

**6TH INTERNATIONAL CONFERENCE ON STABILITY
AND HANDLING OF LIQUID FUELS
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Abstract Summaries

SESSION 1: AVIATION FUELS I

**REMOVAL OF COPPER FROM FUEL BY IMMOBILIZED HETEROGENOUS
CHELATING AGENTS**

*Dhanajay B. Puranik, Yan Guo, A. Singh, Robert E. Morris, A. Huang, L. Salvucci,
R. Kamin, Janet Hughes, V. David, and E. L. Chang*

As a potential alternative to the addition of metal deactivating additives to jet fuels, the removal of dissolved copper by passing fuel over a solid surface functionalized with an optimized chelant structure has been investigated. This approach allows for the use of optimized insoluble chelants with very high binding constants. Since nothing is added to the fuel, the impact of the resulting complex on fuel thermal stability is not a concern. A direct benefit of solid-supported heterogeneous chelant technology is that copper removal is achieved without introducing surface-modifying soluble chelants which can affect the outcome of thermal stability qualification tests that employ heated metal surfaces. Several different substrates have been functionalized with polyamine ligands. Copper extraction from JP-5 and dodecane with surfaces functionalized with a macro cyclic ligand, 1,4,7,11-tetraazacyclotetradecane, and an acyclic ligand, N-3-trimethoxysilylpropyl diethylenetriamine, are reported in this paper. Initial uses are targeted towards cleanup of contaminated fuel stores, with the ultimate goal of applying this technology to perform in-line copper removal at aircraft fueling points. The performance of these chelant systems in both static and flow tests demonstrates the potential of immobilized chelants to accomplish these goals.

**EFFECTIVENESS OF MDA ON JET FUEL THERMAL STABILITY AS
DETERMINED USING THE GRAVIMETRIC JFTOT: EFFECTS OF EXTENDED
DURATION TESTING AND TIME OF ADDITION OF MDA**

Seetar G. Pande and Dennis R. Hardy

Two studies were conducted on the effects of the metal deactivator, N,N' -disalicylidene-1,2-propane diamine (MDA) on jet fuel thermal stability. Study 1 focused on the effects of MDA on extended duration thermal stability testings ranging from 120 to 152 hours. The test fuel was a Jet A, and the effects of MDA were examined with and without the addition of the antioxidant, BHT (2,6-di-tert-butyl-4-methyl-phenol) as well as with and without added copper. For study 2, the thermal stability test duration was 2.5 hours, and the effect of time of addition of MDA, which was also investigated in study 1, was further examined in a test matrix that comprised two JP-5 fuels, two sources of copper and three concentrations of MDA. Thermal stability was

determined using the gravimetric JFTOT. The results of the extended duration testings indicate that even at the relatively high MDA concentrations examined (15 and 35 ppm), MDA exhibited a beneficial effect in the non-copper doped commercial (Jet A) and Navy type fuel (Jet A +BHT): The results of the time of MDA addition studies indicate that early addition of MDA is more effective than late addition for copper-contaminated stored jet fuels.

RETENTION OF METAL DEACTIVATOR ADDITIVE PERFORMANCE DURING STORAGE OF AVIATION TURBINE FUELS

Cyrus P. Henry Jr.

The use of Metal Deactivator Additive (MDA) in aviation turbine fuels has continued to be controversial following the publication of Shell Thornton Research Centre data, which were presented in a paper at the 3rd International Congress. While benefits from MDA may be overstated in fuels with undetectable dissolved metal content in the ASTM D 3241 JFTOT test, there is also no question that use is fully merited when dissolved copper is present. Arguments have been presented that the allowed level in jet fuel should be significantly reduced, because the potential for copper contamination is lessened by the virtual disappearance of copper sweetening processes. There were concerns, however, about the possible loss of the additive during fuel storage, such that re-doping may be appropriate but not accommodated by reduced maximum use levels. To address that concern, samples of jet fuel containing MDA were stored and then challenged by the addition of soluble copper, followed by ASTM D 3241 JFTOT testing to determine whether the additive is still active.

