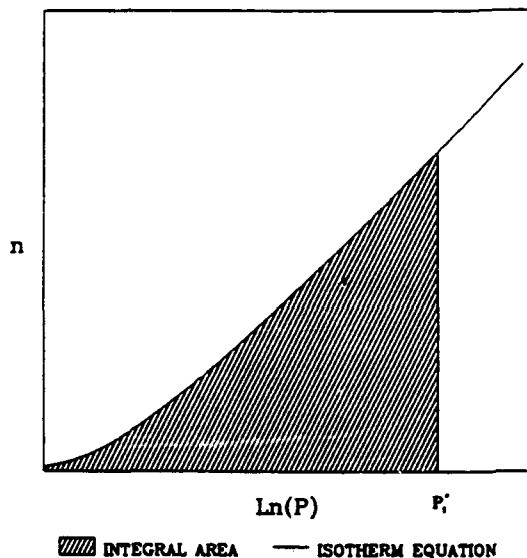


FIGURE 1

SELECTIVITY OF XYLENE AND NONANE
ON BPL CARBON
25 deg C

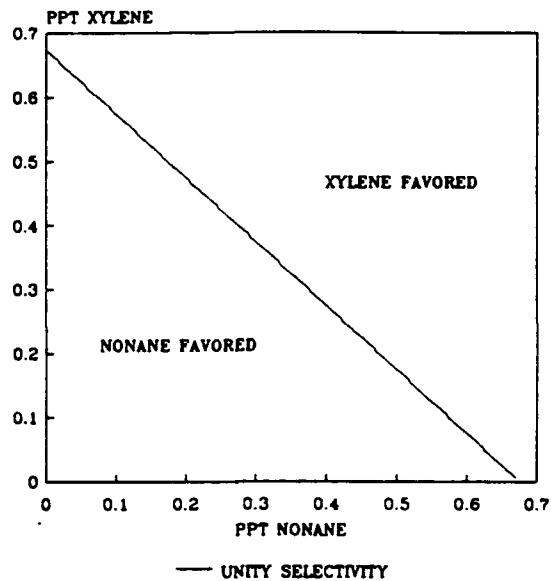


FIGURE 2

XYLENE AND NONANE ON BPL CARBON
200 PPM CHALLENGE
25.7 deg C

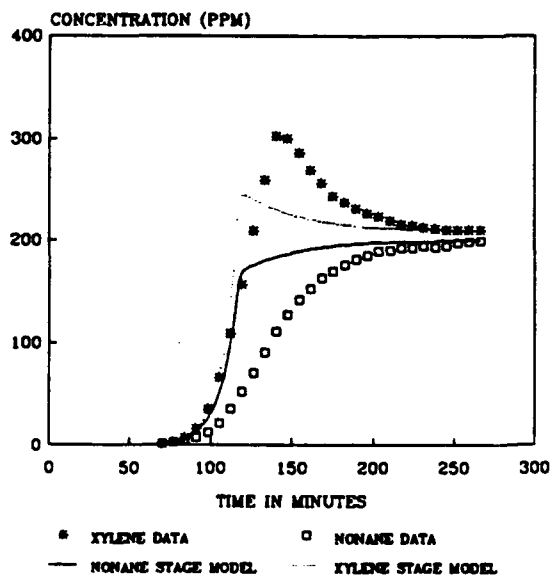


FIGURE 3

XYLENE AND NONANE ON BPL CARBON
3000 PPM CHALLENGE
24.3 deg C

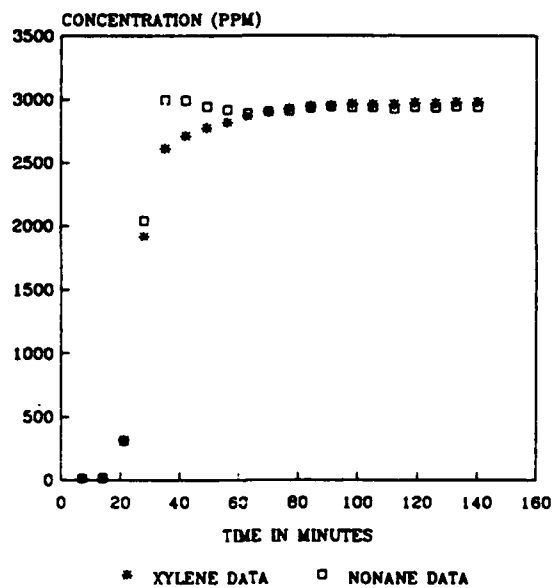


FIGURE 4

Presented at the 1989 CRDEC Conference on Chemical Defense,
Aberdeen Proving Ground, MD, November, 1989, proceedings to be
published in 1990.

