

**2<sup>nd</sup> INTERNATIONAL CONFERENCE ON LONG-TERM STORAGE  
STABILITIES OF LIQUID FUELS  
San Antonio, Texas, USA  
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**Abstract Summaries**

**SESSION 1: FUEL SURVEYS AND LONG-TERM STORAGE STUDIES**

**STORAGE STABILITY OF RESIDUAL FUEL OILS**

*R. P. Anderson, D. W. Brinkman, J. W. Goetzinger and J. W. Reynolds*

The increasing use of low quality heavy crudes in refinery feedstocks has been paralleled by increasing problems in both processing and product quality. Lower product quality is evidenced by increased problems with product stability and compatibility. The problems are particularly severe with residual materials which contain the highest levels of problem components such as asphaltenes or heteroatom compounds. Problems with stability are increased as the refiner resorts to increasingly severe processing to increase distillate yields as the demand for residual fuels decreases. Experience has shown that conventional fuel oil analyses are inadequate to allow prevention or prediction of handling difficulties due to problems with instability or incompatibility. A number of "problem" and "nonproblem" fuel oils have been analyzed in an attempt to understand the reasons for the reported problems. In addition to chemical and physical characterization, these and additional fuels and blends have been subjected to baseline tests for measuring stability. These baseline tests have been used as a basis for initial evaluation of rapid tests which might be used for the prediction of potential problems.

**LONG-TERM STORAGE STABILITIES OF CRUDE OIL RESERVED BY JAPAN  
NATIONAL OIL CORPORATION**

*T. Hara*

Japan National Oil Corporation has been practicing the long-term strategic storage of crude oil since 1978, and the total amount of reserved crude oil now exceeds 20 million kl (130 million bbl). The crude oil storage in above-ground, floating-roof tanks (0.1 million kl in volume) has begun since 1982 at three storage bases located in northern part of Japan. Five kinds of crude oils received in the tanks for the period of 2-3 years are chosen for the analysis of storage stabilities. There are 'sole' crude oils with different API gravities. There are 'mixed' crude oils consisting of light and heavy crude oils at different ratios. Samples have been drawn at different height positions in the 25 m-high tanks of still crude oils at each periodic storage term. Distillation behavior of the crude oils as well as the GPC profiles and hetero-atom functionalities of the vacuum residues separated from the reserved crude oils are monitored for the analysis of chemistry involved in the long-term storage of crude oil. The oxygen and nitrogen functionalities involved in vacuum residues as well as in sludges formed during long-term storage are particularly discussed in relation to the formation mechanism of sludge during long-term storage of crude oil.

## **TEST METHODS AND EXPERIENCE OF SWITZERLAND ON LONG-TERM STORAGE STABILITIES OF GASOLINES AND MIDDLE DISTILLATES**

*E. Gartenmann*

In Switzerland, gasolines and middle distillates are stored for ten or more years. Periodic controls are performed at the EMPA. For gasoline, the most important parameters for stability are existent gum and oxidation stability. Further indications are obtained from a moderately accelerated test, i.e. the bottle storage test. For middle distillates, the existent stability is measured by the Conradson Carbon Residue, ASTM color, and residue on evaporation. The long-term stability is measured by an accelerated test of storing the gasoil four weeks at 50°C. Typical test results for stored gasolines and middle distillates are given.

## **HIGHLIGHTS OF “FIELD TESTS ON STORAGE STABILITY OF GASOLINE, JET FUEL, AND DIESEL FUEL”**

*D. Luria*

The project discussed in this paper is an expanded and updated report of that given in the First Conference for Long Storage of Fuels in 1963. The paper discusses storage behavior of gasoline, jet fuel and diesel fuel in conventional fuel tanks and in 210 liter drums. Two kinds of samples were tested: (a) Blends which were artificially prepared from various components and additives; and (b) Products from current production of oil refineries. A unique aspect of the work is its long and continuous periods of testing: 60 to 100 months in actual ambient conditions. The most interesting finding in these tests is the fact that for long storage durations oxidation stability of gasoline, diesel fuel and probably jet fuel has cyclic characteristics. This means that at certain times one can find a high rate of oxidation while some months later, a low rate might be found. Furthermore, along the whole period no linear or exponential degradation was found. Only in a few cases catastrophic failure had occurred.

## **STABILITY MEASUREMENTS OF COMMERCIAL MARINE FUELS FROM A WORLDWIDE SURVEY**

*D. R. Hardy, R. N. Hazlett, R. Giannini, R. Strucko and S. Westbrook*

As part of a U.S. Navy mobility fuels flexibility program, the storage stabilities of thirty-six commercial marine fuels from a worldwide survey were evaluated. The fuels were categorized into three broad categories based on physical properties marine gas oils (most similar to current use Naval Distillate fuel - NATO 76), heavy marine gas oils and marine diesel fuels. Accelerated stability tests included 43°C and 80°C bottle tests, and ASTM D2274 tests at 95°C. The results of the accelerated tests from two separate laboratories indicate very good agreement in assigning relative storage stabilities to the fuels in each class. The results indicate that D2274 should be useful as a pass-fail test in the procurement of aged commercial fuels. Thus, this test should provide reasonable protection from instability problems encountered from possible future Navy use of commercial fuel stocks worldwide.

## **A RECENT INSTABILITY OCCURRENCE WITH NAVAL DISTILLATE NATO F-76**

*R. Giannini, H. Modetz*

The object of the U.S. Navy's Fuel Qualification Procedure (FQP) is to develop detailed test protocols to qualify candidate fuels for use in Navy shipboard combustion equipment. The base fuel for this investigative work was to represent a "typical" military specification fuel (MIL-F-16884H Fuel, Naval Distillate (NATO F-76)) which would be blended with other components to formulate test fuels. Two hundred fifty thousand gallons (946 m<sup>3</sup>) were required with specific requirements as follows: sulfur content less than 0.2 wt%, a cetane number between 45 and 48, and a storage capability of 2 to 3 years. All other properties were to fall within the specification limits. The fuel was requisitioned and procured through the Navy Petroleum Office (NPO) in May 1984 and stored in a fuel barge at the Naval Ship Systems Engineering Station (NAVSSSES), Philadelphia, Pennsylvania. Samples taken upon receipt indicated that the fuel met the NATO F-76 specification requirements except for an increase in particulates and darkening color of a grab-sample taken during the barge loading, and a hazy appearance of a batch sent to the Belvoir Fuel and Lubricants Research Facility (SwRI), (BFLRF). Six months later, the fuel was off-specification with respect to color (3.0 maximum color as measured by ASTM D 1500) and contained large amounts of microparticulates as determined by ASTM D 2276 for both the BFLRF batch and the barge. An investigation revealed the following:

- The fuel, before leaving the refinery tanks, met the NATO F-76 specification and contained no additives.
- The fuel contained some fluid catalytic cracked (FCC) light cycle oil (LCO).
- The fuel in the barge and the BFLRF tank
  - was unstable (storage) at 95°C, 80°C, 65°C
  - was unstable (thermal) as determined by ASTM D 3241 JFTOT
  - exceeded the 3.0 maximum color specification
  - had a large amount of microparticulates that could agglomerate in storage or while under engine test conditions
- The fuel would continue to degrade at 43°C.
- The stability of the fuel could be improved with an FOA-3 additive package.

The major conclusion which was drawn from the occurrence was that the NATO F-76 specification in its current form (MIL-F-16884H) is not adequate to protect against the receipt of a fuel which can develop a stability problem.

## **SESSION 2: STRATEGIC AND EMERGENCY FUEL STORAGE**

### **STORAGE STABILITY OF KEROSENE AND A JET FUEL**

*N. Li, J. R. Tzou, H., Chang and S. M. Wang*

Storage stabilities of kerosene and a jet fuel {JP-5) derived from petroleum, both manufactured by the Chinese Petroleum Corporation in Taiwan, were determined using sediment formation, laser light scattering, Raman scattering, inductively coupled plasma-atomic emission (ICP-AES), nuclear magnetic resonance, electron spin resonance, and ESCA measurements. Fuel degradation

was monitored in the presence of the following added specific compounds: phenol, 2,6-dimethylphenol, thiophenol, 2- methylpyridine, copper powder and mixtures of some of these at room temperature and 80 °C. The light scattering technique was used to examine the growth of small particles, which are precursors to deposit formation. As a fuel ages, particles grow in size and scatter light, so that light scattering measurement has greater sensitivity for initial deposit formation and could speed up the determination of fuel stability. We are developing the ICP-AES method, which also has greater sensitivity for initial deposit formation, and has not been reported in the literature. The highly hindered phenol, 2,6-di-t-butyl-4- methylphenol or butylated hydroxytoluene BHT, is a commonly used antioxidant. We have added this compound to mixtures used in accelerated aging of kerosene and JP-5, and determined the effectiveness of this antioxidant in retarding the rate of fuel degradation.

