

# **3<sup>rd</sup> INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS**

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## **Abstract Summaries**

### **SESSION 1: STABILITY OF RESIDUAL FUEL**

#### **RESIDUAL FUEL OIL STABILITY AND COMPATIBILITY STUDIES**

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

Following the introductory study on residual fuel oil stability properties and compatibilities reported at the 2nd International Conference on Long Term Storage Stabilities of Liquid Fuels which took place in San Antonio, Texas in July 1986, further work regarding this subject has been carried out at the Oil Refineries Ltd. Research Laboratory in Haifa. The present work covers an investigation of the relation between the chemical characteristics of residual fuels and their stability and compatibility properties, with emphasis given to the mechanisms of the processes associated with degradation product formation during storage and use. Data reported in this work facilitate the operation of visbreaker processes, not only with respect to their severities but also regarding the visbreaker technologies involved; this study has been made possible by using data concerning intermediate as well as final samples of the products obtained in the recently employed soaker operations and comparing them with similar samples obtained in the formerly used conventional visbreaking process. All the samples have been subjected to conventional as well as specially devised tests and laboratory processes. Data obtained show the advantages of using the asphaltene peptization state phenomenon as an indication of the stability and compatibility properties of the residual fuels; this can also be useful as a controlling parameter for the desired optimized severity of visbreaker operations.

#### **PREDICTION OF STORAGE STABILITY AND COMPATIBILITY OF RESIDUAL FUEL OILS**

*William C. Rovesti and Raymond P. Anderson*

The occurrence of problems in the storage and handling of residual fuel oils in the United States Electric Utility Industry has increased with the increased use of lower quality crudes and with the increased severity of refining which refiners have used to convert residual materials to distillate products. Conventional residual fuel oil specifications and test methods were found to be inadequate to predict or prevent problems due to instability (tendency to form sediment on storage or thermal stress or to undergo other changes such as changes in viscosity) or to incompatibility (tendency to form sediment on blending with a diluent or with another fuel). In the 2nd International Conference on long-Term Storage Stabilities of liquid fuels, we reported on simple rapid test methods which showed promise for the prediction of stability and compatibility characteristics of residual fuels. These tests have been further evaluated. The results of the rapid test methods correlate with baseline laboratory tests for stability and compatibility. The more

promising predictive tests are undergoing implementation in selected electric utility laboratories as part of an overall program to relate the test results to actual plant performance relative to heavy fuel oil blending, storage and handling. This report discusses some of the initial results of this "field evaluation" of the rapid test methods

## **COATING SYSTEMS FOR THE INTERNAL LINING OF METHANOL AND METHANOL-CONTAINING FUEL STORAGE TANKS**

*Olof C. Vorster*

In the past, coating systems were extensively used to coat the insides of steel and concrete crude oil as well as refined liquid fuel storage tanks. These coatings were however not resistant to the methanol/fuel or crude methanol mixtures being stored at present. In this paper an attempt is made to assess the problems associated with the storage of methanol and methanol containing fuel mixtures in both steel and concrete storage tanks.

## **EFFECTS OF STORAGE ON THE STABILITY OF RESIDUAL FUEL OIL**

*C.P.G. Lewis and F. DeJonge*

Postbus 3003, 1003 AA Amsterdam, The Netherlands A stable fuel oil is defined as a fuel that will not throw down significant quantities of carbonaceous sludge during use, even when stored and handled at elevated temperatures. Sludge formation will not take place if the oil phase has sufficient aromaticity to prevent the asphaltenes from flocculating. Asphaltenes are large, complex and highly aromatic molecules that can be distinguished from coke or other contaminants by their solubility in highly aromatic solvents. The stability is governed by a balancing mechanism, which depends on the chemical nature of the asphaltenic molecules present and of the oil surrounding them. This balance is described in terms of the required aromaticity (flocculation tendency) for the asphaltene molecules to remain in solution, and the available aromaticity (peptizing power) of the oil phase. This paper presents the results of investigations into the effects of storage on stability. It has been found that the stability of a stable residual fuel composed of normal refinery streams does not deteriorate perceptibly during storage for two years at temperatures up to 75°C. However, a significant change in the viscosity and in the asphaltenes content is observed as a result of the conversion of resins into newly formed (peptized) asphaltenes due to oxidation/polymerisation reactions. The rate of change depends markedly on the scale and temperature of storage. On a laboratory scale and at elevated temperature (75°C) the increase is significantly more pronounced than in large tanks at more realistic storage temperatures (up to 50°C). A marginally unstable fuel clearly shows additional flocculation of asphaltenes, the extent of which increases with storage temperature. The significant role of oxygen in the flocculation process has been demonstrated, i.e. in its absence flocculation is strongly delayed. The possibility of flocculation inhibition by chemical compounds is discussed. The state of the art of detection of flocculated asphaltenes in opaque media is reviewed. For field measurements a test kit has been developed, based on the Shell Spot Test, and recently obtained experience is presented.

## **THE INFLUENCE OF LUBRICATING OILS ON THE COLLOIDAL STABILITY RESERVE OF RESIDUAL FUEL OILS**

*Wanda Pogonowska-Fabriek, M.Sc., and Paul Holbrook*

In total some 200 blends of 5 residual fuel oils and 4 lubricating oils were prepared and over 500 Total Sediment determinations were carried out. The fuel characteristics covered a wide range of kinematic viscosity from 14.52 to 45.08 mm<sup>2</sup>/s at 100 °C, a variety of asphaltene contents from 0.94 to 12.21 % m/m and aromaticity levels from 22.3 to 45.2 mole % aromatic carbon. The lubricating oils had viscosity indices ranging from 75 to 96 with aromaticity levels from 0 to 16.3 mole % aromatic carbon. The choice of lubricating oils also included varying amounts of TBN additives ranging from less than 0.05 to 28.23 mg KOH/g. The blends prepared for F1 and F5 fuels proved totally compatible and stable, whereas blends of fuels F2, F3 and F4 showed incompatibility as determined by TOTAL SEDIMENT EXISTENT (TSE), POTENTIAL (TSP) and ACCELERATED (TSA) test methods. The analysis revealed that the margin between stability and instability relied on a very small blend concentration, with the addition of 1% by mass being sufficient to cause a sharp increase in the Total Sediment content. It was quite clear that where incompatibility of blend components occurred, the sudden change from stability to instability was always initiated by the chemical ageing method as surprisingly low blend concentrations, followed by the thermal ageing method. It was significant that for blends recording TSP and TSA results above the 0.10% m/m maximum limit, TSE values remained acceptable until much higher concentrations of lubricating oil were reached. A number of additional exercises were carried out to study the relationship of oil adsorption by the upper and lower filter media, the spread of the aged Total Sediment results at various levels and the extent of lubricating oil additive deposition on Whatman GF/A filter media. Also, the rate of sediment change was studied at 1% increments, until the stability reserve of the blend was totally exhausted. In order to create as full a picture as possible, the blends with high concentrations of lubricating oil i.e., 50% and above, were also analyzed. The work has proved extremely promising in respect of the possible use of aromaticity factors determined by the NUCLEAR MAGNETIC RESONANCE (NMR) technique as a tool to assist in the prediction of residual fuel oil stability reserve.

## **QUALITY OF FUELS FORMED BY SEVERE HYDROTREATMENT OF VACUUM RESIDUES**

*Takao Hara, Kazuhiro Yanagida and Asanori Okarx*

Heteroatom functionalities are quantitatively analyzed for vacuum residues of various petroleum crude oil. Distribution of acidic NH group and OH group among vacuum residues has been analyzed by measuring infrared spectrum in very dilute solution using 2 cm KBr liquid cells. The structure and nature of such functionalities have been characterized for petroleum vacuum residues, compared with those involved in other hydrocarbon resources such as oils and bitumen, shale oil, coal liquefaction products and coal pyrolysis tar. Structural change of such polar functionalities caused by various conditions of hydroprocessing has been analyzed in the hydrotreatment of vacuum residues derived from various resources. Petroleum vacuum residue was severely hydroprocessed in various reaction conditions (395-420°C, IHSV=0.20 h<sup>-1</sup>, H<sub>2</sub> pressure=130 kg/cm<sup>2</sup>, feed rate=150 cc/h) in the presence of a hydrodesulfurization catalyst by a

two-stage microreactor. The 538°C+ conversion reached to 57% at the next severe reaction condition. The sludge formed during the hydroprocessing as well as heavy ends (350°C+ and 538°C+) produced by the hydroprocessing were structurally characterized. The storage stability of the products were also discussed.