THE 'BLACK AVTUR' INCIDENT IN NORTHERN AUSTRALIA (1994/95); REPORT ON THE AMRL INVESTIGATION (1995/97)

Alan J Power, Paul M Rawson, Michael G O'Connell, Lance W Hillen and Grier G McVea

The 'Black AVTUR' incident that occurred at a northern Australian Air Force base in late 1994 to early 1995, was the first known example in Australia of an aviation fuel throwing a sediment. The fuel was JET A-I which had been additised to the military specifications of NATO Code F-34. The JET A-I fuel had been refined in Singapore from a Chinese crude oil. The black coloured fuel that formed at low point drains in ten 162,000 litre fuel tanks, after several months of storage, caused significant military logistic problems. From investigations by the above laboratory, it was established that the fuel was storage unstable, a characteristic that was responsible for the black colouration of the fuel. The bulk fuel temperature at the base was 32°C and at this temperature, the sediment particulate matter was apparently being held as a stable colloid that gave the fuel its black appearance. This report describes the investigation of this incident and provides details of work done in an attempt to identify the cause(s) of the 'Black AVTUR' incident. A major finding from this research was that an antioxidant present in the AVTUR fuel lubricity improver additive is strongly implicated as a component involved in the formation of the jet fuel sediment molecules that were responsible for the quarantining of the contaminated fuel for several months, at the military air base.

JET FUEL CONTAMINATION BY DIESEL FUEL DYE

K. H. Strauss

An investigation of jet fuel contamination by diesel fuel dye in the USA has been coordinated by the Coordinating Research Council since April 1994. During that time the CRC was instrumental in getting the dye color changed from blue to red to avoid confusion with aviation gasoline. Subsequent to that change laboratory tests were conducted to establish the effect of red dye on specification properties with high temperature stability being the only affected property. Based on these results, aircraft operation with dye-containing fuel was severely restricted by airframe manufacturers. The paper reviews the test results and traces the chronology of industry actions to control the problem.

IMPACT OF CAUSTIC TREATING ON THE FILTERABILITY OF JET FUEL

Lawrence D. Palmer, Kristina M. O'Callaghan, and Brian C. Springthorpe

Demand for jet fuel in Australia continues to increase, and refiners are seeking low-cost means of expanding their production capability. An existing caustic treater may be undersized and act as a production bottleneck. When the caustic treater is limited by flow rate and the jet fuel has minimal acidity, caustic treatment of only a part of the jet fuel is an attractive option. An Australian refinery performed refinery trials with the aim of proving that this approach could increase its jet fuel production. Filterability of jet fuel was severely affected, and electrical conductivity became more sensitive to light-induced decay. The filterability problems were caused by traces of sodium and calcium naphthenates in the fuel. A filter blocking tendency test was developed, and became an essential tool for developing a modified processing scheme which now produces 50% more jet fuel. During refinery trials, the filterability test minimized filtration problems at distribution terminals and airports, and it continues to serve a useful quality control role. Salt driers, located between the caustic treater and refinery storage tanks, acted as reservoirs for the filter blocking agent, which was released intermittently into jet fuel. Complete segregation of one of the salt driers from the caustic treater provided a simple means of eliminating the filterability problem.

SESSION 2: AVIATION FUELS – II

MEASUREMENT OF DISSOLVED AND TOTAL WATER CONTENT IN ADVANCED TURBINE ENGINE FUELS WITH A GAS-LIQUID CHROMATOGRAPHIC OTC TECHNIQUE

Steven D. Anderson, Wayne A. Rubey, and Richard C. Striebich

Significant capabilities have been developed over the past quarter century for detecting extremely trace quantities of organic compounds in water. However, accurate and precise analyses for water in complex organic mixtures continues to be an analytical challenge. Water is