Environmental Weathering of a Radial Flow Carbon Filter

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Carbon samples from different locations within a radial flow filter exposed to a marine air stream for 21 months were analyzed using surface analysis methods. The effects of weathering resulted in the migration of the impregnants to the external surface of the granule and the formation of metal sulfates. The weathering effects were found to be most severe at the inlet region of the filter. Results pertaining to the chemical and physical changes of the impregnants will be discussed as a function of bed depth.

INTRODUCTION

Activated carbon provides protection against chemical agents by either adsorption of the agent within the micropores and/or chemical reaction with the copper/chromium/silver impregnants. The carbon filter employed on the modern day gas mask is sealed under vacuum and removed/installed only in the event of a chemical threat. In this manner, the filter is not exposed to the environment prior to the threat and loss of performance due to atmospheric weathering need not be taken into consideration. Unlike the gas mask filter, the filter employed for collective protection applications (e.g. fixed installations, armored vehicles, naval vessels, etc.) may be required to function continuously, whether or not a chemical threat exists. This results in the collective protection filter being continuously subjected to environmental contaminants which may reduce the filter performance against a chemical attack.

The objective of this study is to determine in detail the effects of environmental weathering on collective protection carbon filters. This work focuses on the changes in metal speciation and distribution within carbon granules removed from various locations within a radial flow carbon filter following 21 months of weathering in a marine environment. This study is part of an ongoing effort at CRDEC and NRL.

EXPERIMENTAL METHODS

Materials. ASC Whetlerite (Lot # 103) was obtained from Calgon Corporation as 12-30 mesh (U.S. Standard Sieve) granules. This sample contained 8% copper, 3% chromium, 0.05% silver and 2% tetraethylenediamine (TEDA) by weight. This sample will be referred to as ASC-TEDA.

Weathering of ASC-TEDA carbon. The weathered samples of ASC-TEDA carbon were obtained from a radial flow filter which had been exposed to a marine environment in an operational collective protection system. The collective protection filter is shown in Figure 1. This carbon filter was exposed to normal operating conditions representative of the sea going vessel.

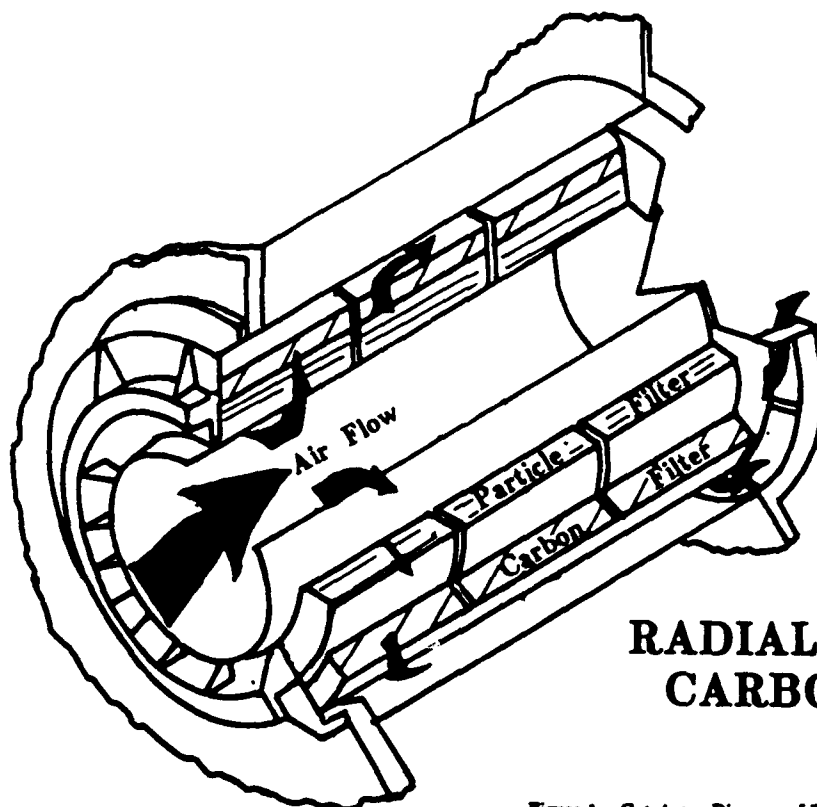
Following weathering, carbon was removed from the radial flow filter and separated into four sections perpendicular to the direction of air flow. The four sections consisted of the inlet most portion of the filter (referred to as INLET throughout the text); a mixture of carbon from the filter inlet to a point extending one-third of the way into the bed (INLET 1/3); a mixture of carbon from a point one-third of the way into the bed to a point extending two-thirds of the way into the bed (CENTER 1/3); and a mixture of carbon from a point two-thirds of the way into the bed extending to the filter outlet (OUTLET 1/3). Samples removed from the inlet most region of the filter were clumped together, while samples removed from the other portions of the bed displayed no evidence of clumping.