### **APPLICATION OF A FIELD FUEL QUALITY MONITOR TO SURVEILLANCE OF PREPOSITIONED FUEL STOCKS**

*S. R Westbrook, L. L. Stavinoha, J. G. Bargee, L. L. Bundy and J. V. Mengenhauser*

Prepositioned fuel stocks and/or extended fuel storage continues to be a requirement for many industrial, government, and military activities. Often this fuel is subjected to adverse storage conditions, such as in vehicle fuel tanks or in contaminated fuel storage tanks. Additionally, the fuel being stored is often of unknown stability and cleanliness. These fuel stocks should be tested periodically to assure proper fuel quality. This testing involves obtaining a sample of the fuel and submitting that sample to a laboratory for analysis. This paper describes a Field Fuel Quality Monitor (FFQM) which can be used to test/monitor fuel stability and cleanliness on site. The FFQM provides a means to sample the fuel, measure the color of the fuel, estimate particulate contamination, and estimate fuel stability. Several programs where the FFQM has been successfully utilized / demonstrated are also discussed. These programs include partially or fully fueled vehicle storage in warehouses (West Germany), at the M-60 tank plant (in Warren, Michigan), and in a Near Term Prepositioned Stocks (NTPS) test of vehicles stored on ships. Also included is surveillance of fuel in underground storage for standby generators at several Air Force bases.

### **A QUALITY CONTROL SYSTEM FOR DIESEL FUEL IN LONG-TERM STORAGE**

*K. H. Strauss*

Nuclear power plants usually include diesel engines to power emergency- generating equipment for shut-down procedures. Fuel for these systems can remain in storage for long periods of time, but full-time operability of the engines and their fuel systems is essential. The configuration of the fuel system posed special requirements which had to be compensated for. A quality control program was designed which is intended to avoid fuel storage stability problems. Portions of the quality control program have been adopted in NRC regulations

## **IN-GROUND OIL STORAGE CONTAINERS "FROM WHENCE IT CAME"**

*J. E. Thrasher, C. S. Dunn*

From late 1976 to 1982 Fenix & Scisson, Inc. provided the project management for the design and construction of large in-ground concrete storage tanks in the Republic of South Africa for the purpose of storing crude oil - putting the oil back "from whence it came". Constructed in balanced cut-and-fill excavations, this high-density polyethylene encased and gravel-covered concrete tanks provide most of the security of an underground storage cavern while being more like extremely large surface storage tanks operationally. Although quite secure from acts of sabotage, the tanks were built with provisions for rapid injection of fire-fighting foam under the tank roofs in the unlikely event a tank roof is ruptured and a fire ignited. The storage space constructed cost less than \$20 per metric ton of storage capacity including general tank farm facilities. Preliminary, pre-construction cost estimates indicated that construction of the in-ground tanks could be accomplished at 60 percent of the cost to construct the equivalent storage capacity in conventional, floating roof, steel surface oil storage tanks. While higher than estimated inflation rates resulted in a higher actual completion cost for the in-ground tanks than indicated in the preliminary estimate, the cost to construct steel surface storage tanks would have been similarly affected by the higher inflation rates. Restrictions imposed by the responsible South African organization prevent revealing the dimensions, volume, number, or specific location of these tanks. However, A Fenix & Scisson, Inc. film entitled, "From Whence It Came" provides details of some of the construction features which are discussed in this paper.

## **SESSION 3: OPERATIONAL STORAGE AND FUEL SYSTEMS**

### **EFFECTS OF POLYMERIC COATING SYSTEMS FOR CONCRETE FUEL TANKS ON THE QUALITY OF JET FUEL**

*B. Polishook, Y. Geva and R. Fass*

Four commercial polymeric coating systems for concrete fuel tanks. were tested for their compatibility with Jet Fuel, and for their potential to accelerate microbial growth on Jet Fuel. Membranes of the coating materials and coated concrete blocks were exposed to environmental conditions prevailing in concrete fuel tanks before and after refueling. Prolonged storage conditions were imitated by heating the fuel to 50°C for two months. The study on stability. experimental system and the results of a comparative the effects of the four coating systems on fuel stability, fuel corrosiveness. and fuel microbial contamination, are described.

### **CONSEQUENCES OF SULPHUR COMPOUND CONVERSIONS IN STORAGE OF JET FUELS**

*J. B. Asher, N. Por and A. B. Shavit*

Factors enhancing or inhibiting the corrosivity of kerosene type jet fuels were studied. It was found, contrary to current belief, that in some jet fuels, containing elemental sulfur, the Copper Strip Tarnish Test ASTM D-130 is more sensitive than the Silver Corrosion Test IP-227. It is

believed that jet fuel corrosivity depends on the crude source and the refining processes, particularly the sweetening process, to which it has been subjected. The effect of organic sulfides and exposure to sunlight on corrosivity of jet fuel containing elemental sulfur has been studied. Experimental results indicated that in some instances jet fuel conforming to all specification requirements, while containing elemental sulfur, may become corrosive during storage or pipeline transportation. This transformation is most probably governed by environmental conditions affecting the transition of heteroatomic compounds from one type to another. Based on this study, corrosive jet fuels, in field storage, containing elemental sulfur have been rendered non-corrosive by blending with an acid treated jet fuel containing evidently certain heteroatomic constituents inhibiting this sort of corrosivity.

## **STABILITY PROPERTIES AND COMPATIBILITIES OF RESIDUAL FUELS**

*N. Por, R. Brauch and N. Brodsky*

The increasing need for producing more distillates from each barrel of crude oil necessitates employment of more severe conversion processes for increasing distillate yields. Alternative energy sources, diminishing the residual fuel demands, contribute also to the need of increasing production of distillates at the expense of residues. More severe visbreaking processes will have to be therefore employed, adjusting the yield demand, but resulting in residual fuels of a lesser stability. Vacuum residues, when serving as fuel oil base stocks rather than as visbreaker feed or asphalt base stocks, have to be backblended with diluents because of viscosity requirements; compatibility problems may be expected in this case, especially when relatively high asphaltene content stocks are blended with diluents of an insufficient aromatic reserve. Deposition of sludges may also be expected in blends of two or more residual fuels forming a combined continuous phase of too low a peptizing power. The use of fuel oil in marine engine systems, instead of marine diesel fuel or middle distillates, brought along problems of fuel system clogging by excessive formation of sludge and deposits. The main purpose of this work is to study the mechanism of residual fuel instabilities and incompatibilities, as well as the factors affecting them, so that means for minimizing these undesirable processes may be recommended.

## **OPERATIONAL PROBLEMS WITH MARINE FUEL OILS**

*M. F. Winkler*

Over the years, Marine (Residual) Fuel Oils have represented the bottom of the barrel. Since ocean-going vessels do not have environmental air quality restrictions, the most heavily cracked, highest sulfur, lowest quality residual fuel oils have been routed into the Marine Bunkers. Typically, the residual fuel oils with the poorest ignition properties, the highest levels of sulfur, metallics, contaminants, and the highest boiling point hydrocarbons have created many difficult Marine operational situations resulting in fouling, deposits, corrosion, incompatibility, and instability. The paper presents an overview of Marine Residual Fuel Oil stability and the operational problems that can result from the use of these fuel oils in diesel and steam turbine-powered ships

## **SESSION 4: MICROBIAL ASPECTS OF FUEL STABILITY**

### **MICROBES IN FUEL: AN OVERVIEW (WITH A NAVAL FLARE)**

*R. A. Neihof*

A brief review of the history of microbial contamination of hydrocarbon fuels is followed by descriptions of the genera responsible for the major objectionable effects and a discussion of selected aspects of growth requirements of the organisms, interactions among different organisms and methods of control

### **THE IMPACT OF MICROBIAL ACTIVITY ON THE QUALITY OF JET AND DIESEL FUEL STORED IN MODELS FOR WET ROCK CAVERNS**

*R. Fass, Y. Geva, A. Mizrahi and Y. Henis*

Unlined rock caverns below the water table are used for long term storage of several petroleum products in Sweden and Norway, Microbiological aspects of the application of this storage system, for Jet and Diesel fuel ,in selected sites in Israel, were studied in pilot rock models simulating the environmental conditions at a sedimentary rock format1on, Results of five years of follow up on the microbial activity and its impact on the stored fuels, indicated that aerobic-anaerobic microbial sequences may induce fuel acidity and corrosiveness. Attempts to exclude the microbiological impact on stored fuel by water exchange and aeration, were unsuccessful. It is concluded that fuel and water soluble biocides must be added while using such a storage technology, in order assure the long-term storage stability of the stored fuel.

### **MICROBIOLOGICAL STUDIES IN ROCK CAVERNS WITH JET FUEL, HEAVY FUEL OIL AND CRUDE OIL**

*A. Norqvist, R. Roffey and A. Edlund*

In Sweden a large number of rock caverns have been used for long-term storage of different petroleum products. The storage system is based on the principle that the products are stored on a waterbed. The caverns are situated below the groundwater table so the water pressure prevents the products from leaking out of the caverns. During the last years some microbial problems have been observed in caverns with jet fuel and heavy fuel oil. In caverns with jet fuel, sulfide was produced which gave rise to corrosive fuel. When heavy fuel oil, microbially produced methane has been the problem. In order to understand the factors responsible for the microbial activities, physio-chemical and microbiological analysis of the bedwater in the caverns and the groundwater surrounding the caverns have been performed. Similarities and differences in activities between caverns with different petroleum products are discussed.