omnipresent and a thin film of adsorbed moisture usually coats every type particle and surface. The analysis for water content in a complex turbine engine fuel is complicated by water sorption onto fine particulate matter and also the presence of numerous fuel additives, e.g., corrosion inhibitors, fuel system icing inhibitors, static dissipators, metal deactivators, detergents, dispersants, etc. Many of these additives affect the interfacial surface tension and the water coalescing properties of the bulk fuel. Instrumental approaches for measuring water content in complex organic mixtures include titration techniques, optical spectroscopy, humidity sensing devices, diode lasers, light emitting diodes, liquid chromatography, and gas chromatography. There has been a real need for a laboratory technique that can provide appropriate water content measurements for turbine engine fuels which contain extensive additive packages. Accordingly, we pursued the gas chromatographic approach for measuring dissolved and free water. Initially, a reaction gas chromatography (RGC) technique was investigated in which water was converted to acetylene by way of a temperature-controlled calcium carbide reactor. Although this RGC procedure exhibited considerable sensitivity via detecting water as acetylene using hydrogen flame ionization detection, significant irreproducibility was encountered. Accordingly, various gas-solid chromatographic (OSC) and gas-liquid chromatographic (OLC) scenarios were investigated. It was found that when a modified high-temperature splitter injector assembly is used in conjunction with a highly deactivated and low 13 value GLC open tubular column, that water can be well-behaved (symmetrical zone profile) and separated from other constituents. Measurement of water content in a variety of turbine engine fuels while using a modulating thermal conductivity detector was found to be both precise and sensitive, even into the sub-ppm region. Using standard addition procedures along with an internal standard, it is anticipated that this GLC analytical method can be simplified for eventual field-scale testing.

AVIATION FUEL HANDLING: NEW MECHANISTIC INSIGHT INTO THE EFFECT OF SURFACTANTS ON WATER COALESCER PERFORMANCE

Victor B. Hughes

Aviation fuels may contain trace polar materials of a type and at a concentration sufficient to impair the performance of filter-water-coalescers in the removal of dispersed droplets of free water from the fuel. This process, commonly called "coalescer disarming" may cause the transmission of unacceptable levels of free water. There are a number of proposed mechanisms for this phenomenon, one of which invokes a change in "(water-)wettability" of the coalescer fibres as a result of surfactant adsorption. In this paper the results of fibre wettability changes observed using an Environmental Scanning Electron Microscope (ESEM) are presented. Bundles of fibres may be observed in the ESEM whilst the water vapour pressure is varied. Precipitation of water droplets onto the fibres may be induced by cooling the stage holding the fibres and increasing the water vapour pressure. Thence the contact angles made by water droplets may be assessed for fibres exposed to fuels with and without potent surfactants. Droplet growth may also be observed until coalescence occurs. Surprisingly the observations reveal that the trend in fibre wettability as a function of surfactant exposure does not go the way expected from considerations of currently proposed mechanisms. Fibres exposed to surfactants appear to be prone to water swamping rather than becoming hydrophobic. The implications of this observation will be discussed in terms of macroscopic coalescer performance observations.

AN ANALYTICAL APPROACH TO WATER SEPARATION FROM JET FUELS AND COALESCER DISARMING

Peter David, Spencer E. Taylor and Andy J. Woodward

An analysis is presented of some aspects of fibre wetting and the possible implications for the operation of filter-coalescers. Two experimental approaches have been adopted in the present work. In the first, pre-treatment of single fibres by a Merox fuel and by a JP8+ 1 00 dispersant additive was followed by dynamic wetting measurements in water. The second approach, which is more representative of the practical situation, involves a "dual-liquid" system, in which the fibre first passes through an oil phase directly into water, via an oil/water interface. Specific wetting-related features arising from these single-fibre experiments have been identified.

STADIS® 450 IN AVIATION FUEL APPLICATIONS – UPDATED

Cyrus P. Hemy Jr.

At the October, 1994 International Conference in Rotterdam, information was presented on the use of Stadis® 450 in certain fuels, mainly chemically sweetened, which contain interacting trace impurities resulting in several difficulties. A slightly modified product has now been introduced which overcomes a potential to form a precipitate containing a dodecylbenzenesulfonate. This modified additive has now been fully accepted by airframe and turbine manufacturers and is fully commercialized; production of the old formulation ceased in December 1996. The status of the transition to the modified product is reviewed. Additionally, progress has been made in understanding the relationship of the results from ASTM D 3948 water separation tests, and the actual performance of coalescers in the industry. This has led to changes in aviation fuel specifications, and to a program in ASTM to better define an improved test method to predict coalescer performance. Overall, fewer difficulties are expected in the future.