Equipment. X-ray Photoelectron Spectroscopy (XPS) spectra were recorded using a Perkin-Elmer Phi 570 ESCA/SAM system employing MgK- α X-rays. Samples were analyzed for carbon, oxygen, copper, chromium and sulfur. No silver could be detected, likely due to the low quantity (0.05 wt%) associated with the sample. All binding energies reported are referenced to the carbon 1s photoelectron peak at 284.6 eV. The fraction of chromium(VI) was determined by subtracting the spectrum of chromate from that of the carbon granule¹. Atomic ratios pertaining to elements of interest were determined by correcting peak areas using instrument supplied sensitivity factors.

Energy Dispersive X-ray Spectroscopy (EDS) was performed using a Tracor Northern 5700 EDS/WDS automation system interfaced with a JEOL 35CF scanning electron microscope. Cross sectional analysis was performed on single carbon granules bisected with a diamond knife. Analyses of the bisected carbon granules were performed by collecting spectra from a 100 μ m by 100 μ m square area stepped across the largest sample diameter.

Cyanogen Chloride Reactivity. The reactive properties of the unweathered and weathered samples of ASC-TEDA were determined by a cyanogen chloride (CK) breakthrough test. Approximately 18 g of carbon were placed into a glass bed and equilibrated with 80 % RH air at 80 °F overnight. The CK test was performed at 80 %RH, 80 °F with a CK feed concentration of 4 mg/l air and a linear bed velocity of 9.6 cm/s. The breakthrough time is defined as the time the effluent CK concentration exceeds 8 μ g/l.

Surface Area Determination. The surface areas of the unweathered and weathered samples of ASC-TEDA were determined using a Quantasorb Surface Area Analyzer. This instrument provides nitrogen BET surface areas using the desorption behavior of nitrogen from the carbon samples.



RADIAL FLOW CARBON FILTER

Figure 1. Cut-Away Diagram of Radial Flow Carbon Filter.

RESULTS

XPS analyses of the carbon samples are reported in Figures 2 and 3. In addition to carbon, copper, chromium and oxygen (as detected on the unweathered sample), a significant fraction of sulfur was detected on the samples from the filter INLET and INLET 1/3. Surprisingly, no sodium was detected, as one might expect due to the salt water environment. No silver was detected on either the unweathered or weathered sample, likely because the concentration of silver (about 0.05%) is below the detection limit of the instrument. Figure 2 compares the XPS spectra of the copper 2p photoelectron region of the weathered carbon granules from the different filter locations. The position of the copper 2p_{3/2} photoelectron peak corresponding to the unweathered sample is indicative of copper in the +2 oxidation state^{1,2,3}. Figure 2 shows the position of the copper 2p peak to be shifted to a higher binding energy for carbons from the INLET and INLET 1/3 region of the filter relative to that of the unweathered sample. These peaks also appear broader than the peak corresponding to the unweathered sample. Note also the changes in the satellite shake-up region (about 939 to 947 eV) of the spectrum corresponding to the INLET sample. Spectra corresponding to the CENTER 1/3 and OUTLET 1/3 samples appear identical with that of the unweathered sample.