## **SESSION 2: MICROBIOLOGICAL GROWTH IN FUELS**

### **BIODEGRADATION OF STORED HEAVY FUEL OIL WITH PRODUCTION OF METHANE IN UNLINED ROCK CAVERNS**

*R. Roffey and A. Edlund*

During storage of heavy fuel oil on a waterbed in unlined rock caverns for long periods of time problems with degradation of oil and production of methane gas have been observed. In order to understand the factors responsible for the microbial methane production and to find methods to inhibit the methanogenic bacteria a study was undertaken. Chemical and microbiological investigations at two storage plants where problems had occurred showed that anaerobic conditions existed in the bedwater and that a complex microbial community was present. The methane production was calculated to be 2-37 91day, ml bedwater. To study methods to inhibit the methanogenic activity laboratory model systems were used. Four methods were evaluated which were increasing the oxygen level in the bedwater, increasing the pH to 9, using a biocide an isothiazolone compound or addition of nitrate. It was found that only nitrate addition gave a satisfactory inhibition at a concentration of 0.5 911 in the water.

### **STUDIES ON A U.S. MILITARY APPROVED FUEL PRESERVATIVE AND STABILIZER**

*F. T. Klein*

West Germany Introduction (1) MIL-S-53021 is the military specification for stabilizer additive, diesel fuel. This specification is approved for use by all departments and Agencies of the U.S. Department of Defense. The specification covers a stabilizer additive for use in diesel fuels meeting the requirement of the Federal specifications for fuel oil and diesel which are intended for intermediate or long-term storage. The stabilizer additive shall consist of petroleum-soluble compounds which perform the following functions: (a) antioxidant stabilizer, (b) metal deactivator, (c) dispersant, (d) corrosion inhibitor, and (e) biocide. The reference formulation of the stabilizer additive given in the military specification consists of DuPont Fuel Oil Additive FOA-15 and Biobor JF (U.S. Borax), where the FOA-15 covers, as listed above, the functions (a) through (d), and Biobor JF function (e). ANGUS Chemical Company completed a test program to meet the specifications outlined in MIL-S-53021 for stabilizer additive diesel fuel, as well as tests to show the efficacy of FUELSAVER as a biocide. The combination of DuPont's FOA-15 and FUELSAVER was approved for inclusion in the qualified products list 53021 in October 1986.

## **A SURVEY OF THE MICROBIAL CONTAMINATION LEVEL OF SOME FINNISH FUEL STORAGE SYSTEMS**

*P. Carlson, S. Niemela, E. Tenhunen*

The aim of the project was to estimate the degree of microbial contamination of jet fuel and light heating oil in both long- and short-term storage in Finland. The nine storage systems studied included both rock caverns and above-ground and subsurface steel tanks. Samples were taken biannually. Sampling methods were developed. Certain physical and chemical factors relevant to the appearance of microbiological problems were analyzed, too. No corrosiveness was found in the fuel samples studied in the standard silver and copper corrosiveness tests, nor when a more sensitive Swedish method was applied, utilizing piezoelectric crystals. No water bottoms were found in the jet fuel storage systems and few microbes were found in the fuel itself. In the light heating oil water bottoms the microbial counts were higher. *Cladosporium resinae*, a common fuel contaminant, was absent from the two rock caverns studied. The constantly low temperature in these tends to select an aerobic flora consisting chiefly of cold tolerant gram-negative rods, including some psychophilic forms. Many of the bacteria are pseudomonads, which are especially difficult to eradicate with biocides, because resistant mutants are likely to develop quickly. The water bottoms of the fuel tanks and the bed waters of the caverns, as well as the fuels, were analyzed for C2-C11 saturated aliphatic straight chain carboxylic acids. These compounds are likely to accumulate in fuel-water systems, where microbial growth has taken place. They were found in low concentrations usually not exceeding those of fresh products and, with a few exceptions, are not thought to be of microbiological origin.

## **THE USE OF BNPD TO CONTROL MICROBIAL GROWTH IN DIESEL FUEL SYSTEMS**

*R. Elsmore & W.G. Guthrie*

Microbial deterioration of hydrocarbon-based products has been known for many years and the field of biodeterioration of petroleum products has been reviewed by several workers. In the case of distillate fuels, microbial problems such as biocorrosion, filter blockage, coalescer malfunction and water entrapment have been of great concern, principally in the aviation industry. In more recent years, however, microbiological problems have been associated with other fuel systems such as tractor vapourizing oil, diesel, paraffin and gas oils. Particular note has been paid to the increase in microbiological problems in marine applications. The reasons for the apparent increase in microbiological problems may be due to changes in crude source, refining and blending techniques, storage and handling facilities and the increased use of fuel additives. In addition, there has been a change in the type of organism causing microbiological problems away from *Hormoconis resinae* (*Cladosporium resinae*) to bacteria and yeasts. To minimize microbiological problems in fuel systems several methods have been suggested, including good housekeeping, production of microbiologically harder fuels, physical control, e.g. heat treatment and chemical control, e.g. the use of chemical biocides. Bronopol (2-bromo-2-nitropropane-1,3-diol, BNPD) is a versatile antimicrobial agent traditionally used as a preservative to control bacterial growth in pharmaceuticals, cosmetics and toiletries. In recent years its use in controlling industrial biofouling problems, either alone or in combination with

other biocides, has been grown significantly. This paper reports studies to evaluate its potential as a biocide for microbial contamination in fuel systems.

## **A BIOLOGICAL MONITORING AND CONTROL STRATEGY FOR LARGE DIESEL FUEL STORAGE FACILITIES**

*M. P. Reynders, P. Stegmann*

Large diesel fuel storage containers are subject to microbiological related problems, i.e., biofouling, biocorrosion and degradation of the fuel. Micro-organisms are able to use diesel fuel as carbon and energy source. Four fungi and nineteen bacteria species were isolated from contaminated diesel fuel and blocked filters, all proved to be primary users of diesel fuel. Two bacteria species specifically were found to be the most common cause of microbial induced filter blockages due to their ability to form spores and to inhibit the growth of other hydrocarbon utilising micro-organisms. It was shown that one of these was capable of excreting a gummy substance which was able to rapidly block fuel filters. Factors which contribute to the development of a biological treatment strategy are the presence of water with readily available nutrients and carbon source within the tank, cost of treatment and operational considerations. The use of a water-soluble biocide treatment programme in these storage facilities has proved successful and has prevented the establishment of a food chain which can cause the blockage of fuel filters, the corrosion of containers, pipelines and meters and the degradation of the fuel.

## **MICROBIOLOGICAL TEST METHODS FOR FUELS IN THE LABORATORY AND ON SITE**

*E. C. Hill, G. C. Hill and D.A. Robbins*

Microorganisms can proliferate in free water associated with distillate fuels and subsequently may become dispersed in the fuel phase. Both aqueous and fuel phase samples may be presented for microbiological examination. In general, the typical Gram-negative spoilage bacteria rapidly lose viability in the fuel phase whilst moulds, particularly spores, tend to pass readily into the fuel phase and survive there; yeasts may exhibit better fuel tolerance than Gram negative bacteria. Thus, the result of any test for viable microbes in the fuel phase is influenced by the age of the sample as well as the extent of aqueous phase growth and the intensity of agitation. We have noticed an increased incidence of Gram-positive sporing bacilli in fuel systems. These organisms seem to be more common in long established infections, presumably stimulated by the metabolic products of primary spoilage organisms, and they may be found in large numbers (in excess of  $10^2 \text{ mL}^{-1}$ ) after sub-optimal applications of biocides. Spores of bacilli can be found in the fuel phase but we have not yet systematically investigated their survival or significance. The testing for microorganisms in the fuel phase is itself a challenge to microbial technologists but the subsequent interpretation requires knowledge of the system, the exact location of the sampling point and the history of the sample. Unfortunately, very frequently the only sample available is the fuel phase.