### **EFFECT OF MICROBIAL CONTAMINATION IN STORAGE TANKS ON THE LONG-TERM STABILITY OF JET FUEL**

*R. Fass, J. B. Asher and A. B. Shavit*

The stability of jet fuel stored for long terms in contact with active microbial cultures, was studied in bench scale simulations of storage tanks in which enhanced microbial development took place, and in storage tanks where natural occurring microbial flora developed for four years. Results of the bench scale experiments indicated that active microbial cultures may deteriorate some fuel properties, such as Total Acidity, WSIM and Corrosiveness. Other fuel properties remained in the range of specification limits, following five years of storage under favorable conditions for microbial growth. Field investigations showed that jet fuel stored in large storage tanks equipped with floating roofs, became heavily contaminated by microbial cells. However, no deterioration of fuel properties could be detected. Silver Corrosion and tendency in WSIM decrease were observed in bottom-bottom samples taken from a contaminated storage tank. Hence, the main risk to jet fuel stored for long periods, without biocide treatment, is the formation of corrosive sulfur compounds, and surface-active materials by the combined action of microorganisms feeding on hydrocarbons and Sulfate Reducing Bacteria, which flourish at the tank's bottom. However, it may be anticipated that such risks may be minimized by draining operations which remove the whole bottom layer from the storage tank

#### **METHODS TO MONITOR BIODETERIORATION OF JET FUEL DURING LONG-TERM STORAGE IN ROCK CAVERNS**

*R. Roffey, A. Norqvist and A. Edlund*

During long-term storage of jet fuel on a fluctuating waterbed in rock caverns, the fuel can become corrosive due to the activity of sulfate reducing bacteria which produce hydrogen sulfide. In order to study the problems with biodegradation and increased corrosivity of jet fuel during storage, it was necessary to develop more sensitive methods to monitor these processes. It was found that the standard silver strip test (IP 227/73) was not sensitive enough to, at a very early stage, indicate if there was risk for a fuel becoming corrosive. This led to the development of a more sensitive and quantitative method to measure corrosivity based on piezoelectric crystals. Elemental sulfur in the range of 1-5 mg/l was found to be important for the corrosive effect, why a polarographic method was developed with a sensitivity down to 0.1 mg/l. Different methods to monitor the microbial processes in the waterbed will be discussed. The use of these developed methods to monitor the situation in a rock cavern is presented.

#### **UPDATE ON LONG-TERM DISTILLATE FUEL STORAGE PROGRAM FROM 1992. PROBLEMS WITH INTERNAL TANK CORROSION**

*H. L. Chesneau*

In 1980, a large utility in the Southeast United States discovered what appeared to be microbial slimes appearing in bottom fuel samples taken from gas turbine distillate fuel storage tanks. Because of a floating feed system, problems involving filters were not being encountered. Increased efforts were made to remove as much water from the system as possible. Early in 1981 the floating booms of two of the tanks sank to the bottom. As a result, tank bottom debris was pulled into the filters and turbine shutdown was experienced. The immediate solution was to attach cables to the booms and pull them about 10 feet from the tank bottom. A testing program



was conducted utilizing standard microbial test methods and the DuPont 300 F. stability test. The results showed heavy microbial activity combined with an apparent unstable fuel condition. It was then decided that an additive program using specifications under Hil-S-53021 would be started. This specification calls for the use of a fuel biocide and a fuel stability package. Several items became apparent as the program progressed. To begin with, it was impossible to remove all the water present in the system because of "puddles .. existing throughout the tanks. In addition, the low usage of the fuel made it clear that it might be several years before the system was low enough to be able to clean the tanks. These are large 180,000 bbl tanks.

## **EFFECT OF MICROBIAL CONTAMINANTS ON THE CORROSION OF FUEL STORAGE TANKS**

*E. H. Reinoso, O. Fleischmacher, S. M. DoValle, P. Guiamet and H. A. Videla*

The electrochemical behaviour of SAE 1020 steel and 2024 aluminum alloy was studied to estimate the corrosion hazard in storage tanks due to the presence of microbial contaminants of kerosene type fuels. Electrochemical potentiostatic polarization techniques and current transients were made in the presence of sterile and microbially contaminated fuel to evaluate the role of the microorganisms in the corrosion process. SEM observations and EDAX analysis were also made. Gas chromatography was used to follow the attack of hydrocarbon chains during incubation time. Microbial contaminants (fungi and bacteria) were isolated from fuel storage and distribution systems and correspond to commonly reported microorganisms. Microbial growth facilitates the corrosion process mainly through the accumulation of aggressive metabolites in the medium near the metal surface. In the presence of these metabolic products the breakdown of passivity occurs at more cathodic values than in the absence of microbial contaminants leading to localized corrosion, preferentially pitting. The effect of adhesion processes and structured microbial consortia on the metal surface, facilitating the metal attack are also analyzed.

## **IN VITRO BIODEGRADATION OF CRUDE OILS**

*K. Bosecker, M. Teschner and H. Wehner*

Crude oils from the Gifhorn Trough (Lower Saxony, NW-Germany) and from the Maracaibo Basin (Venezuela) were analysed for their content of microorganisms capable of biodegrading crude oils. In incubation experiments genetically related oils were treated with the cultures isolated and the progress of biodegradation was followed by chromatographic techniques. Parameters important for the course of the reaction (pH-value, oxygen-, nitrogen-, phosphorus-supply, type of reaction medium) were checked and optimized. The degradation of n-alkanes was followed closely. It was shown that the microorganisms active in degradation (yeasts, bacteria) could easily survive a period of inactivity due to missing nutrients and could be reactivated within hours to degrade newly added crude oil. Under oxygen-limiting conditions selectivity of degradation was found, destroying short-chain n-alkanes (C20, C21) at a faster rate than long-chain n-alkanes (C30, C31). The alteration of physical parameters of the crude oils (density, 4veriled molecular weights) shifted as expected during the course of degradation.

## **SESSION 5: BIOCIDES AND MICROBIOLOGY OF FUELS**

### **MICROBIOLOGY OF HYDROCARBON FUELS**

*S. Holmes*

An introduction to the types of microorganisms found in fuel oil systems. The types of fuel systems attacked by microorganisms will be described together with the most common types of problems caused by microorganisms. Microbiological control measures will examine physical as well as chemical, e.g., the use of biocides, methods for controlling degradation and fouling of fuel oil systems.

### **FUEL-SOLUBLE BIOCIDES FOR CONTROL OF FUNGAL CONTAMINANTS IN HYDROCARBON FUELS**

*G. Andrykovich and R. Neihof*

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.

### **MICROBIOLOGICAL CONTAMINATION CONTROL IN NAVAL DISTILLATE FUEL**

*R. M. Morchat, A. J. Hebda, C. D. MacGregor and R. Brown*

In an attempt to identify a suitable biocide, to treat a microbiological contamination (MBC) problem in fuel on ships which use the coalescer principle for water removal, five commercial products based on benzimidazoles, pyridinethiol-1-oxide, imidazoline, dioxaborinanes and isothiazolones, have been examined. The efficacy of the commercial products to suppress the growth of the fungus *Cladosporium resinae* in naval distillate fuel was evaluated. Both pure cultures of *C. resinae*, and mixed cultures started from untreated sea water inoculated with *C. resinae*, were treated at three different concentrations of the biocides. Four materials suppressed microbiological growth of the pure cultures at the concentrations tested. Both the rate of growth and the total quantity of *C. resinae* mat produced decreased as the concentrations of the biocides were increased. However, for the mixed culture system the rate of growth and the production of fungal mat was suppressed only slightly, if at all, by the biocide treatments evaluated. The surface tension measurements of these materials in fuel and the partitioning in fuel/water

mixtures have been evaluated. The effects of temperature, water and oxygen content and pH of the water on the biocide activity was also studied. In addition, samples from the bottom of naval distillate fuel tanks were collected and treated with biocide to enable correlation of the laboratory findings with results from samples from the "real" system.

### **THE USE OF DIOXABORINANES TO CONTROL MICROBIAL GROWTH IN LIQUID FUELS**

*C. R. Bennett and E. L. Docks*

Microbial growth can occur in liquid fuels contaminated with water. Depending on the severity of microbial contamination, tanks corrode, gaskets and coatings are attacked, valves and gauges plug, fuel deteriorates, etc. Eliminating water from the fuel handling system would be one way of preventing the above problems. However, since this is virtually impossible, organoborates can be used to control the growth of microorganisms in water contaminated fuels. In particular a mixture of dioxaborinanes is currently used for this application. The experimental results of their use to control microbial growth in Jet A fuel/water mixtures will be reviewed in this paper.

### **THE USE OF METHYLCHLORO/METHYLISOTHIAZOLONE IN CONTAMINATED DISTILLATE FUELS**

*J. A. Meeks, C. T. Kuhar and D. E. Greenley*

Methylchloro/methylisothiazolone biocide treatments of distillate fuels were evaluated in both laboratory and field trials. The effect of biocide treatments on chemical and physical characteristics of the fuel and on fuel additives were measured in ASTM 01655, DERD 2494, ASTM 0975 and ASTM 04054 tests. Biocide treatments (1.4 and 5.6 ppm w/w active ingredients) resulted in no measurable effects on the physical or chemical characteristics of Jet A or No. 2 diesel fuels. Biological efficacy of methylchloro/methylisothiazolone in contaminated distillate fuels was determined in laboratory tests by measuring the concentration of viable microorganisms in the aqueous phase at regular time intervals. Microbial contaminants in distillate fuels were reduced by 99% in 24 to 48 hours after treatment with 1.4 ppm active ingredient of biocide; long-term biological efficacy (30 days) was demonstrated with methylchloro/methylisothiazolone treatments in both laboratory and field trials.