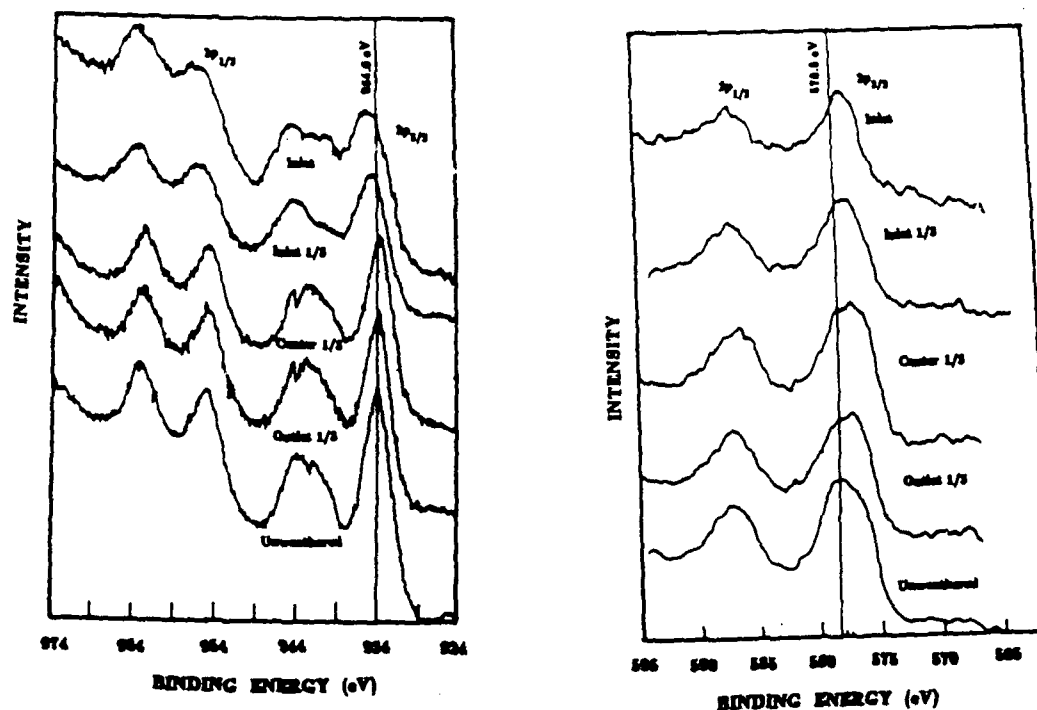


Figure 2. XPS Spectra of the Copper 2p Photoelectron Region for Fresh and Weathered Carbon Samples.

Figure 3. XPS Spectra of the Chromium 2p Photoelectron Region for Fresh and Weathered Carbon Samples. All samples analyzed as a powder.

Figure 3 compares the XPS spectra of the chromium 2p photoelectron region of the weathered carbon granules from the different filter locations. The spectrum corresponding to the unweathered carbon sample is shown for comparison. The position of the chromium $2p_{3/2}$ photoelectron peak corresponding to the unweathered sample is 578.5 eV, indicative of chromium in the +6 oxidation state^{2,3,4}. The shoulder, present at about 576.5 eV, is due to the presence of chromium(III) species. For the unweathered carbon sample, approximately 60% of the chromium associated with the sample was determined to be in the +6 oxidation state. The spectrum corresponding to the INLET carbon exhibits a $2p_{3/2}$ peak approximately 1.0 eV lower than that of the unweathered sample. Note also that the signal 578.5 eV is very weak, indicating that virtually no chromium is present in the +6 oxidation state. Moving further into the filter (INLET 1/3), the chromium $2p_{3/2}$ peak remains at a lower binding energy, but is much broader than that corresponding to the INLET sample. Moving still further into the filter (CENTER 1/3), the chromium $2p_{3/2}$ peak exhibits a strong shoulder at about 578.5 eV,

suggesting that a significant ^{3/4} fraction of chromium(VI) is associated with this sample. The spectra from the CENTER 1/3 and OUTLET 1/3 are nearly identical. Approximately 40% of the chromium associated with each of these samples was determined to be in the +6 oxidation state.

Figure 4 shows a backscattered electron image (BEI) of a representative INLET carbon granule. The BEI is similar to an SEM; however, the BEI highlights high concentrations of metallic elements. Note from the figure that large regions of the weathered granule appear covered with an amorphous overlayer. EDS microbeam analysis of the amorphous overlayer revealed it to consist primarily of copper and sulfur; only a trace amount (<5%) of chromium was present.