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

*R.M. Morchat, A.J. Hebda and G.M. Jones, R.G. Brown*

Microbiological contamination (MBC) in naval fuels can cause serious operational problems, particularly if coalescers are used for water removal and if the fuel is to be used in gas turbine engines with their intricate fuel control units which are easily blocked. In order to identify a biocide which could be used to treat MBC problems in fuel on ships, five commercial biocides have been evaluated. These biocides include compounds based on benzimidazoles, pyridinethiol-1-oxide, dioxaborinanes, morpholines and isothiazolones. The degree of susceptibility of microorganisms, in naval distillate fuel, to the specific biocides was evaluated. Pure cultures of *Cladosporium resinae*, *Yarrowia lipolytica*, *Pseudomonas aeruginosa* and mixed cultures in fuel/water mixtures were treated with the manufacturers recommended concentrations of the biocides.

## **EVALUATION & COMPARISON OF MICROBIAL GROWTH IN DISTILLATE FUELS**

*P.J. Miller-David and Gary G. Pipenger*

Microbial contamination of fuel tanks and systems has been blamed for fuel system corrosion, filter and line plugging, and fuel degradation. Of the fuel samples in this evaluation, bacterial growth has been isolated from as many as 56% of stored fuel systems in the United States. Since most storage tanks were underground and maintained a relatively constant temperature year-round, microbial proliferation was neither regional nor seasonal. Although microbial growth in fuel systems is an area of concern involving both users and suppliers of distillate fuels, this study limits its scope primarily to users of distillate fuel and further attempts to categorize microbial isolates of fuel systems and their deleterious effects to fuel by: Frequency of appearance; Colony forming units per milliliter (cfu/ml) quantitated; Amount of growth byproduct generated; and Physical appearance of the water, fuel, and interfacial phases. Samples of fuel were collected from a twenty-three state geographical area east of a line from New Mexico to the Dakotas. The states sampled most heavily were Indiana, Ohio, Michigan, Kentucky, Illinois, Tennessee, New Jersey, Florida, and Texas. This study limits its attention to aerobic organisms, initially cultured and isolated on Tryptone, Yeast, Dextrose agar, then subcultured to appropriate media for identification. Inoculation, culturing, identification and isolation were performed according to guidelines established for clinical pathogens. Statistical evaluations were used to compare specific organisms isolated (genus and species) along with amount of colony formation units generated to amounts of growth by-products, physical appearance of the fuel, and physical appearance of the water phase in samples collected (if present). By isolating specific organisms from fuel which have been statistically shown to affect the condition of stored distillates, the fuel user can select treatment methods most effective against those organisms.

## **SESSION 3: JET FUEL STABILITY**

### **NUCLEAR MAGNETIC RESONANCE TECHNIQUES FOR PREDICTING THERMAL STABILITY OF JET AND DIESEL FUEL**

*J. A. Russell, B. K. Bailey and J. P. Buckingham*

A wide variety of distillate hydrocarbon fuels were characterized as to thermal stability breakpoint (JFTOT, ASTM D 3241) and chemical structure parameters directly measurable by Proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR). Materials included coal-derived distillates subjected to three levels of hydrotreating severity, specification-quality military diesel and jet fuels, special high-energy density and high-thermal stability jet fuels, and pure hydrocarbons. Regression modeling resulted in one general model and three sub-models for three distinct temperature regimes. The coefficients of the NMR terms appearing in these equations have provided valuable information on molecular structure factors which enhance or degrade thermal stability.

### **OLD AND NEW WAYS OF USING THE JFTOT FOR AVIATION FUEL STABILITY RESEARCH**

*G. Datschefski*

The Jet Fuel Thermal oxidation Tester (JFTOT) is normally operated under standard conditions required by international specifications for qualification of production batches of jet fuel. Because the test can discriminate between fuels of poor and good high temperature stabilities, it has a valuable role in its present form for quality assurance of fuels. However, it can also be used under a wider range of operating conditions for research into high temperature thermal stability behaviour of aviation fuels. Some typical research investigations are reviewed in the paper to illustrate this point. When used in the research mode, several shortcomings of the JFTOT became evident, particularly in the areas of tube deposit assessment and tube surface metallurgy. Improvements are proposed to overcome these shortcomings, e.g., measuring tube deposits quantitatively by carbon burnoff, or by recently developed methods utilizing light interferometry and breakdown of dielectric potential. JFTOT breakpoint temperature is a very important concept for establishing the level of fuel thermal stability quality, and this is discussed in detail. Some single test predictive methods for measuring breakpoint temperature are outlined, which are aimed at shortening the usual lengthy multi-test determination of this parameter.

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

*R. E. Morris, R.N. Hazlett and C. Linden McIlvaine*

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.

## **THERMAL STABILITY MEASUREMENTS USING THE FIBER OPTIC MODIFIED JET FUEL THERMAL OXIDATION TESTER**

*R.A. Kamin, C.J. Nowack and S. Darrah*

An experimental study was conducted to evaluate the use of fiber optics to measure Jet Fuel Thermal Oxidation Tester (JFTOT) tube deposition. Eight fiber optic probes, connected to a data acquisition system, were embedded into a standard JFTOT tube housing. This modification, based on the theory of light interference phenomena, provided real time quantitative measurements (in microns) of the deposit thickness formed on the tube during testing. A single probe off-line fiber optic unit was also constructed to make deposit thickness measurements spatially along the tube at the completion of the test. Six fuels, with breakpoint temperatures ranging from 216 °C (420 °F) to 263 °C (505 °F), were tested over a tube temperature range of 204 °C (400 °F) to 316 °C (600 °F). Arrhenius plots of the data allowed a comparison of the fuel deposition rates over a range of temperatures above and below the fuels respective breakpoint temperatures. Interpretation of the initial results indicates that the fiber optic modification enhances the capabilities of the JFTOT as a research tool.

## **THE ROLE OF ALKYLPEROXY AND ALKYL RADICALS IN FUEL DEPOSIT AND GUM FORMATION**

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

The thermal stability characteristics of n-dodecane and n-dodecane plus heteroatomic species were studied after aerating the fuels and stressing them on a modified Jet Fuel Thermal Oxidation Tester (JFTOT) facility. Fuel degradation mechanism(s) were hypothesized, based on the quantification and identification of the soluble degradation products using Gas Chromatography and Mass Spectrometric techniques. The mechanism suggests that in the autoxidation regime ( $T \leq 300\text{C}$ ), the alkylperoxy ( $\text{R}\text{O}_2\bullet$ ) radical reactions appear to dominate the alkyl ( $\text{R}\bullet$ ) radical reactions. Conversely, in the intermediate temperature regime ( $300 \leq T \leq 400\text{C}$ ), the  $\text{R}\bullet$  radical reactions appear to dominate the  $\text{R}\text{O}_2\bullet$  reactions. The predictions of the fuel degradation mechanism were compared with actual fuel derived deposits and gums. Data from similar JFTOT experiments performed at the Naval Research Laboratory and from flask oxidation studies conducted at Stanford Research Institute were used to test the validity of the hypothesized mechanism. The data correlation showed that the hypothesized fuel degradation mechanism is valid. Thus, if the  $\text{R}\text{O}_2\bullet$  and  $\text{R}\bullet$  can be suitably scavenged in the appropriate temperature regimes using anti-oxidants, inhibitors, radical scavengers, etc., it may be possible to inhibit fuel degradation.

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

*R. E. Morris, R. N. Hazlett and C. Linden Mcilvaine*

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 °C 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.

## **FURTHER STUDIES OF THE EFFECTS OF POLAR COMPOUNDS ON THE THERMAL STABILITY OF JET FUELS**

*R. H. Clark and L. Smith*

The influence of polar compounds on the high temperature degradation mechanism of jet fuel has been studied using a number of experimental techniques. The deposition characteristics of the fuel were assessed by the Jet Fuel Thermal Oxidation Tester (JFTOT), whilst a flask oxidation test was used to probe the initial stages, that is liquid phase oxidation. The results of these tests have given an indication as to where polar compounds act within the overall degradation mechanism. The studies employed a dual strategy using both polar compounds and extracts obtained from commercial jet fuels. The model compounds encompassed sulphur, nitrogen and acidic species, whilst the use of ion exchange chromatography provided acidic extracts from commercial jet fuels. The work examined not only the individual effect of each compound class, but also their pairwise interactions. From these studies, we have developed an improved means of predicting, from compositional information, fuel degradation rates in service.