## **SESSION 6: METHODS FOR CHARACTERIZATION, ANALYSIS AND TESTING**

### **METHODOLOGY FOR IDENTIFICATION OF DIESEL FUEL SYSTEM DEBRIS RELATED TO PROBLEMS IN THE FIELD**

*S. R. Westbrook, J. G. Barbee, L. L. Stavinoha, S. J. Lestz, M. E. LePera and J. V. Mengenhauser*

Field problem surveillance for the Army has identified vehicle power loss due to premature fuel filter plugging as a major maintenance and readiness problem. A systematic approach to the

analysis of fuel system debris has been partially developed. First, a set of reference materials was gathered based on the most commonly encountered fuel system debris. The most useful microscopic and spectroscopic techniques and their utility for examining the various types of debris were identified. The individual reference materials were characterized for use in comparison to actual field samples. Sample preparation procedures were developed for fuel filters, fuel samples, and fuel tank sludge samples. A scheme for the final analysis of the prepared fuel samples was devised and applied to two different field samples. This methodology requires some technical judgment in assessing the relative amounts of some of the debris types; however, this methodology provides a step-by-step means of determining the identity and thereby diagnosing probable causes of fuel filter plugging. This methodology has been applied to a number of Army field-related problems.

### **ATTEMPTS TO STANDARDIZE FUEL/WATER EMULSIONS FOR THE ASTM COALESCENCE PROCEDURE**

*G. S. Sprenger*

Emulsion size and stability affect fuel/water coalescer performance greatly. Size and stability of the emulsion are a function of the liquids, their interfacial nature, and the mixing device used to create the emulsion. Using standard liquids, which are reproducible in physical, chemical, and interfacial properties, emulsion size is a function of the mixing device solely. In this study, Jet A fuel and water were used. Various mixing devices were analyzed as to the relative size of the emulsion they produce. Centrifugal pumps, eductors (or venturis), and valves were tested. The relative size of the emulsion was determined using a turbidimeter, which measured an "average" drop size. Using high speed centrifugal pumps (3450 rpm), average drop size was a function of the impeller diameter; larger impellers (i.e., larger pumps) produced smaller diameter drops. This property made centrifugal pumps unattractive as a standard emulsion-producing device. Testing of eductors indicated emulsion size was a function of the pressure differential across the eductor and the size of the orifice. Smaller orifices produced a larger drop-size emulsion, as indicated by the turbidimeter, even at the same pressure differential across the eductor. Various valves were also examined. Globe and ball valves were first tested due to their availability, low cost, and consistency in design from size-to-size. Emulsions were produced using different size valves, varying the pressure differential across the valve and the flowrate through the valve. For the globe valve, emulsion size was only a function of pressure differential across the valve. Flowrates and valve size had no effect. This was the desired result for a device to be considered in the standard. Further testing is required, but tests to date show that a globe valve produces a consistent emulsion of water in Jet A, independent of valve size and flow rate, making it an excellent choice for emulsion production in a fuel/water coalescer standard.

### **FUEL SYSTEM DESIGN CONSIDERATIONS FOR DIESEL AND GAS TURBINE ENGINE POWERED MILITARY VEHICLES**

*M. Treuhart, S. R. Westbrook, L. L. Stavinoha, M. L. Valtierra and W. R. Williams*

Considerations are provided for the following vehicle fuel system components: fuel tanks, sensors, filters, fuel lines, fuel system heaters, and fuel transfer pumps, with major emphasis on

their impact on fuel quality. Requirements with respect to materials, geometry, integrity, durability, and effect on fuel quality are explored. Status of fuel filter bench test design is also summarized. While many of these considerations are not unique to military engine systems, unique military environmental conditions and stand-down requirements are more demanding on the overall fuel system in order to maintain operability.

## **FILTERABILITY OF DEGRADED FUELS**

*R. W. Hiley*

Rapid blockage of the coalescing fuel filters of RN gas turbine powered warships burning distillate diesel fuel has led to a study both of the filters and of the materials which cause blockage. The most common cause of blockage was found to be fuel which has degraded in storage, producing fine particulates. Existing prefilters, intended to protect the coalescing filters from blockage, permit the majority of this material to pass. A shipboard test procedure has been developed which can quantify the blocking effect of fuels and this is described in detail. The test has been successfully used to monitor F-76 fuel cleanliness in warships and a commercially produced version is to be deployed for this purpose. Blockage tests of full-scale single coalescer elements have shown that some increase in lifetime would be obtained by the adoption of a slightly more porous element. Investigation of improved prefilter designs has shown that a considerable improvement can be made, and that the best of these will provide complete protection to coalescer filters.

## **APPLICATION OF THE FILTERABILITY INDEX TEST METHOD TO EVALUATE DIESEL ENGINE OPERABILITY**

*G. Irish and K. Bell*

A test method is presented for measuring the filterability of diesel fuel through a 5-micron filter. Results of these measurements are related to the performance of fuels in diesel equipment.

## **APPLICATION OF STABILITY ADDITIVES UPON DISTILLATE FUEL FILTERABILITY**

*R. K. Solly, W. Arfelli*

The effect of commercial fuel stability additives upon the amount of particulate matter and fuel filterability has been determined for the thermal ageing of automotive distillate fuel composed of a mixture of straight run and either catalytically or thermally cracked petroleum distillate. Suspended particulate matter was determined by filtration through 0.8  $\mu\text{m}$  absolute filters, 2.5, 8 or 20-25  $\mu\text{m}$  nominal filters. The amount of particulate was independent of the filter pore size for all filters with the exception of the 20-25  $\mu\text{m}$  size. Tertiary alkyl amine antioxidant additives reduced the amount of particulate matter with all fuel mixtures. A long chain polymer dispersant additive increased the amount of particulate collected on all filter membranes compared to the reference fuel without additive. A commercial additive containing amine antioxidant, metal deactivator, polymer dispersant and corrosion inhibitor yielded increased particulate values with

some samples and decreased values with others. For all samples, the formation of particulate matter was approximately linear with time for periods up to 32 days ageing at SOC. Fuel filterability was determined as the time of filtration for measured volumes of fuel through the filter media at a fixed pressure differential. The correlation between particulate matter and filterability was poor. With all fuel mixtures, the addition of the dispersant alone resulted in a significant increase in filtration times with all filtration membranes. Upon the addition of amine antioxidant, most test fuel samples showed little change in fuel filterability from the reference fuel without additive. Most samples containing composite additive with the dispersant showed increased fuel filtration times. It may be concluded that fuel stability tests based solely on particulate matter are unlikely to be fully indicative of filterability problems which may arise from ageing of distillate fuels.

## **FUEL FILTER PLUGGING BY INSOLUBLE SEDIMENT IN DIESEL FUELS**

*S. R. Reddy*

Diesel fuels contaminated with insoluble sediment and water have caused problems for light-duty diesel engines by plugging fuel filters. The sediment consists of either aggregated gum particles resulting from fuel oxidation or biological slime produced by microorganisms which grow at the water/fuel interface. Laboratory experiments were conducted to understand the mechanism of filter plugging by these sediments. Gum particles tend to be hard and spherical in shape, while biological growth tends to consist of long, stringy, fibrous material. Biological slime plugged both the 10  $\mu\text{m}$  engine filter and the 130  $\mu\text{m}$  tank sock filter; gum particles, which individually were less than 3  $\mu\text{m}$  in diameter, plugged the 10  $\mu\text{m}$  engine filter by forming aggregates of several hundred particles; these aggregates readily passed through the 130  $\mu\text{m}$  tank sock filter. However, plugging with these aggregates was not very severe because a porous cake formed on the surface of the filter paper which allowed some fuel to flow. Filter plugging was very severe when gummy fuel was contaminated with water because the particles flocculated and plugged both of the filters. Prevention of water contamination and treatment of diesel fuel with additives to prevent gum and biological growth formation are necessary to avoid filter plugging problems.

## **FUEL FILTERABILITY PROBLEMS AFTER STORAGE**

*D. W. Brinkman, O. Bhan and B. Carley*

Most of the storage stability research has been focused on the formation of gums and solids, usually accompanied by darker coloration. This degradation can result in the plugging of filters when the fuel is used. However, there are fuels which look acceptable visually and which have no solids present, yet they do not filter readily. In some cases, no material is observable on the filter, even under an electron microscope. This paper will present the results of a study conducted to investigate the cause(s) of high filtration time observed in some jet fuels. Our work indicates that the presence of organic sediments and gums in these fuels is the principal cause of their poor filterability. Metals and inorganic contaminants present also contribute to the filtration problem by adhering to the filter medium, although their significance is diminished unless there are organic gums and sediments bonding and holding them together on the filter surface.

## **SESSION 7: THEORETICAL ASPECTS OF FUEL STABILITY**

### **CHEMISTRY AND MECHANISM OF DISTILLATE FUEL STABILITY**

*W. F. Taylor and J. W. Frankenfield*

The paper reviews the current state of knowledge relative to the chemistry and mechanism of distillate fuel stability. Fuels covered in the review include aviation turbine fuel, diesel fuel and heating oil. Research on both the effect of storage at ambient conditions for prolonged periods of time, i.e., storage stability, and on the effect of short exposure to higher temperatures in end use equipment after storage, i.e. thermal stability, is discussed. Storage and thermal stability effects on sediment, peroxide, color and surface deposit formation are reviewed. Relevant pure compound autoxidation kinetic studies as well as studies with actual fuels are covered, and the current state of knowledge on the effect of fuel composition on the rate of autoxidation and on stability properties such as sediment and surface deposit formation rates is reviewed. The interactions between chemical kinetic and physical rate processes in the overall sediment and surface deposit formation process is discussed.