THE EFFECT OF PHENOLIC IMPURITIES IN JET FUEL ON THE BEHAVIOUR OF CONDUCTIVITY IMPROVERS

Brian Dacre and Janice I. Hetherington

The conductivity improver Stadis 450 is known to give a variable conductivity response in jet fuels which come from different crudes and refinery processes. The present work shows that certain phenolic impurities in the jet fuel may be responsible for these variations and that fuels with a high phenolic content could be particularly prone to poor conductivity response with Stadis. Conductivity measurements on Stadis in model systems have shown that certain phenols interact with Stadis to cause considerable reductions in the conductivity. The magnitude of the effect is highly dependent on the concentration and the structure of the phenol and especially on whether the phenol is hindered or unhindered. Unhindered simple phenols such as m-cresol, p-cresol and phenol, at concentrations above 50ppm, cause a large reduction in the conductivity response with Stadis. Highly hindered phenols, such as the types used as antioxidants (2,6-ditert-butyl-4-methylphenol), cause almost no reduction in the conductivity. This confirms the findings of the antioxidant suppliers. Partially hindered phenols such as 2-tert-butyl-4-methylphenol are intermediate in their effect on the reduction of the conductivity. Jet fuels analysed by BP revealed total phenol concentrations as high as 700ppm, which is considerably higher than had

previously been expected. Of these phenols, 80% were found to be of the simple, low molecular weight, unhindered type, such as m-cresol, which were found in the model systems work to have the most damaging effect on the conductivity of Stadis. The conductivity of Stadis was measured in fuels of known phenolic content. The response was found to be lower in fuels of high phenolic content, thus confirming the behaviour predicted from model phenol systems. The role of the phenols on the conducting mechanism of Stadis is discussed. It is proposed that the phenol is involved in a proton donor interaction with a component of the Stadis, possibly the sulphone and that this interferes with the normal ion producing mechanism which imparts conductivity to Stadis-doped fuels.

COPPER CONTAMINATION OF JET FUEL FROM SHIPS' HEATING COILS

Peter David, Alan Goddard, Spencer E. Taylor and Andy J. Woodward

Metal contamination of aviation fuels can sometimes occur during distribution to the extent that the fuel is rendered off-specification with respect to thermal stability. Such problems can occur during sea transportation and the effects can often be traced to on-board copper dissolution from ship's heating coils, employed for shipment of more viscous cargoes, such as residual fuel. Verification of the metal-leaching propensity of fuels has been based for the most part on the results from tests involving controlled storage of fuels over specimens of representative metallurgies, followed by metal analysis to determine the levels of contamination. Often these experiments are lengthy and by the time the results of the extended tests are known, failures in the JFTOT or other indicators of contamination are also known. There is therefore a requirement for a method which will rapidly determine a fuel's propensity for copper leaching, especially in cases where it is known that the likelihood is high of the fuel coming into contact with copper alloys. A simple laboratory test based on copper strip immersion with determination of fuel copper by a new in-house colorimetric method has been devised to predict the aggressive nature of fuels towards copper alloys. The relationship with fuel composition and processing route has been investigated. The quartz crystal microbalance (QCM) with copper crystals has also been used to study copper dissolution from fuel systems; results are generally in agreement with the immersion tests. Details of the studies are presented in the paper, together with recommendations on test implementation.

SESSION 3: AVIATION FUELS III

CHARACTERISATION AND QUANTIFICATION OF DEPOSITS FROM THERMALLY-STRESSED AVIATION FUELS

Clive Baker, Peter David, Ian Love, Robin Mogford, Spencer E. Taylor and Andy J. Woodward

Using a combination of the Ellipsometric Tube Analyser (ETA), SEMIEDX analysis and the Jet Fuel Thermal Oxidation Tester (JFTOT), three aspects of thermally-induced deposit formation in jet fuels have been studied. These are (i) the quantification of surface deposits and bulk insolubles generated in the JFTOT test, and the extent to which metal deactivator additive affects deposition rates; (ii) the feasibility of characterising fuel thermal stability from single JFTOT runs; and (iii) a preliminary analysis of the composition and nature of abnormal deposits generated in JFTOT tests and the mechanism by which they are formed. The analyses have been based on results from a variety of fuel types.