## **THE ROLE OF METAL DEACTIVATOR IN IMPROVING THE THERMAL STABILITY OF AVIATION KEROSENES**

*R.H. Clark*

Under the high temperatures encountered in certain parts of a gas turbine fuel system, aviation kerosene undergoes thermal degradation to form deposits. Ultimately, these will impair the operation of the engine and require the premature servicing of the affected components. To

ensure adequate thermal stability, fuels are certified by testing in the Jet Fuel Thermal Oxidation Tester (JFTOT). Kerosines which fail this test must either be discarded to a lower value pool, or may sometimes be upgraded by the use of an approved stability enhancing agent. In the case of civil fuels, the sole such approved additive is N,N'-disalicylidene 1,2-propane diamine, which functions as a metal deactivator and is commonly known as MDA, This paper describes studies conducted to identify the mechanisms by which MDA acts. The experimental techniques employed were as follows; a flask oxidation test to investigate the effect of MDA on the oxidation mechanism and thence to establish a binding ratio between MDA and dissolved copper; the JFTOT and thirdly fuel system simulators designed to examine oil-cooler lacquering and injector feed-arm fouling. The results confirm that MDA acts to chelate dissolved metals in a near 1:1 mole ratio and thereby reduce their catalytic activity towards radical initiation; as such, therefore, they are highly effective at reducing fuel oxidation and thence deposition. At the same time, the JFTOT and rig tests show that MDA produces a beneficial effect even for fuels containing little or no dissolved catalytic metals, This phenomenon is attributed to a second beneficial mechanism, namely, surface passivation, When compared to more realistic rigs, the JFIOT appears to be over-responsive to this passivating aspect of MDA's action, The results are discussed in terms of the criteria for the appropriate application of MDA,

## **JET FUEL INSTABILITY: ORGANO-SULPHUR HYDROPEROXIDE INTERACTIONS**

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

The role of organosulfur 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 on 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. am a model fuel, tetradecane. The relationship between organo-sulfur compounds and the peroxidation of JP-5 have been studied under conditions of accelerated storage.

## **HYDROPEROXIDE FORMATION AND REACTIVITY IN JET FUELS**

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

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 analyzed 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.

## **THE CHEMISTRY OF ANTIOXIDANT ADDITIVE DEPLETION IN JET FUELS**

*F. D. Sutterfield, D. W. Brinkman, O.K. Bahn, J. B. Green, J. W. Goetzinger, G. P. Sturm, G. Speck and L. Turner*

Fresh samples from two West Coast (U.S.A.) refinery hydrocracker streams with boiling ranges similar to JP-5 fuel were aged at temperatures of 60° and 80° C neat and after blending with two hindered phenol-type antioxidants. Additive concentration, peroxide number, color, filterable sediment, and adherent sediment were determined periodically. Also, fresh and aged samples of the two hydrocracker streams without additive and sediments produced by the aged samples were analyzed in detail by gas chromatography /mass spectrometry, probe microdistillation/high resolution mass spectrometry, and infrared spectroscopy. The data from the aging experiments indicated an initial induction period followed by a period of rapid depletion of antioxidant and an increase in peroxide. This was followed by a final period of decreasing peroxide content, increasing color formation, and increasing filterable and adherent sediment formation. The additives were effective in delaying the onset of peroxide, color, and sediment formation. Results from detailed analyses of the additive-free fresh and aged fuels and sediments indicated that the gums or sediments apparently result primarily from oxidation of alkyl-substituted indans, tetralins, indenenes, dihydronaphthalenes, naphthalenes, and benzenes. In the next phase of the study, corresponding samples from the fuels with antioxidants will be analyzed and the results compared with those reported here. Overall results to date support a free radical chain oxidation mechanism as a primary mechanism operative in formation of sediment in these two fuels. The presence of dimers is consistent with mechanisms involving the condensation of oxidation products and the coupling of substrates by peroxides.

## **EFFECT OF PEROXIDE ON THE THERMAL STABILITY OF HYDROCRACKED AVIATION FUEL**

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

Extensive research efforts have been conducted to study the chemistry of both storage and thermal oxidation stability little work has been done to relate these two areas. Recent findings however have indicated that there may be a relationship between the two stability temperature regimes similarity in chemical composition of the gum deposits formed during accelerated storage stability tests obtained by thermal stressing in the Jet Fuel Thermal Tester (JFTOT). Accelerated storage stability hydrocracked aviation fuels with and without antioxidant. Samples were analyzed for peroxide number, total acid, existent gum and thermal oxidation stability (JFTOT) regularly over a period of 16 weeks. A link was developed relating the increase in peroxide concentration of the fuel during storage with the increase of deposition in the JFTOT.

## SESSION 4: STABILITY OF GASOLINES

### STABILITY PROPERTIES OF GASOLINE-ALCOHOL BLENDS

*N. Por*

The lead phase down for motor gasolines resulted in a search for alternative octane boosters, some alcohols and ethers being the most favoured candidates. The advantages and disadvantages of each of the oxygenates have been extensively studied, but the effect of oxygenates on the stability properties and long-term storage stability of motor gasolines has been neglected. This paper summarizes the work done on the effect of some alcohols and ethers on degradation product formation in motor gasolines containing oxygenates. Following are some specific points which have been investigated in the present work: Effect of oxygenates on the conventional stability estimates and on stability properties of different types of gasolines has been examined; A reduction of methanol concentration has been noted during storage of some motor gasolines containing methanol, especially in case of catalytically cracked gasolines. It has been investigated whether this phenomenon is associated with formation of ethers due to a reaction of methanol with olefins present in some severely cracked stocks or whether this is due to common phase separation; The effect of peroxy radicals in gasolines containing alcohols on the behaviour of gasolines in storage and in use, such as formation of gum-like substances in inlet manifold systems of car engines, has been studied and is described in this paper;

### EVALUATION OF MOTOR GASOLINE STABILITY

*D. L. Morris, J. N. Bowden and L. L. Stavinoha*

This paper presents current results of an on-going storage program whose primary Goal is the development of improved methods for evaluating motor gasoline stability. Several existing and potential predictive tests were applied to both individual refinery components of gasoline, selected laboratory blends, and commercial gasolines for which ASTM D 525 induction periods ranged from 75 to >5000 minutes. Darkroom storage was commenced at 43 °C, 54 °C, and ambient temperatures, for varying periods which will ultimately reach 4 years. Results to date confirm the findings of earlier researchers that ASTM D 525 is not viable as a predictive device by virtue of a low coefficient of determination between induction period and gum formed in storage at 43 °C for periods up to 1 year. It is recognized, however, that ASTM D 525 is not likely to be abandoned as a specification stability test. Based upon the data generated to date under the four phases of this storage stability program including supporting data obtained from literature sources and current surveillance information on both military and industry practices, the method to be adopted for evaluating stability of commercial/military motor gasoline will consist of the modified ASTM D 873 Method using a 6-hour aging existent gum maximum limit of 20 mg/ 100 mL. The ability of this test to distinguish between stable and unstable low induction period fuels and/or components is discussed. In evaluating the individual potential gasoline components, a pyrolysis naphtha was shown to be generally an order of magnitude less stable than all other streams, and coker naphtha was shown to possess poor stability characteristics. LCC and HCC naphthas which make up the bulk of unleaded gasoline have lower stability than the remaining components. Reformate showed definite acceleration of

deterioration during storage. Synergistic effects exist, particularly between LCC and HCC naphtha blends.

## **STORAGE STABILITY OF AVIATION GASOLINE**

*R. Dekel*

Aviation gasoline specifications include accelerated ageing tests with the intention to forecast in advance the storage life of the fuel and to ensure its stability for a reasonable period of time (1 -2 years). The problematic question in this matter is for how long the fuel would be suitable for use if it is stored under adverse and unusual conditions and how the deterioration, if any, would influence the engine performance. The purpose of this study is to find the answer to these questions when the storage conditions are set in advance. Aviation gasoline according to MIL-G-5572 grade 100/130 with and without 5% lubricating I preservative oil are stored under regular and severe conditions in two kinds of containers: (1) 200 liters steel drums (2) 2 liters polyethylene bags. A test program for the different samples include gasoline specification properties, analytical methods to record possible chemical changes in the gasoline and functional tests. Parallelally, a two-stroke cycle engine will be run with the fuels under test and its performance recorded and correlated against laboratory test data. At each stage of the study the test results would be compared with the starting properties and chemical composition of the fuel. Finally the data would be statistically elaborated in order to establish the influence of the different parameters and the expected stability of the gasoline under specified storage conditions

## **SESSION 5: STABILITY OF DIESEL FUELS**

### **EVALUATION OF COMMERCIAL STABILITY ADDITIVES FOR NAVAL DISTILLATE FUEL**

*D. R. Hardy, E. J. Beal, R.N. Hazlett and J.C. Burnett*

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 02274 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.