### **LIQUID PHASE OXIDATION OF SULFUR COMPOUNDS**

*G. W. Mushrush, R. N. Hazlett, D. R. Hardy and J. M. Watkins*

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

### **CHEMICAL CHARACTERIZATION OF FUEL SEDIMENTS USING ANALYTICAL SUPERCRITICAL FLUID METHODOLOGIES**

*B. W. Wright, H. R. Udseth, R. D. Smith and R. N. Hazlett*

A manifestation of fuel instability is the formation of sediments and insoluble organic materials. Chemical analysis of the fuel degradation products may help establish the identity of the reactive components in the fuels and lead to a better understanding of the mechanisms involved in middle distillate storage instability. The generally intractable nature of these residues makes analysis by conventional methods difficult. However, new analytical methods that exploit the high solvating power and mass transport properties of supercritical fluids can be applied to these problems. Direct supercritical fluid extraction-mass spectrometry (SFE-MS) provides a means of extracting high molecular weight material with direct introduction to the mass spectrometer for on-line analysis. Supercritical fluid chromatography (SFC) and SFC-MS provide high resolution separations of nonvolatile and thermally labile analytes. SFE-MS utilizing ammonia as the

solvent was applied to the sediment from an unstable diesel fuel and compared to "model" sediments formed from stressing fuels doped with additives believed to induce sedimentation. The extract from the natural sediment contained significant quantities of alkyl indoles and alkyl carbazoles with the matrix consisting of a pyrrole-like polymer extending to masses of over 900 dalton. The model sediment extracts consisted mainly of oxidation products and dimers and trimers of the oxidation products of the additives. SFC-MS analysis of the polar fractions of the unstable diesel fuel found significant quantities of alkyl carbazoles with lower concentrations of numerous other nitrogen heterocycles and oxygen-containing compounds.

## **GUM AND DEPOSIT FORMATION FROM JET TURBINE AND DIESEL FUELS AT 100° C**

*F. R. Mayo and B. Y. Lan*

Rates of oxidation and gum formation for six hydrocarbons, three jet turbine fuels, and three diesel fuels have been measured at 100°C in the presence of t-Bu<sub>2</sub>O<sub>2</sub> as initiator. Four of the six fuels oxidize faster at 100° than in previous work at 130° without initiator. For any single substrate, the amount of gum produced for the oxygen absorbed tends to be similar at 100° and 130°, even with large changes in rates of oxidation and gum formation and t-Bu<sub>2</sub>O<sub>2</sub> concentration. Thus, one mechanism of gum formation is intimately associated with oxidation. The effects of t-Bu<sub>2</sub>O<sub>2</sub> concentration on rates of oxygen absorption and gum formation show that gum formation is associated with chain termination by two peroxy radicals, but that the efficiency of this coupling to dimer and gum varies greatly with the substrate. In general, the pure hydrocarbons have long kinetic chains and give good yields of hydroperoxides. Most of the fuels have short kinetic chain lengths and produce little hydroperoxide but such gum for the oxygen absorbed. Another mechanism of gum formation is the coupling of substrates by peroxides in the absence of oxygen. This is an efficient mechanism for coupling, and the products contain little or no oxygen. This mechanism is replaced by the oxidation termination mechanism when oxygen is present. A third mechanism, condensation of oxidation products from alkylnaphthalenes, is also proposed.

## **ACID-BASE PHENOMENA IN DISTILLATE FUEL STABILITY**

*R. N. Hazlett and G. Kelso*

Carboxylic and organic sulfonic acids, added to distillate fuel blends containing catalytically cracked stock, increase deposit formation, sometimes very dramatically. The carboxylic acids data fitted into a unified treatment in relationship to hydrogen ion concentration calculated from PKa values for aqueous solutions. These acids enhance deposit formation by catalytic action and are not incorporated into the deposit. Organic sulfonic acids may fit into the unified acid catalysis pattern but await resolution of ionization phenomena in non-aqueous solution. A tertiary aliphatic amine stabilizer was effective for reducing deposit amounts from fuel blends containing acids. This amine acts on a stoichiometric basis to counteract strong acids in the fuels. For weak acids, the amine stabilizer exhibited an effect greater than that for a 1:1 basis with the amount of acid in the fuel. Other amines exerted favorable behavior only if they were strong organic bases.



## **THE ROLE OF PHENOLS IN DISTILLATE FUEL STABILITY**

*R. N. Hazlett and A. J. Power*

The influence of naturally occurring phenolic compounds on the stability of some diesel distillates has been examined. Quite stable straight run automotive distillate oil (ADO) and hydrotreated light cycle oil (HT-LCO) were doped with 0.2 wt% of a caustic extract from an unstable catalytically cracked LCO. Total insolubles which formed during accelerated ageing at 65 and 80°C, for periods equivalent to two years ambient storage, increased by 2.5 and 3.5 times, respectively for the ADO and HT-LCO. The LCO caustic extract was found to comprise phenolic components almost exclusively, as a complex mixture of homologous series of alkylphenols, -naphthols and J -phenylphenols. The estimated concentration of thiophenol in the extract was ' about 14 ppm, a level too low to have a significant effect on fuel stability. Infrared spectroscopic evidence indicated that phenolic oxidative coupling during fuel ageing was responsible for the increased amounts of deposits formed in the test fuels.

## **FORMATION OF INSOLUBLES DURING STORAGE OF NAVAL FUELS**

*R. W. Hiley and J. F. Pedley*

Insoluble particles formed during the storage of naval distillate diesel fuels (NATO F-76) have been identified as a major cause of fuel filter blockage in gas turbine powered warships. The paper describes the course of five trials, in which stable and unstable fuels were stored in 1000 gallon steel tanks under ambient conditions. The formation, agglomeration and settling of insoluble particles in the unstable fuels were monitored over a period of a year, while one stable fuel acted as control. Particular attention was paid to the tendency of the degrading fuels to block filters, which was monitored using a novel method. Two of the fuels contained stability improving additives, which failed to have the desired effect, and were deleterious to the filter-blocking tendency. Insolubles harvested from the fuels by settling and filtration were subjected to a range of analytical techniques, including thin-layer chromatography, pyrolysis/gas chromatography/mass spectroscopy and nuclear magnetic resonance spectroscopy. Results of the analytical work will be presented, leading to various conclusions regarding the chemical mechanisms of insolubles formation. Some studies of insolubles formation from combinations of various precursors in model hydrocarbon systems, with analyses of the products formed, will also be reported

## **STUDIES RELATING TO THE MECHANISM OF DIESEL FUEL DETERIORATION AND ADDITIVE INHIBITION**

*G. H. Lee, II and L. L. Stavinoha*

The formation of deleterious products in diesel fuels has become an increasing problem which can have a significant adverse effect on vehicle operation through fuel filter plugging and/or injector nozzle fouling. Fuel deterioration manifests itself in two stages. First are the chemical reactions between constituents present in the fuel at concentrations of parts per million or less, which lead to formation of fuel insoluble materials. Second is the formation of solid or semi-

solid particulate matter. The effect of fuel additives on particle distribution and growth has been determined in selected fuels. It appears that dispersants in some fuel stabilizers act to control particle size, thus making it appear that reactions have been minimized where, in fact, the chemical mechanism of particle formation has not been altered. The relationship between particulate and wall-adherent formation has been studied using time, temperature, and container size as variables. Here it has been found that the quantity of particulates remains larger and wall adherents smaller as container size increases. Wall adherents, in most cases, appear to form after particulate formation first takes place. These determinations were accomplished using particle in liquid measurement, as well as gravimetric determination of the fuel insoluble materials. A mathematical determination of particulate weight from number/size data was developed. Other chemical parameters, such as peroxide number, bromine number, and elemental analyses were also determined.

## **THERMAL STABILITY DEPOSIT MONITORING DEVICE**

*L. L. Stavinoha and J. G. Barbee*

In a cooperative Belvoir RD&E Center/US Navy Project, a unique, nondestructive deposit thickness-measuring technique was devised in support of diesel fuel injector/thermal fouling bench test development. A quantitative measure of deposit thickness is critical for meaningful results, and the current method of relating dielectric breakdown voltage to deposit thickness meets that requirement. Selected tubes from a JFTOT test matrix (consisting of 6 test fuels at various D 3241 test temperatures) were coated with a thin silver layer, and nickel plated to trap the varnish-like deposit between the aluminum tube and nickel plate. After placing the specimens in a plastic jacket, this allowed metallurgical grinding and polishing to be performed along the cross section of the tubes. At high magnifications in an electron microscope, the deposit thickness could be measured as the gap between the metals. The longitudinal and radial positions of the tube at each measured location were recorded for comparison with the results of various indirect measurement techniques which were applied to the tubes prior to sectioning (visual rating, TOR, and dielectric strength breakdown voltage). Auger spectrometer/ion milling was also performed on some of the tubes to compare with earlier work using this technique as a means of establishing deposit thickness as a function of milling rate versus time required for deposit removal. Based on an excellent correlation of 3.50 volts (dielectric breakdown) with 1.0 m deposit thickness for a 1 percent sulfur referee fuel, this technique is applied to deposits from other test fuels and is used to calculate deposit thickness and volume. This test methodology has been incorporated into a prototype testing device, the DMD, which, by simply pressing a switch, will gently lower the electrode onto the deposit, apply increasing voltage, detect dielectric breakdown, display detected voltage, and lift the electrode of the manually indexed test tube. The DMD is demonstrated as an invaluable tool for quantitating results in studies of fuel additive effects, reaction kinetics, effects of tube metallurgy and surface finish, and the effects of fuel flow rates or residence time on deposit formation.