IMPACT OF FUEL RECIRCULATION ON THERMAL STABILITY

E. Grant Jones, Walter J. Balster, and Lori M. Balster

Modern military aircraft utilize aviation fuel for combustion energy and also as a heat sink to cool component systems. On-board fuel management must satisfy both combustion and cooling requirements during all phases of a flight. Frequently, fuel that has been subjected to thermal oxidative stress must be diverted from combustion and recirculated back to the fuel tanks. The resultant pre-stressing can significantly reduce fuel thermal stability. Through an isothermal simulation under well-defined reaction conditions, the thermal stability of neat and pre-stressed or recirculated fuels has been measured. It was found that fuel recirculation seriously degrades thermal stability. The results of this study are reported, and possible corrective measures are discussed.

COMPARISON OF THE EFFECTS OF STORAGE CONDITIONS, TYPE OF SOLUBLE COPPER, AND MDA ON JP-5 FUEL THERMAL STABILITY

Seetar G. Pande and Dennis R. Hardy

The effects of the type of storage and the source of soluble copper on fuel thermal stability were examined using five JP-S fuels. The effects of the metal deactivator, MDA (N,N'-disalicylidene-1, 2-propane diamine) were also examined in the comparative studies using two of the five test fuels. Thermal stabilities were determined using the gravimetric JFTOT, which gives a quantitative measure of the total deposits formed. A copper concentration/storage effect was observed, which necessitated evaluations at similar copper concentrations. However, the source of copper appears not to be important. Instead, the main operative factor affecting the thermal stability of stored fuels appears to be the combined effect of long-term ambient storage in the presence of copper. Good correlations were obtained between the thermal stabilities of fuels that were stored in the presence of 400 ppb copper from copper IT ethyl acetoacetate (CuEA) at 90°C/50 psig air/24 hr versus comparable field conditions, which approximated an ambient storage period of six months in the presence of copper from 90:10 copper-nickel alloy. These results are significant for the following reasons: (1) they validate the use of the specified laboratory test conditions as being realistic; (2) they support our premise that the precursors that lead to thermal deposits are formed primarily on storage in the presence of copper; and (3) they offer a rigorous method for predicting the thermal stabilities of jet fuels. The MDA/Cu/storage studies also indicated good agreements between the thermal deposits of fuels stored using accelerated vs ambient conditions for periods equivalent to - six and twelve months in all the cases examined, which include with and without added copper from CuEA or Cu-Ni.

INVESTIGATION OF THE EFFECTS OF TIME ON THE PHYSICAL COLLECTION OF AVIATION FUEL DEPOSITS IN A SCALED TURBULENT FLOW SYSTEM

John E. Colbert and Clarence J. Nowack

The Fuels & Lubricants Division of the Naval Air Warfare Center has developed and verified a hypothesis which models the collection and buildup of aviation fuel carbon deposits as a function of time in a turbulent flow simulator (i.e., fuel injector nozzle). These deposits are the result of thermal oxidative breakdown that typically occurs when aviation fuels are exposed to the

different heat loads rejected into various parts of an aircraft fuel system (viz., fuel injector nozzles) during flight operations. This paper presents experimental data that supports the use of a proposed mathematical model used in describing the fuel thermal deposition process and provides theory upon which the model is based. Assumptions are made which enable this model to be used in calculating the deposition rate within a turbulent simulator over a wide range of typical temperature conditions of an aircraft fuel system. The intended use of this work is to develop a test protocol that will require less test time and fuel in order to study the effects of fuel thermal stability using a high fuel flow unit.