Figure 4. Backscattered Electron Image (BEI) of an ASC-TEDA Carbon Granule from the Filter Inlet following Weathering.

The surface area and CK breakthrough time of the unweathered and weathered samples are reported in Table 1. No CK data regarding the INLET sample was recorded, as there was not enough sample from the inlet most region of the carbon bed to perform the CK test.

DISCUSSION

The changes which have occurred in the carbon granules as a result of atmospheric weathering were found to be a function of location within the filter. Samples removed from the inlet region of the filter were much more severely affected by weathering than samples located further into the bed, similar to the observations of Deitz et al.⁴. Apparently, the inlet region of the filter rather effectively removes the airborne contaminants, preventing them from interacting with carbon further into the filter.

Table 1: Surface Area and CK Breakthrough Time for
ASC-TEDA Samples From Different Filter Locations.

Sample	Surface Area (M ² /g)	CK Breakthrough Time (min)
INLET	37	—
INLET 1/3	241	< 5.0
CENTER 1/3	497	24.2
OUTLET 1/3	611	24.6
Unweathered	712	37.8

Freshly prepared ASC Whetlerite is believed to contain copper-ammonium-chromium complexes⁵. These complexes possess chromium in the +6 oxidation state and are postulated to be responsible for the destruction of light gases; namely cyanogen chloride and hydrogen cyanide^{2,5,6}. Changes in the impregnant speciation are expected to reduce the reactive properties of the carbon. It is evident from the data presented in Figures 2 and 3 that large scale changes in the copper and chromium speciation have occurred as a result of the marine weathering for samples located at the inlet region of the filter. The impregnants associated with carbon from the inlet regions of the filter have been transformed into metal sulfates as a result of weathering, based on the XPS analyses. Past the inlet third of the filter, virtually no sulfur was detected, suggesting that the airborne sulfates have been removed at the filter inlet. It was also evident that the impregnants associated with the inlet carbons have migrated from within the granule to the external surface (see Figure 4). EDS analysis of the bisected granule from the filter inlet revealed that virtually no impregnants were present within the granule.

EDS analyses of the CENTER 1/3 and OUTLET 1/3 samples indicated that metal migration did not occur to a significant extent. This suggested that leaching of metals was a result of sulfate formation and therefore confined to only the filter inlet. No change in the copper speciation was detected for samples located at the CENTER 1/3 and OUTLET 1/3 of the filter. However, a reduction of chromium(VI) to chromium(III) is evident. Quantitative XPS analysis of these samples indicates a decrease in the fraction of chromium(VI) from 60% to 40%, compared to the unweathered sample. The decrease in the fraction of chromium(VI) was expected to reduce the CK breakthrough time, as the chromium(VI) fraction has been linked to CK destruction.

Cyanogen chloride breakthrough times for the weathered carbon samples were recorded in an effort to determine the reactive properties of the weathered carbon from the different bed locations. These data are reported in Table 1. The INLET 1/3 sample possessed a small fraction of chromium in the +6 oxidation state. The cyanogen chloride breakthrough time indicated that carbon from this region of the filter provided virtually no protection against light gases. The breakthrough time for carbon located at the center and outlet of the filter were identical. Note that both samples possess approximately 40% of the chromium in the +6 oxidation state. Breakthrough times for both these samples, however, were about 35% less than that of the unweathered sample. It is interesting to note that the decrease in the chromium(VI) fraction (about one-third) corresponds to a proportional decrease in the CK breakthrough time. This is consistent with recent studies which have linked CK reactivity to the chromium(VI) content of the carbon sample^{2,7}

CONCLUSIONS

- 1) The inlet portion of the filter was severely affected by weathering.
- 2) Weathering resulted in the formation of metal sulfates at the filter inlet. These sulfates leached impregnants to the external surface of the granule. No sulfates were detected past the inlet third of the filter.
- 3) Past the inlet third of the filter, approximately one-third of the chromium(VI) fraction had been reduced to chromium(III) species.
- 4) Weathering reduced the effectiveness of the filter against removal of light gases by approximately 50%.

Acknowledgements: One of us (J.A.R.) wishes to thank the National Research Council for financial support on this project. R.A.L and L.I. thank NAVSEA for financial support. The authors wish to thank J. Rehrmann for providing the surface area measurements and R. Grue for providing the CK data.

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