## **SESSION 8: TEST METHOD DEVELOPMENT AND EVALUATION**

### **METHODOLOGY FOR EVALUATING THE STABILITY OF MOTOR GASOLINES**

*D. L. Morris, J. N. Bowden, L. L. Stavinoha and M. E. LePera*

This paper outlines interim results of a storage program aimed at developing improved methods for evaluating motor gasoline stability. A parallel effort within this program will define the engine-related operating problems when utilizing a stored gasoline with an original induction period (ASTM D 525) of approximately 360 minutes. A stable leaded gasoline was blended with varying amounts of unstable, catalytically cracked naphtha. A range of induction periods resulted. Several existing and potential predictive tests were applied to these blends. Darkroom storage was commenced at 43°C, 54°C, and ambient temperatures, for varying periods which will ultimately reach 4 years. Results to date show that a new test (Oxidation Stability: Total Gum Method; a modification of ASTM D 873) is a viable alternative to existing methods and warrants consideration by ASTM for adoption as a standard. This test is being used in Europe, and has been applied to evaluate the effectiveness of antioxidants in various refinery blend stocks in the United States.

### **DEVELOPMENT OF A TEST METHOD TO DETERMINE POTENTIAL PEROXIDE CONTENT IN TURBINE FUELS**

*G. E. Fodor*

Through the generally accepted 43°C bottle storage method of accelerated aging, the relative ratings of four selected fuels' oxidative tendencies were established. In this test, storage for about 12 weeks produces results that are comparable to a full year's storage under ambient conditions. To develop a practical test method for the prediction of peroxide potential of fuels, experimental conditions were sought so that the oxidative tendencies of fuels could be assessed within a reasonable time, i.e., less than 48 hours. Accordingly, a matrix of experiments was designed to allow selection of reaction conditions that would give results comparable to the 43°C bottle storage experiments. Additionally, the results of experiments should allow the development of global reaction kinetics to aid the determination of fuel peroxidation potential and to shed light on the reaction mechanism. The oxidations were carried out in a stirred pressurized reactor at 60°, 80°, and 100°C under oxygen pressures of 138, 690, 1034 kPa (20, 100, 150 psig) for periods of up to 70 hours. From the partially completed experimental matrix, fuel stressing was done at 60°, 80°C, and 100°C under an oxygen pressure of 690 kPa (100 psig), and at 80°C under 1034 kPa (150 psig) of oxygen. Additional experiments were carried out at 80°C and 100°C under 138 kPa of oxygen. Experiments conducted at 60°C for up to 48 hours gave low reaction rates. Results of experiments at 80°C/690 kPa oxygen were promising, but the reaction rates were still too slow. Oxidation rates at 100°C were acceptably high, and the results agreed with those of the bottle storage for the most and least stable fuels. Results for the two intermediate fuels, however, were interchanged. Interpretation of Arrhenius plots offers a solution to project objectives.

## **A STUDY OF TEST VARIABLES AFFECTING RESULTS OBTAINED IN THE ASTM D 2274 ACCELERATED STABILITY TEST**

*E. W. White*

Poor reproducibility among laboratories using the ASTM D2274 test for the storage stability of distillate fuels has long been a problem. Several years ago, David Taylor Naval Ship Research and Development Center (DTNSRDC) initiated a study to ascertain critical variables in the test. This paper discusses the results of three major areas of that study. First, the responses to a questionnaire issued by an ASTM working group show major variations in practices among laboratories using the method. A few of these variations appear to represent significant differences. Second, when five operators each tested eight replicates of a single fuel, their averages and associated standard deviations were sometimes significantly different. This implies that part of the poor reproducibility of D2274 may lie in operator idiosyncrasies. Third, when the major specified process variables (bath temperature, oxygen flow rate, and time in bath) were studied experimentally, the results indicated that these variables had only minor effect on the insolubles measured, if the variables were kept within prescribed limits. However, plots of time in bath versus insolubles formation for several fuels indicated that a single test time, such as the 16 hours of D2274, does not adequately define how the fuel will behave in storage

## **SUMMARY OVERVIEW OF SOURCES OF ERROR IN ACCELERATED STABILITY TEST METHODS FOR DIESEL FUELS**

*G. H. Lee, II and L. L. Stavinoha*

Ten test methods (including ASTM D 2274) used to determine the accelerated oxidation stability of middle distillate fuels were reviewed. A critique of various procedures (such as weight and volume measurements) within these test methods is summarized, including an estimation of which procedural steps have the greatest potential affect on final test results. Subsequent laboratory work allowed more definitive conclusions to be made on the effect of particular procedures on test results using a small set of test fuels. Changes in particulate filtration procedure and adherent fuel insolubles determination were suggested and submitted for ASTM cooperative "round robin" testing. These data are also illustrated in this report.

## **EFFECT OF NITROGEN AND SULPHUR CONTAINING COMPOUNDS ON THE DETERIORATION OF FUELS AT ELEVATED TEMPERATURES**

*K. T. Reddy, N. P. Cernansky and R. S. Cohen*

Fuel deterioration problems are expected to become severe in the future due to the anticipated usage of broadened specification and alternative fuels and increased demands on aircraft performance. Future fuels will tend to have relatively high contents of heteroatomic species (nitrogen, sulfur and oxygen containing compounds) which are reactive constituents and are known to promote fuel degradation. Past work, emphasizing research on actual fuels and dopants, has yielded unclear and, at times, contradictory information regarding the effects of certain dopants on fuel degradation. Consequently, the study of a single component model fuel, n-dodecane, singly and in combination with heteroatomic species, was undertaken, motivated

largely by the simplifications in degradation chemistry inherent in such systems. The fuels, n-dodecane and n-dodecane plus dopants, have been stressed on a modified Jet Fuel Thermal Oxidation Tester facility between 200 - 400 °C. Gas chromatography and mass spectrometry analysis of the control and stressed samples yielded reaction mechanism information. The soluble products (in the polar fraction) consisted mainly of tetrahydrofuran derivatives, dodecanol and dodecanone isomers, and dodecylhydroperoxide (ROOH) decomposition products. The major soluble products, as mentioned above, were always the same, with and without dopant addition, but their distributions varied considerably. 2,5-dimethylpyrrole and 3,4-dimercaptotoluene dopants individually added to n-dodecane introduce cooxidation reactions and consequently inhibit ROOH formation. Dibutylsulfide dopant added to n-dodecane promotes dodecanol and dodecanone formation and inhibits ROOH formation.

## **THE INFLUENCE OF POLAR COMPOUNDS ON THE STABILITY OF JET FUEL**

*D. R. Kendall and P. A. Stevenson*

Development of a flask oxidation test to measure directly the oxidation rate of kerosine jet fuels at high temperatures has permitted resolution of the oxidation process into initiation and inhibition stages. The observed rate of initiation provides a good indication of the tendency of fuels to form deposits under thermal stress. In addition, fuel trace polar compounds have been extracted and their influence on fuel stability determined in the flask oxidation test and the Jet Fuel Thermal Oxidation Tester (JFTOT). The polar extracts comprised a sulphur-rich and three acidic fractions. When added to a low sulphur content fuel the sulphur-rich extract was found to impart antioxidantancy in the flask test but, conversely, encouraged deposit formation in the JFTOT. In contrast, two of the acidic fractions had a markedly pro-oxidant influence in the flask test but their presence yielded only slightly greater amounts of deposits in the JFTOT. A combination of the polar extracts, however, promoted a significant increase in deposition in the JFTOT, suggesting that highly deleterious interactions occur between sulphur and acidic species. Work with model sulphur compounds has confirmed the possibility of strong interactions with fuel acid fractions but has highlighted the importance of acidic species and source. Of greater significance is the finding that acids are strong promoters of deposition in their own right.

## **THERMAL STABILITY OF DIESEL FUELS**

*L. L. Stavinoha, J. G. Barbee and D. M. Yost*

In a cooperative Belvoir RD&E Center/US Navy Project, a unique, nondestructive deposit thickness-measuring technique was devised in support of diesel fuel injector/thermal fouling bench test development. A quantitative measure of deposit thickness is critical for meaningful results, and the current method of relating dielectric breakdown voltage to deposit thickness meets that requirement. Selected tubes from a JFTOT test matrix (consisting of 6 test fuels at various D 3241 test temperatures) were coated with a thin silver layer, and nickel plated to trap the varnish-like deposit between the aluminum tube and nickel plate. After placing the specimens in a plastic jacket, this allowed metallurgical grinding and polishing to be performed along the cross section of the tubes. At high magnifications in an electron microscope, the deposit thickness could be measured as the gap between the metals. The longitudinal and radial positions

of the tube at each measured location were recorded for comparison with the results of various indirect measurement techniques which were applied to the tubes prior to sectioning (visual rating, TOR, and dielectric strength breakdown voltage). Auger spectrometer/ion milling was also performed on some of the tubes to compare with earlier work using this technique as a means of establishing deposit thickness as a function of milling rate versus time required for deposit removal. Based on an excellent correlation of 3.50 volts (dielectric breakdown) with 1.0 m deposit thickness for a 1 percent sulfur referee fuel, this technique is applied to deposits from other test fuels and is used to calculate deposit thickness and volume. This test methodology has been incorporated into a prototype testing device, the DMD, which, by simply pressing a switch, will gently lower the electrode onto the deposit, apply increasing voltage, detect dielectric breakdown, display detected voltage, and lift the electrode of the manually indexed test tube. The DMD is demonstrated as an invaluable tool for quantitating results in studies of fuel additive effects, reaction kinetics, effects of tube metallurgy and surface finish, and the effects of fuel flow rates or residence time on deposit formation.