## **DISTILLATE FUEL STABILISATION IN A MAJOR EUROPEAN REFINERY**

*P. B. Mahley and G. M. Wallace*

This paper illustrates how a complex European conversion refinery was able to maximize distillate production through the use of a specifically designed multi-functional stabilizer package. The first section of the paper deals with the profile of the Refinery in terms of operating capacity and processing units available. The economic drive to increase conversion products in the middle distillate pool is discussed. This increase was achieved by producing fuel closer to the required specification in terms of sulphur and cetane number. Key stability test requirements and performance parameters which this Refinery had to meet are then detailed. These included short term thermal and oxidative stability tests commonly employed in quality control applications and long-term storage trials used to ensure good field performance. Latterly the approach to develop a multifunctional distillate stabilizer package specifically to meet the severe refinery requirement is described. Test data from the use of this package in the variety of stability test parameters is related. These results showed that balanced multifunctional additive packages added to fresh high severity conversion streams inhibit colour degradation and sediment formation. This benefit allowed the refiner to optimize distillate production which was previously not possible due to constraints on the hydro-processing route. Field experience including engine testing has shown excellent correlation with the results from the initial study.

## **MIDDLE DISTILLATES STABILITY: COMPOSITION AND ADDITIVE UTILIZATION EFFECTS ON THEIR AGING AT DIFFERENT TEMPERATURES**

*C. Bernasconi, A. Chaffardon, P. Charleux, J. Denis, J. Gaillard and J. P. Durand*

The storage stability of middle distillates is of great importance in France, because, on one hand, of their increasing demand and, on the other hand, of the evolution of refining processes towards producing more and more unstable cracked products leading to gum and sediment formation. In this field, our work has consisted in evaluating middle distillates stability and additive effectiveness. Several mixtures of Straight Run Gas Oils and cat-cracked Light Cycle Oils have been subjected to different aging methods (2 hours at 120°C, 12 weeks at 43°C, 1 year at ambient temperature) followed by color and gravimetric determinations. The first method (120 °C) has to be used as a screening test while the second method (43°C) appears closely correlated with the actual storage. Unaged and aged middle distillates and sediments were analysed by gas chromatography and mass spectrometry. Alkylindoles appear to be involved in L.C.O. degradation. L.C.O. fractionation has allowed to show the important degradation tendency of heavy 315+ fraction. Stabilizers such as aliphatic tertiary amines with a metal deactivator minimize the gum and sediment formation, but their action is more obvious if measured by accelerated aging methods; however, color darkening is harder to control

## **SOLID ABSORBENTS AS DISTILLATE FUEL STABILITY AGENTS**

*W. Arfelli, A. J. Power and R. K. Solly*

Summary Fuel Stability Foam (FSF) formulated from polyurethane was found to be very effective in greatly reducing the degradation of unstable diesel fuel on ageing. When present in the fuel during the ageing process at amounts of 0.2g per litre of fuel, reductions in total particulate greater than 90 per cent, improvements in fuel filterability approaching that of unaged fuel and reduction in fuel darkening were obtained. After insertion in fuel systems, FSF will displace less than 0.5 per cent of the fuel volume and provide continued protection against fuel degradation over a long period for each batch of fuel with which it is in contact. The high level of protection against fuel degradation provided by FSF is effective in the presence of diesel fuel deposit promoters such as organic acids, aromatic thiols and fuel soluble copper. The major fuel stabilization mechanisms of FSF are proposed to be adsorption of fuel deposit precursors, soluble particulate species, insoluble particulate and degradation catalysts. Following from these adsorption processes, FSF is also effective in reversing the degradation of degraded fuel with which it is in contact.

## **STORAGE STABILITY CHANGES WITH COMMERCIALY AVAILABLE DIESEL FUEL WINTERIZING ADDITIVES IN THE UNITED STATES**

*G. G. Pipenger*

Commercially available winter additives for diesel fuel claim to correct a variety of fuel-related problems, including long term storage instability. The flow and cetane improvement claims of these products have been tested and in some cases documented. Correction of these stability problems with these commercially available additives may not be possible and testing must be accomplished to verify any claims. A total of twenty-nine (29) commercially-available additive treatments were tested on three untreated consumer-available fuels. Samples were blind-labelled to ensure objectivity and were sent to independent testing facilities for evaluations of the following properties: 1. Stability Improvement 2. Biocidal Effectiveness 3. Cetane Number 4. Cloud Point 5. Pour Point The diesel fuel test samples purchased were obtained from three different suppliers in the midwestern United States. The fuels selected were typical of the grade of No-2 diesel fuels supplied to the United States transportation markets, all meeting the current American Society for Testing and Materials (ASTM) specification D975 for diesel fuels. The additive treatments were purchased in the continental United States and were selected using the following criteria: 1) Readily available in the United States; 2) Winterizing benefits advertised; 3) Multifunctional capabilities promoted. Conclusions were made based on the statistical comparison of ASTM D2274 oxidation stability test results, incorporating effectiveness on each product in the three base fuels. Specific additive brand names are omitted from the study.



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

*E. J. Beal, D. R. Hardy, R. N. Hazlett, J. C. Burnett, R. Giannini and R. Strucko*

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 categories of fuel will be presented along with conclusions based on fuel type and geographical location.

## **COMPARISON OF THERMODYNAMICS OF NITROGEN AND SULPHUR COMPOUNDS IMPLICATED IN FUEL STABILITY PROBLEMS**

*F. D. Satterfield, W. V. Steele, D. G. Archer, R.D. Chirico and M. M. Strube*

Processing of crudes containing increasing levels of sulfur and nitrogen compounds using present-day technology has produced fuels with higher heteroatom and aromatic contents and a tendency toward instability. The literature of hydrodesulfurization chemistry and technology has been reviewed by McKinley, Schuman and Shalit and Schuit and Gates. Recent literature reviews of hydrodenitrogenation chemistry and technology include those of Katzer and Sivasubramanian and Ledorix. In addition, the recent literature contains a number of studies on the mutual effects of sulfur and nitrogen compounds on the chemistry of the heteroatom removal. Of note in this area is the series of papers by Satterfield's research group at the Massachusetts Institute of Technology on the catalytic hydrodenitrogenation of quinoline in the presence of hydrogen sulfide and water. These studies demonstrate that all the hydrogenation reactions among the heteroatomic species are reversible over a wide range of industrial processing conditions. Therefore, a knowledge of the thermodynamic equilibria among the species is necessary for the proper interpretation of reaction data, for comparing different catalysts, and for accurate modeling of the overall reaction.

## **STUDY OF FUEL DEGRADATION PROCESSES BY UV LASER TECHNIQUE**

*M. Rotel, J. Zahavi, N. Por and Y. Ben-Asher.*

Irradiation of diesel fuel drops by an excimer laser working at 193nm was used to stimulate degradation processes with a view to evaluating relative instabilities of the fuel and insight into the processes involved. Two aspects were studied: deposits produced on microscope slides, and the changes in composition following the irradiation. Deposits obtained from partially-cracked stock were darker and denser and had higher weights than those obtained from straight-run stock. Correlation between the deposits and laser conditions was investigated. Analysis of the irradiated fuel revealed an increase in gum and peroxide content.

## **INVESTIGATION OF “SEDIMENT PRECURSORS” PRESENT IN CRACKED GAS OIL**

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

At the 2nd International Conference, we reported the discovery of ~sediment precursor compounds. It was suggested that these compounds occur in solution in degrading fuel and are converted to insoluble sediment by the action of strong acids. In this paper we describe the isolation of two related groups of the compounds from a degrading catalytically-cracked gas oil using combined normal and reversed phase chromatography. The isolated groups were characterised using principally mass spectrometry and the precursor compounds were tentatively identified as consisting of indoles linked to polycyclic aromatic hydrocarbons. A subsequent search showed that the corresponding aromatic hydrocarbon species could be found in degrading cracked gas oil. We conclude that the precursor compounds could have been formed by the condensation of these oxidation products with indoles.