## **EFFECTS OF AN UNSTABLE DIESEL FUEL ON INJECTOR COKING AND VEHICLE PERFORMANCE**

*R. Halsall*

The short-term effects of an oxidatively unstable diesel fuel were investigated in a 1982 General Motors 4.3-L V-6 diesel vehicle in city-suburban service. Effects on injector coking, FTP emissions, fuel economy, cold-idle passenger compartment sound pressure, and driveability were monitored. The unstable test fuel caused frequent severe vehicle fuel filter plugging, despite the fuel having been pre-filtered with a filter having a pore size half that of the vehicle fuel filter. Filter plugging caused by fuel gum resulted in excessive smoke emission and power loss in highway operation and a tendency for the engine to stall easily when cold. It was concluded that vehicle fuel filter plugging can cause some of the complaints (e.g., poor driveability and excessive smoke) attributed to injector coking. Injector coking was also observed, but the extent was insufficient to cause adverse effects on the measured parameters.

## **SESSION 9: SHALE/COAL LIQUIDS AND ADDITIVE CHEMISTRY**

### **INFLUENCES OF SULPHUR, NITROGEN AND OXYGEN BEARING COMPOUNDS ON DIESEL FUEL STORAGE STABILITY**

*R. E. Morris and K.W. Flohr*

Effects exerted by selected sulfur, nitrogen and oxygen-bearing compounds on the storage stability of a shale-derived diesel fuel have been examined. Fuel samples were stressed at elevated temperatures in vented borosilicate glass vessels, utilizing quantitative determinations of insoluble reaction products as a measure of inherent storage stability. Sulfur-bearing dopants included sulfides, disulfides, thiols and a sulfonic acid. None of the sulfur compounds examined significantly degraded fuel stability when used alone, but in combinations with an active nitrogen

compound they were found to exert differing influences on insoluble products formation. The ratios of sulfur to active nitrogen from selected dopants were found, in some instances, to influence the distribution of products between filterable particulates and gum deposited on vessel walls. The effects of fuel acidity on degradation phenomena.

## **EFFECTS OF SHALE-DERIVED POLAR COMPOUNDS ON DIESEL FUEL STABILITY**

*J. V. Cooney, E. J. Beal, G. W. Mushrush and R. N. Hazlett*

Polar compounds, particularly nitrogen heterocycles, frequently have been implicated in the chemical processes involved in middle distillate fuel instability. Nitrogen-rich polar fractions were isolated and characterized from two unstable shale diesel liquids produced during the ' U.S. Navy's Shale-I and Shale-II exercises and from the high nitrogen hydrocracker intermediate stream from the Caribou (Utah) refinery. The identification of the extract components was accomplished by combined GC/MS. These extracts were added as dopants to a stable shale diesel fuel in an effort to produce instability under accelerated storage conditions. These experiments were designed to provide information about stability in an actual fuel where a range of polar species is present. The results demonstrate that the total nitrogen content in a fuel does not control the amount of sediment formation in a fuel. Further, the more polar extracts exhibit the greatest effect in decreasing fuel stability.

## **STORAGE STABILITY OF COAL-DERIVED LIQUIDS**

*B. Hoesterey, W. H. McClennen, G. R. Hill and H. L. C. Meuzelaar*

Pyrolytic coal tars and other coal-derived liquid fuels are notoriously reactive, especially with regard to regressive ("retrograde") phenomena. As a result, coal liquefaction experiments have often produced tars which reverted to black, coal-like solids within a matter of days or weeks. The high reactivity is a serious stumbling block on the road to synfuels production from coal. Even hydrotreatment, unless carried out under the most severe conditions, does not prevent coal liquids from becoming darker and more and more viscous upon storage. Fresh coal tars from three Western coals of different rank (lignite, subbituminous, and high volatile bituminous) were obtained from a Wellman Galusha fixed bed gasifier and stored at temperatures ranging from -180°C (in LN<sub>2</sub>) to +60°C (in o<sub>2</sub>) for periods up to several months. Stored tar ., samples were analyzed by means of Curie-point desorption mass spectrometry followed by factor analysis and discriminate analysis of the mass spectral pattern. This enabled the detection and interpretation of minute changes in chemical composition. Other analytical methods used include thermogravimetry and Fourier Transform Infrared Spectroscopy. Dihydroxybenzenes and hydroxynaphthalenes were found to be among the most reactive tar components. The reaction mechanisms, although still incompletely understood, appear to involve primarily condensation reactions. A storage temperature of -90°C (under nitrogen) was found to be effective in preventing measurable changes in tar composition over periods up to several months. Storage at regular refrigerator or freezer temperatures, however, did not completely prevent the occurrence of regressive changes. Our results confirm the extreme reactivity of coal-derived tars and caution against the effects of storage under less than optimal conditions. Computerized mass

spectrometric analysis techniques were shown to be quite effective in detecting and monitoring storage effects. Some proposed mechanisms for regressive reactions in coal tars will be discussed as well as possible procedures for increasing storage stability.

### **FATES OF HETEROATOMS WHEN PROCESSING CRUDES**

*D. Sutterfield, J. Wells, F. S. Manning*

There are significant interactions between compound classes during hydrotreating. These interactions make compositional studies of synthetic crude hydroprocessing of great importance. Although specific compound identification is neither necessary nor practical, compound-type separation and identification as practiced at NIPER are particularly well suited for improving the understanding of the chemistry of synthetic crude hydroprocessing. This paper presents and compares the results of hydrotreating coal liquids and shale oil. Compound classes are identified and quantitated with emphasis on the heteroatoms which are particularly deleterious to quality and processing.

### **THE ROLE OF ANTIOXIDANTS IN IMPROVING STABILITY PROPERTIES OF SHALE OIL AND ITS PRODUCTS**

*N. Por, N. Brodsky, D. Givoni and A. Raweh*

The subject of this paper is to establish the effect of various types of antioxidants on stabilities of shale oils produced in the Mishor Rotem pilot plant, and on its blends with conventional crude oils in various ratios. The purpose of the first phase of this investigation is to establish the possibility of achieving a sufficient stability of this shale oil or its blends with crude oils for limited storage periods by adding antioxidants instead of hydrotreating it at the oil shale retorting site, which means delaying this operation until the shale has reached the more convenient facilities of an oil refinery. The goal of the second phase of this investigation is to define the response of shale oil fractions and their blends with parallel fractions of conventional crude Oils to the various types of antioxidants and also to establish their respective concentrations needed to improve 1 their stabilities. After commissioning the pilot plant at Mishor Rotern, which is producing several gallons of shale oil per day, it has been made possible to study in more detail the properties of the so-obtained shale oil and its products.

### **ADDITIVE EVALUATION FOR SHALE JP-4 JET FUEL**

*T. A. Boos and T. L. Dues*

This paper summarized work performed 1n the Shale JP-4 Additive Evaluation Program. In this program, shale JP-4 jet fuel was obtained as the test fuel from the Caribou Refinery at Woods Cross UT (Reference 1). Combinations of antioxidants, 1ubricity enhancers, anti-static additive, Fuel System Icing Inhibitor {FSII), JFA-5 and metal deactivator were blended with the fuel fn varying concentrations to make the test samples. The thermal and storage stability, lubricity, conductivity and water separation characteristics of the samples were studied at four intervals over 15 months. The test results showed that a minimum amount of antioxidant was required for



the fuel to maintain acceptable thermal and storage stability, and a maximum amount of lubricity enhancer was required for the fuel to maintain good lubricating quality. JFA-5 and metal deactivator had minimal effect on fuel stability. Few fuels met the electrical conductivity requirement, which was attributed to several changes in sample containers. Water separation characteristics were acceptable overall, with only fuels containing maximum lubricity enhancer and/or JFA-5 obtaining failing ratings. All fuels containing maximum lubricity enhancer but no JFA-5 had at least one acceptable rating.

## **SESSION 10: EFFECT OF REFINERY PROCESSING AND ADDITIVES ON STABILITY**

### **ADDITIVES FOR MIDDLE DISTILLATE AND KEROSENE FUELS**

*C. P. Henry*

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

### **STORAGE CHARACTERISTICS OF ADDITIVE-TREATED DIESEL FUEL**

*J. J. Weers*

A study was conducted to determine the influence storage conditions have on the ability of stability additives to hinder formation of insoluble residue in diesel fuel. Residue levels as a function of storage duration, temperature, and additive concentration were determined on a number of fuels. Accelerated stability test data was also obtained on the additive treated fuels and compared to the results generated actual storage conditions. The data suggest addition of an additive to a diesel fuel may result in a dramatic decrease in the residue-forming tendency of the fuel a variety of conditions.

### **EFFECTIVENESS OF ANTIOXIDANTS IN JP-5**

*L. M. Turner, G. E. Speck and C. J. Nowack*

Hydroperoxides in jet fuel are the cause of degradation of aircraft fuel system elastomers. The JP-5 military specification requires the addition of an antioxidant to insure the protection against peroxide formation in the fuels. Fuels processed by different refinery methods were evaluated for their tendency to peroxidize under accelerated storage conditions of 100°C. JP-5 produced via hydrocracking or severe hydrogenation peroxidized at a rate 300 times greater than that of a straight run distillate. The effectiveness and optimum concentration of some of the approved antioxidants was evaluated in several JP-5 fuels at 100°C and 60°C. The antioxidants which

showed the greatest effectiveness in controlling peroxidation were the hindered phenols having a tertiary butyl group at both ortho positions. At accelerated storage conditions of 60°C and 8 weeks and 8 ppm concentration of this totally hindered phenol proved to be as effective as a 24 ppm concentration of a partially hindered phenol.

## **DEVELOPMENTS IN HANDLING LONG-TERM STORAGE PROBLEMS IN JET FUELS**

*N. Por and N. Brodsky*

Since the validity of long-term stability testing used in this country has been further established, more insight into the behaviour of various types of jet fuels and additives used in jet fuels has been gained. The main endeavour regarding studies on long-term stabilities of jet fuels during the last two years has been directed to an evaluation of the following points: a. Long-term stability of jet fuels containing various antioxidants and lubricity-improving additives: a relative superiority of certain phenolic antioxidants, in relation to other additives of this type, has been observed. On the other hand, use of lubricity-improving additives seems to create some problems in long-term storage of jet fuels containing them. Factors governing these processes have been studied and are discussed in the framework of this study. b. Effect of processing methods and conditions on stability properties of jet fuels: stability problems arising as a result of certain jet fuel processing methods have been defined and possible remedies are discussed. A further evaluation of laboratory prediction testing of long-term storage stability of jet fuels by establishing the rate of change with time of the resistivity of jet fuels to break-down when exposed to degradative processes, has been achieved and is also dealt with in this paper.

## **STORAGE STABILITY OF HYDROTREATED RESIDUAL OIL**

*H. Kaminyama, H. Ishikawa and C. Sera*

Our attention was paid to the stability of hydrotreated residual oils produced by pilot plant from high sulfur heavy residue. The stability, causes of the instability and improvement of the stability were investigated. The following results will be presented and discussed: The stability of the hydrotreated residual oils depends upon kind of the feedstocks and pilot plant operating condition. In the case of the oil being unstable, the increase of organic sludge is observed during storage. The stability closely relates to polar fraction content and solvent power of maltene in the hydrotreated residual oils. The stability can be improved by adding a very small amount of the polar fraction.

## **AUTOMOTIVE DIESEL FUEL STABILITY- AN AUSTRALIAN VIEWPOINT**

*R. J. Smith and L. D. Palmer*

Historically, numerous tests have been used to assess the long-term storage stability of automotive diesel fuel in the Australian marketplace. With varying degrees of success, these have included the more reliable oven storage tests at 110°F or 175°F as well as other more accelerated tests incorporating copper metal or soluble copper at higher temperatures. The

reliability of such tests in predicting long-term field storage stability of diesel fuel has been studied in detail, with the internationally accepted 110°F/13 week test being the most satisfactory indicator. Apart from the 175°F/7 day stability test, other methods (particularly those incorporating copper) are generally unreliable and easily affected by such influences as light exposure. The effectiveness of techniques of caustic washing and additive treatment in improving storage stability of diesel fuel containing various levels of light cycle oil is discussed. Excellent results have been obtained, particularly in reduction of deposit formation tendencies. However, despite literature claims and accelerated test indications, additive treatment offers little in terms of prevention of colour degradation, a property of some importance in the Australian market-place. Certain additives for storage stability enhancement, however, have been found to aggravate other problems, most notably the retention of water haze and formation of stable emulsions. In addition, a negative influence on diesel fuel storage quality has been observed with certain biocides containing bis(trichloromethyl)sulfone, which reacted with pyrrolic compounds to produce black deposits. Overall, it is possible to use additive treatment to achieve excellent storage properties in terms of deposit formation in Australian ADO containing cracked stock. However, to produce colour stable product it is necessary to involve other processes such as hydrotreatment of light cycle oil.

#### **ASSESSMENT OF STORAGE STABILITY ADDITIVES FOR NAVAL DISTILLATE FUEL**

*R. N. Hazlett, D. R. Hardy and E. W. White*

This paper summarizes the effectiveness of five of six allowed military specification stabilizer additives and of five proprietary commercial stabilizer products in five military fuels. This work emphasized evaluations of aged fuels which exhibited poor or marginal stability behavior during long-term storage. The fuels contained a range of catalytically cracked stock from less than 10% up to 30%. The results of accelerated storage stability tests run under a variety of test conditions with temperature and storage time being the main variables will be discussed. Test temperatures varied from 43° to 95°C. In addition to gravimetric tests, the results of the effect of the additives on important fuel properties will be presented and discussed. The effects of the commercial additives added at 24 to 50 mg/liter on selected fuel properties will also be presented and discussed.

#### **HYDROTREATMENT OF LIGHT CYCLE OIL FOR STABILIZATION OF AUTOMOTIVE DIESEL FUEL**

*L. D. Palmer and B. V. Copson*

Hydrotreatment of only the light cycle oil LCO component of automotive diesel fuel has been studied as a means of achieving high deposit and colour-stability for diesel fuel derived from Australian crude oil. Light cycle oil was hydrotreated using a 300 g/h pilot reactor at a range of severities. Total reactor pressures were in the 600 to 1000 psig range generally employed for conventional refinery hydrodesulfurization processing. The stability of automotive diesel fuels consisting of 35 percent LCO and 65 percent straight-run distillate was addressed by 175°F/7 day and 110°F/13 week accelerated storage stability tests. Hydrotreating LCO at all of the severities studied resulted in automotive diesel fuel blends of exceptionally high colour and deposit stability. Following storage stability tests, concentrations of particulate deposits were

around the limit of detectability (<0.1 mg/100 mL), and colour increases due to the tests were only slight. Concentrations were determined for two of the compound classes considered to be strongly implicated in the formation of insoluble deposits in diesel fuels. Pyrrole/indole-type nitrogen compounds were present at concentrations of approx. 25 mg/kg in untreated LCO. This type of nitrogen was relatively easily removed by hydrotreating, resulting in concentrations of <5 mg/kg in hydrotreated LCO's. Thiophenols, present at concentrations of 65 mg/kg in untreated LCO, were also reduced to <5 mg/kg. Total nitrogen content, taken by itself, was shown to be a poor indicator of fuel stability. The abilities of hydrotreating and stabilizing additives to yield highly stable fuels were compared. For the low sulfur/nitrogen diesel fuel studied, a selected additive system is capable of efficiently reducing sediment formation to acceptably low values. Hydrotreating, although a much more expensive option, offers the advantage of very high colour stability. Australian experience has shown that while colour cannot be considered to be a genuine fuel quality property, consumers show a strong preference for lightly coloured, colour-stable diesel fuel. In such circumstances the more costly option of LCO hydrotreating as opposed to chemical additives may be warranted.

## **CAUSES OF COLOR CHANGES AND PARTICULATE FORMATION IN NAVY DISTILLATE FUELS**

*D. W. Brinkmann, O. Bhan and B. Carley*

The military has unusual requirements for storage of large quantities of fuel for long periods of time as strategic war reserves. Because of the location of these supplies, it is often expensive to remove old fuel and refill the tanks. Thus, recent experience in which Navy distillate fuels have been going off color and showing a tendency to form unacceptable levels of solids in a relatively short period of time has drawn serious attention. This paper will describe the detailed compositional studies of companion diesel fuels that did and did not exhibit problems, with a discussion of the differences observed and the probable mechanisms leading to the problems. Our work suggests that oxidation of neutral components present in fuel to polar intermediates may be a major pathway for sediment formation and darkening of diesel fuels. Within a given compound class, the more aromatic, higher molecular weight members were usually more active in sediment formation.

## **SESSION 11: POSTER SESSION**

### **ENHANCED METHODOLOGY FOR JET FUEL CLEAN AND BRIGHT EVALUATIONS**

*J. G. Bargee, R. S. McInnis, K. B. Kohl, L. L. Stavinoha and W. R. Williams*

Many common types of debris were encountered during the course of a recent investigation to identify an unusual contaminant present in jet fuel (JP-4) at three Army locations. Most of the other debris were materials commonly found in fuel samples, e.g., metal flakes, rust, fibers, dirt, etc. Various analytical techniques indicated that the unusual flake-like organic debris was probably a manmade (synthetic) organic component and is not a fuel product. It had a high melting point (>200°C) and was insoluble in most common solvents. The physical appearance of

the flake (thin and flat while floating in the fluid) indicated that the material was originally formed or deposited in a thin layer prior to its introduction into the fuel. The most likely source of a material with these characteristics was an unpigmented paint or protective coating from one of the epoxy or similar resin families. Such a material could be introduced into the fuel by debonding or delamination of the contaminant from any handling, storage, or transportation equipment that contains such a coating. The elements, chemical bonds, and functional groups detected by the various analytical tests were consistent with this conclusion. The use of a lightbox for enhanced visual ("Clean and Bright") evaluation is presented in this paper. Also discussed is an approach for isolating similar debris (from fuels) to provide for scanning electron microscopic, auger, and electron spectroscopy for chemical analysis (ESCA) evaluations.

## **PYROLYSIS/FIELD IONIZATION MASS SPECTROMETRIC ANALYSIS OF FUEL SEDIMENTS**

*R. Malhotra*

Pyrolysis/field ionization mass spectrometric analysis of a sediment from a shale-derived fuel doped with 2, 5-dimethylpyrrole shows peaks in the 50 to 300 amu range. Most of these peaks can be assigned to the dopant and derived coupling materials. The spectra of sediments from undoped fuels are very different, spanning a much wider mass range and showing features characteristic of polymerization products. Methylindoles or dihydroquinolines are strongly implicated in sediment formation.