## **SYNTHESIS OF “SEDIMENT PRECURSOR” COMPOUNDS AND SIMULATION OF SEDIMENT FORMATION IN CRACKED GAS OIL USING MODEL SYSTEMS**

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

Compounds which are closely related to the ‘sediment precursor’ species extracted from degrading catalytically-cracked gas oil have been synthesised by the condensation of indoles with polycyclic aromatic ketones. Spectral data including proton NMR for these compounds will be presented and possible structures discussed. Sediment formation has been simulated in model systems which contained various combinations of pure compounds representing suspected active species. The active components, which included an indole, thiol and polycyclic aromatic hydrocarbon, were dissolved into a stable straight-run gas oil at concentrations representative of those in finished fuels and the blends stored at 25°C for 6 months. The results of these tests including characterisation of the sediments formed will be reported and their significance in the context of sediment prevention will be discussed.

## **EXAMINATION OF FUEL DEPOSITS FROM VARIOUS SOURCES BY PYROLYSIS/FIELD IONISATION MASS SPECTROMETRY**

*R. Malhotra and G. A. St. John*

Deposits that often build up in fuels under prolonged storage, and sometimes even under relatively short storage cause problems with filtration and pumping of the fuels. Furthermore, some soluble gum is also formed that subsequently forms deposits on the hot engine parts causing additional problems. Numerous tests have been developed to predict the tendency of a fuel to form deposits. Often, these tests require stressing the fuel at elevated temperatures, and the relevancy of such tests to storage conditions is not clear. Studies have also been conducted with dopants, but again it is unclear whether the deposits formed in the presence of the dopant are the same as those formed under storage. An improved chemical understanding of the nature and causes of deposit formation is clearly needed. We have previously shown the applicability of pyrolysis/field ionization mass spectrometry (Py/FIMS) for characterizing the deposits. We now

wish to report results obtained from a variety of deposits. The objectives of the present study were to determine the variability in the nature of deposits and to answer some chemical questions relating to their formation.

## **STUDIES OF FUEL DETERIORATION AND ADDITIVE INHIBITION MECHANISMS**

*S. R. Westbrook, L. L. Stavinoha and J. P. Hsu.*

Insolubles in diesel fuels are known to occur through several mechanisms, some of which include polymerization, condensation, and acid base reactions. Recent studies have revealed that acid base reactions (or acid-catalyzed reactions) are especially important in the formation of sediments in fuels containing catalytically cracked stock. Evidence also exists that simply removing the acid and base fractions of the fuel does not completely eliminate sediment formation, which would indicate some sort of preliminary reaction, such as oxidation. Fuels containing little or no cracked stock are usually subject to different reactions to form insolubles. The type of additive that used to reduce insolubles formation depends on the reactions that occur to produce the insolubles. For these reasons, additive efficacy will vary between fuels. During this study, the formations of fuel insolubles in a straight run fuel, a light cycle oil, and a blend of the two were studied. The test fuels were stored at 800e for periods up to 28 days. The effects of several commercial fuel stabilizer additives and one pure compound on sediment formation were also studied. The fuels and fuel sediments were analyzed, and the results were used to develop a model system. Studies of the formation of insolubles during the aging of the model system showed the importance of acids in sediment formation. The inhibition mechanism of one fuel stabilizer, N,N'-dimethylcyclohexylamine, was also studied. The usefulness of the model system for evaluating stabilizer additive effectiveness was also demonstrated.

## **THE DEVELOPMENT OF REFERENCE FUELS FOR USE WITH THE ASTM D2274 TEST FOR FUEL STORAGE STABILITY**

*M. D. Klinkhammer, E. W. White and K. W. Flohr*

The reproducibility of ASTM D2274 method for evaluating the stability of middle distillate fuels is poor. Differences between results obtained by two laboratories or by two operators in one laboratory may be large. A significant portion of the difference rests with operator idiosyncrasies and failure to follow the procedure. Reference fuels are needed to qualify apparatus and to train and check operators. DTRC and ARTECH CORP. are engaged in the development of such reference fuels. Because a petroleum-based fuel set aside as a reference would be subject to aging and to the effects of shipping conditions, we have based our reference fuels on a small number of pure compounds that can be blended in a series of standard ratios. immediately prior to use. Initially, n-dodecane, t-amylbenzene, and 1-dodecene have been chosen to represent the paraffinic, aromatic, and olefinic components of diesel fuels. These are blended in a 75/22.5/2.5 volume ratio to form a base fuel. A known sediment former (1,2,5-trimethylpyrrole) is added in various concentrations to produce a series of reference fuels. The resultant reference fuels have been subjected to stressing in the D2274 apparatus for periods between 4 and 96 hours, in addition to the standard 16-hour period, by four analysts to develop a sense of repeatability. Precision and agreement for experienced D2274 operators was good. Curves showing total

insolubles as a function of D2274 test time or as a function of initial 1,2,5-trimethylpyrrole will permit the fuel stability community to use these reference fuels for training personnel and for checking personnel and equipment. The "shelf life" of the 1,2,5-trimethylpyrrole, the use of other sediment forming compounds, synergistic effects, and an ASTM round-robin study are possible areas for further work.

## **A STUDY OF PRECURSORS IN THE FORMATION OF INSOLUBLE PRODUCTS DURING THE AGING OF MIDDLE DISTILLATE FUELS**

*M. D. Klinkhammer, E. W. White and K. W. Flohr*

The identification of precursors to insolubles formation in middle distillate fuels during storage may be the key to an improved method for identifying unstable fuels. Consequently, DTRC and its contractor, ARTECH CORP., conducted a gas chromatographic (GC) study of both unstressed fuel and fuel and insolubles following various bottle storage regimes, viz. 43°C for eight weeks, 65°C for one, three, and eight weeks, and 95°C for one week. Three types of detectors were used with the GC unit, a flame ionization detector, an electron capture detector, and a thermionic-specific (nitrogen-phosphorous specific) detector. Prior to stressing, all three fuels used in the program contained detectable amounts of material similar to the major components later found in the filterable and adherent insolubles. These precursors increased in concentration in the filtered fuels following stressing as the stressing conditions became more severe. It was found that the adherent insolubles and the filterable insolubles were almost identical by gas chromatographic techniques. It is thought that further development may well result in a test which will supplement the currently-used AS1M D2274 procedure or other accelerated stability test.

## **MEASUREMENT OF LOW LEVELS OF STRONG ACIDS IN GAS OILS**

*S. J. Marshman*

Chemical species which have been reported to affect the storage stability of diesel fuels include organic acids, and phenalene and its homologues. In storage stability studies reported elsewhere, the addition of organic acids has been shown to enhance the production of insoluble degradation products from gas oil. The strength of the acids added is also considered to be a factor affecting sediment formation. Methods currently used to determine acidity, such as ASTM D664, are not sufficiently sensitive to determine the levels of strong acids in gas oils. New conductometric and potentiometric titration methods have therefore been developed to measure the type and quantity of organic acids present. These techniques are sufficiently sensitive to detect low ppm levels of strong acids. The results from each of these methods were compared for a number of gas oils. Acidity measurements for a straight-run and a catalytically-cracked gas oil were obtained during ambient storage studies. Phenalene and its homologues have been detected in a catalytically cracked diesel fuel and quantified by means of a two-stage chromatographic procedure utilizing oxidative electrochemical detection.

## **DEVELOPMENT OF PREDICTIVE TESTS FOR FUEL STABILITY**

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

Heteroatoms (O,N,S) and unsaturated compounds exert deleterious effects on the stability of a liquid fuel by promotion of deposit formation on storage. Since deposit techniques for determination of fuel stability require long times of storage, predictive tests should be developed in order to save observation time. Light scattering measurements, before onset of sedimentation, is a predictive test. Inductively coupled plasma atomic emission (ICP-AES) and atomic absorption (AA) are very sensitive methods for measuring trace amounts of metal and constitute other predictive tests for fuel stability. A metal powder, Cu, Al or Fe, is added to the fuel. Various amounts of unsaturated and S,O,N-containing compounds are added to the fuel to accelerate aging. After standing for various short intervals, again before the onset of sedimentation, the metal powder is removed and the metal content in the fuel is determined by ICP-AES or AA. The predictive tests show that the deleterious effects of metals are in the order  $Cu > Al, Fe$ . The extents of light scattering and of metal drawn into the fuel from added metal powder are correlated with the extent of deposit formed in degradation of the fuel, and a mechanism is suggested for sediment formation with sulfur compounds. We have applied Raman spectroscopy, nuclear magnetic resonance, electron spin resonance, and electron spectrum for chemical analysis (ESCA) techniques to the characterization of deposits.

## **STUDY OF STABILITY OF DIESEL FUELS UNDER OPERATIONAL CONDITIONS**

*E. Zahavi, A. B. Shavit, J. Ben-Asher and N. Por*

Although no significant degradation of diesel fuel quality has been observed in conventional storage of locally produced straight run stocks, formation of degradation products in bus engine fuel systems has been observed by filter clogging and deposit formation. The main cause for these field operational problems may be attributed to the fact that diesel fuel, which serves also as an injector coolant, most probably deteriorates at the relatively high temperatures prevailing in part of the fuel system. Two different straight run diesel fuels, a blend of light cycle oil and straight run diesel fuel with and without a stabilizer additive (qualified by U.S. Department of Defence according to MIL-S-53021), have been studied in buses of the public transportation system during actual road service. The initial fuel properties of the gas oils have been tested, and finally the 10% of the remaining unconsumed gas oils, which were taken from the systems, were evaluated in view of stability by four different stability tests. It was found that diesel fuel types, tested during this study, deteriorated upon actual road service. The loss in stability resulted in formation of insoluble sediments, increase in acidity and low filtration rates. Addition of fuel stabilizer, qualified under MIL-S-S3021, induced a better filterability on the two straight run stocks, accompanied by a reduced rate of filtration of the unstable blend.

## **ASSESSING DISTILLATE FUEL STORAGE STABILITY BY OXYGEN OVERPRESSURE**

*D. R. Hardy, E. J. Beal, R. N. Hazlett and J. C. Burnett*

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 100°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 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.

## **A STUDY OF VARIABLES AFFECTING RESULTS OBTAINED IN THE ASTM D2274 ACCELERATED STABILITY TEST. PARTS 2 & 3 - EFFECTS OF SELECTED CHEMICAL AND PHYSICAL FACTORS**

*Dr. E. W. White and Robert J. Bowen*

This paper examines selected chemical and physical variables that could possibly affect results obtained in the ASTM D2274 accelerated stability test. It is a continuation of the work reported as the 2nd International Conference in San Antonio, Texas. Together, the two papers summarize the results of a David Taylor Research Center study of critical factors in the D2274 procedure. The chemical factors addressed are the concentration of oxygen in the gas that is introduced into the fuel and catalysis of the instability reaction. The aspects of the oxidation cell that are addressed include the method of introducing oxygen; the wetted surface-to-fuel ratio; and the cell age (number of prior uses). Oxidation bath factors include the location of the cell in the bath; the speed of temperature recovery following introduction of the cells; and a comparison of an 8-cell with a 12-cell bath. The single post-stress factor addressed is the drying time of the filterable solids. We recommend that users of the D2274 procedure use only high purity oxygen; refrain from the use of unlined metallic shipping containers; and protect samples from UV radiation and excessive agitation. The effects of the wetted surface-to-fuel volume ratio and of cell age are not critical in the D2274 procedure. Different baths give different results, probably the result of different temperature recovery rates following cell introduction. The current one-hour drying time specified for the filterable insolubles is not adequate and probably should be increased to at least 2.5 hours.

## **OPERABILITY OF AUTOMOTIVE DIESEL ENGINES WITH UNSTABLE FUELS - ACCELERATED STABILITY TEST RELEVANCE**

*B. Martin, X. Montagne and C. Bernasconi*

Operability problems (filter plugging or injector fouling) may encounter when unstable fuel is used. The aim of this work is to study relevance of accelerated tests for prediction of these operability problems. So 50 liters of fuel have been aged in steel tanks at different temperatures. Evolution of quality during storage is monitored by filterable sediments weights, filter blocking tendency and injector fouling tendency. At the same time, observation of sediments by SEM permits us to see the influence of temperature on size and shape of particles. The results confirm that degradation of fuel is different according to the temperature. It is important to notice that a fuel may present a high filter blocking tendency despite a low weight of sediments produced during storage. Ageing affects the thermal stability of fuels and their injector fouling tendency.

## **SESSION 6: FUEL STORAGE, HANDLING AND FILTRATION**

### **FUEL FILTRATION CHARACTERISTICS OF VEHICLE FILTER MEDIA**

*G. G. McVea, M. E. Medwell, A. J. Power and R. K. Solly*

Clusters of 1-2 micron spherical particles of organic matter formed by storage degradation of diesel fuel were found to pass through vehicle filter media of 1 micron nominal pore size but to be retained by filters of 2 micron nominal pore size. In contrast, a suspension of a silica dust of similar particle size to the organic particulate matter, was largely retained by the vehicle filters. As a result of the dust particles being retained in the voids of the filter media, the vehicle filters were more rapidly blocked by the silica dust than the organic particulate. The probability of the clusters of organic particulate matter passing through a filter paper are reduced by the presence of other insolubles such as microbiological and inorganic material. Once retained, the clusters of small spheres may be moulded to fill voids in the filter media. In these circumstances, the presence of organic particulate matter in fuel will lead to very rapid filter blockage.

### **BIOGEOCHEMISTRY OF SLUDGE THAT FORMS IN SALT DOME CAVERNS USED FOR STRATEGIC STORAGE OF CRUDE OIL**

*H. N. Giles, P. W. Woodward and R. A. Neihof*

In many salt dome solution-mined caverns used for the strategic storage of crude oil, a sludge or emulsion layer accumulates over time at the oil/brine interface. This layer typically comprises less than 0.5 percent of the volume of crude oil stored. Relative to the overlying crude oil, the sludge is enriched in trace metals and acidic components; has a high sediment, water, salt, and ash content; exhibits a bimodal distribution of the paraffins, with maxima at about nC17 and nC45; and is depleted in basic components, nitrogen, and sulfur. The apparent depletion in nitrogen and sulfur is probably a result of dilution by water, waxes, and the heterogenous components comprising the sludge rather than an actual loss. Some of the water is present as a very stable emulsion, contrary to the normal tendency of emulsions to be relatively unstable in

highly saline systems. Viable aerobic and anaerobic bacteria have been found in some storage caverns despite the hypersalinity of the environment but all physical and chemical evidence to date demonstrates that these bacteria are not degrading the stored crude oil. Under storage conditions, the bacteria are apparently dormant. Carbon and deuterium stable isotope ratio analyses of methane present in the sludge layer indicate that it is of petrogenic origin and not formed by bacterial alteration of the crude oil. The sludge does not appear to be a result of incompatibility between the various crude oil streams typically commingled during cavern fill. In fact, sludge also forms in caverns with only a single crude oil stream in storage. The formation of sludge is likely a natural phenomenon resulting from settling out of suspended and agglomerated colloidal constituents of the crude oil.

## **WATER SENSITIVITY OF DIESEL FUELS: EFFECTS OF COMPOSITION AND AGEING**

*C. Bocard, G. Castaing and C. Bernasconi*

It has long been recognized that filter plugging in diesel engines is often caused by the growth of micro-organisms when water has entered storage or ship tanks but little is known about the physico-chemical effects of water and specially the interactions between water and gums which form by ageing of fuels. The water-sensitivity of six fuels (straight-run distillates and mixtures containing low-sulfur and high-sulfur Light Cycle Oil distillates) is studied by contacting fuel with water according to different methods; emulsification by mechanical mixing at different energy levels, condensation caused by temperature changes, static contact with a water phase while ageing at 43°C. The effect of water on the filterability of fuels is characterized by a Filter Blocking tendency (FBT) value determined in a pressure-volume test using two membranes: a Whatman GFA filter (1.6 micrometers glass fiber) and a diesel Purflux filter (5-10 micrometers paper). It is shown that GFA filters are very sensitive to both water and gums independently or associated and that their plugging by water could be enhanced by a high paraffin content. Plugging of paper filters, caused mainly by gums, can be enhanced or mitigated by water, depending on the conditions of mixing and on the nature of fuel. Water has only little effect on the effectiveness of an antioxidant additive.

## **USER GUIDELINES FOR DIESEL FUEL HANDLING AND STORAGE**

*S. R. Westbrook and L. L. Stavinoha*

Contaminated or degraded fuel can plug filters, foul injectors, or cause other types of operational problems. For this reason, it is critical that diesel fuel handling and storage procedures provide maximum protection against contamination and deterioration of the fuel. This paper is a summary of guidelines for handling and storage of diesel fuel. Topics discussed include contaminants, specifications, acceptance criteria, fuel and fuel system monitoring, additives, and corrective actions.



## **INGROUND CONCRETE TANKS FOR STORAGE OF PETROLEUM PRODUCTS**

*K. J. Duncan*

Oil and its by-products are strategic materials vital to the vast majority of the world's nations. The bulk storage of strategic materials for quick availability, is of major concern to governments. Policy on this matter is usually influenced by the amount of oil produced locally, the amount imported, the assessed security risks and the internal distribution requirements. Traditional storage methods have recently been proved to be costly and inadequate to meet these requirements and new and improved methods of storage have been investigated. As a result, the concept of inground concrete storage tanks has been developed. This concept has been fully proven through the construction of a major tank farm resulting in unit storage costs substantially lower than conventional storage methods, making its use viable for normal operating, commercial and strategic purposes. This paper deals specifically with the storage of petroleum products in concrete tanks and provides economic and technical data on the subject.

## **SESSION 7: POSTER SESSION**

### **ADDITIVE RESPONSE AND THE EFFECT OF THE CHEMICAL COMPOSITION ON STORAGE STABILITY OF DIESEL FUELS**

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The American Society for Testing and Materials has accepted the Oxidation Stability of Distillate Fuel Oil Test (ASTM D-2274) as the standard test for assessment of inherent stability of diesel fuels. Nevertheless, its reproducibility and predictive potential are still in doubt. There is a need for an improved test technique to monitor diesel fuel stability during production, distribution and storage. Two alternative stability test techniques were chosen for evaluation. The results were compared to results obtained by the ASTM D-2274 test. Oven Storage Test method at 50 °C provided inherent fuel stability base-line comparison data for assessment of the results obtained by the other accelerated stability test methods. Five diesel fuels were subjected to the different testing procedures: three fuels were straight run products typical of local production, two fuels were unstable blends containing LCO. The potential stability of the fuels has been evaluated as such and in the presence of five different multifunctional additives. For the first time, to the best of our knowledge, the Rapid Oven Test at 200°F for evaluating the storage stability of gasolines has been used to evaluate the storage stability of diesel fuels. The results obtained by this accelerated technique served for clarification of the breakdown mechanism of diesel fuels under study. A new stability criterion has been proposed and employed for ranking the fuels according to their stability.

## **ANALYTICAL TECHNIQUES FOR MONITORING ANTIOXIDANT DEPLETION IN JET FUELS**

*C. D. Pearson, J. W. Vogh, O. K. Bhan and D. Sutterfield*

Antioxidants are used at low ppm levels to protect jet fuels against peroxide and sediment formation. The low levels used (ca. 20 ppm) make quantitation very difficult. Our research interests are primarily in following reactions leading to additive depletion and subsequent fuel degradation. To assist in this objective, we have developed two analytical techniques that can accurately and reproducibly determine the level of hindered phenol antioxidants in jet fuels. Specific antioxidants addressed here are 2,6-di-tert-butyl-4-methylphenol (BHT) and 2,4-tert-butylphenol supplied by the DuPont Company as AO-29 and AO-33 commercial antioxidants. The two approaches involve the use of 1) a gas chromatograph/quadrupole mass spectrometer and 2) an HPLC with an electrochemical detector. The techniques have been tested on a range of jet fuels and appear free from interference. A comparison between the techniques showed agreement within the limits of experimental error. Additionally, the techniques were able to pinpoint the time of additive depletion, which corresponded directly with the onset of deposit formation.

## **THERMAL INSTABILITY MECHANISMS OF JET FUELS**

*D. W. Brinkman, O. K. Bhan, J. B. Green, J. W. Goetzinger, R. D. Grigsby and R. Kamin*

Six jet fuels were thermally stressed in a JFTOT apparatus, resulting in the formation of tube deposits and filterable sediments. Liquid chromatographic separation was used to produce fractions and subfractions from the fuels before and after thermal stressing. An acidic subfraction from one of the fuels was analyzed by GC/MS, and significant differences in the concentrations of hydroxyaromatics were found. High resolution mass spectrometry was used to analyze the tube deposits and filterable sediments. In addition, several of the sediments were analyzed by GC/MS. Numerous compound types were identified. Especially prominent were aromatic hydrocarbons and aromatic compounds containing oxygen, nitrogen, and sulfur. A number of significant differences were found in comparing the analytical results from the deposits and sediments from the same fuel and in comparing results between fuels.

## **CHARACTERISATION OF PARTICULATE MATTER IN AGED DIESEL FUEL**

*I. J. Baran, A. J. Power and R. K. Solly*

Organic particulate matter formed in both naturally and thermally accelerated aged diesel fuel has been characterized with the aid of an electron microscope. All particles formed as a result of chemical degradation of the fuel were spheres of 1-2 microns diameter, with most being approximately 1 micron in diameter. The spherical particles clustered together to form chains, with chain lengths up to 25 microns being observed in this study. Particle counts were determined on a HIAC Particle Counter during the mild thermal accelerated ageing of fuel at 43C in the presence and absence of polyurethane Fuel Stability foam (FSF). In the reference fuel, the number of particles registering as less than 1 Omicrons in size reached a maximum after 5 weeks, then decreased. Species registering greater than 10 microns increased in number

throughout the 8 week experimental time as would be expected from the clustering of the smaller spherical particles. In the presence of FSF, the number of particles less than 10 microns remain virtually unchanged from the initial unaged fuel, while the number of clusters greater than 10 microns showed a gradual increase. Mycelia from the common fuel fungus, *HORMOCONIS resinae* (*CLADOSPORIUM resinae*), were branched and linear structures to lengths exceeding 0.5 mm, whereas the spores were ovals, approximately 2 by 4. microns in size.

## **FUEL RELATED PROBLEMS AT A NUCLEAR POWER PLANT OF THE EMERGENCY DIESEL GENERATOR SYSTEM**

*H. L. Chesneau*

This paper deals with the response to a problem that developed in an emergency generator system at a nuclear power plant in the Southeast United States. On January 28, 1987, the power plant formed an Event Response Team (ERT) responding to a notification that a sample from the Emergency Diesel Generator (EDG) Diesel Fuel Oil Storage Tank (DFOST), was above the plant's technical specification limits for water and sediment. The report indicated that a fuel sample from the Diesel Fuel Oil Storage Tank contained water and sediment equal to 0.15%. The technical specification limit for water and sediment is less than or equal to 0.05% by volume. The ERT quickly directed and managed the immediate actions necessary to ensure that the quality of fuel in the DFOST would assure reliable and continuous operation of the emergency diesel generators. At the same time, a Diesel Fuel Oil Task Team (DFOTT) was formed by the ERT to evaluate the root causes of the out-of-specification sample and to develop recommendations to prevent a recurrence. Fuel Quality Services, Inc. became involved at that time to assist the DFOTT to determine both the causes of the problem and to develop the means necessary to correct the current situation.

## **FIELD TRIALS ILLUSTRATING THE LONG TERM EFFECTIVENESS OF METHYL-ISOTHIAZOLONES IN THE PRESERVATION OF LIQUID FUELS**

*M. M. Dorris, D. P. Carmody and D. G. Pitcher*

Methyl-Isothiazolone biocides have been used in both Europe and the United States for the last five years. During this period, many field trials have been performed to demonstrate the Methyl-Isothiazolone's performance. This poster describes the biocide's performance features and illustrates two field trials (one with a utility and one for the French Navy). In these field trials, one single dose of biocide (2.8 ppm active ingredient based on the total tank volume) protected stored fuel from microbiological contamination for at least two years. This illustrates the long-term effectiveness of Methyl-Isothiazolone biocides.