EVALUATION OF JP-8 + 100 FUEL COMPATIBILITY WITH AIRCRAFT FUEL SYSTEM MATERIALS: THE EFFECT OF DETERGENT DISPERSANT ON AIRCRAFT MATERIALS

Dexter H. Kalt

Within airframe and engine fuel systems, materials including metallics, composites and non-metallics are found in contact with aircraft fuel. This paper describes a few of these materials and physical property changes observed in these materials after thermal aging in specific aircraft fuels in a laboratory setting. These changes are evaluated in comparison to physical properties of materials before fuel aging and with different test fuels and additives. The laboratory tests are designed to reasonably replicate temperatures to which the materials and the specific fuels would be subjected in airframes and engines. The 28 day aging test temperatures range from ambient to 400 °F. The materials are identified according to use categories in aircraft fuel systems. The materials include those used in fuel system tanks and in associated components (bladders, sealants, locking devices) as well as alloys and sealing materials used in fuel lines and components up to the engine combustion chamber. Included in the test data points are the materials' effects on the fuel i.e. conductivity, elements, gums, acid number and hydroperoxides. This paper describes aircraft fuel system materials and their compatibility with a new higher thermal stability fuel. The improved thermal stability JP-8 fuel is obtained by incorporating a fuel additive package commonly referred to as JP-8 +100. The effects of this fuel additive on the aircraft fuel systems materials are measured and determined by comparing their effects to that of a baseline JP-8 fuel. The +100 refers to the increase in the expected thermal stability range of the fuel by 100 °F over that of a JP-8 baseline fuel. The +100 fuel additive package incorporates dispersant / detergent, metal deactivators and antioxidant compounds which are incorporated to reduce the rate of oxidation and deterioration of fuel at higher temperatures.

JP-8+ 100: THE DEVELOPMENT OF HIGH THERMAL STABILITY JET FUEL

Shawn P. Heneghan and William E. Harrison

Jet fuel requirements have evolved over the years as a balance of the demands placed by advanced aircraft performance (technological need), fuel cost (economic factors), and fuel availability (strategic factors). These challenges include: maintaining availability while minimizing the cost; maintaining flammability and heat content while minimizing fire and explosion hazards; allowing cold weather and high-altitude operations by restricting flow characteristics, improving storage lifetimes, improving handling and improving refueling safety. To meet these evolving challenges, the Air Force over the years has developed fuels and fuel additive packages for both general (JP-4 and JP-8 fuels) and specialized (JPTS and JP-7) use. In a modern aircraft, the jet fuel not only provides the propulsive energy for flight, but also is the

primary coolant for aircraft and engine subsystems. To address this particular requirement, the U.S. Air Force, industry, and academia have teamed to develop a new additive package for kerosene jet fuels that offers increased heat sink and thermal stability. This advanced additive package when added to jet fuels enables improved aircraft design and decreases fuel system maintenance due to fuel fouling/coking. This paper describes the development of an improved JP-8, named "JP-8+100", that offers a 55C (100F) increase in the bulk maximum temperature (from 325F to 425F), wetted wall temperature (from 400F to 500F) and improves the heat sink capability by 50%. Included are sections that detail the problem definition, the additive selection and design process, and flight and field-testing and evaluation. Field-testing in current front line Air Force aircraft has shown that an improvement in thermal stability of JP-8 fuel reduces fuel-related maintenance, reduces replacement parts requirements and increases aircraft readiness. In studies of the design of future advanced aircraft, JP-8+ 100 has been shown to reduce fuel system complexity and weight.

ADDITIVE STABILITY IN JP8 METAL ALLOY SYSTEMS AT ELEVATED TEMPERATURES

Marlin D. Vangness and Shawn P. Heneghan

We have developed a method to determine the concentration of the Betz/Dearbom 8Q462, known as SPEC-AID 8Q462, thermal stability additive in jet fuel samples. Betz 8Q405, the dispersant component, includes a proprietary amount of phosphorus. This technique utilizes the phosphorus content of Betz 8Q405 to estimate the concentration of the complete package in JP-8+100. The precision depends on the availability of base fuel to correct for background and other matrix effects. If the base fuel is available the concentration can be measured with day to day or sample to sample variations less than 5%. Without the base fuel, but using a generic Jet-A or JP-8 as a standard, the sample-to-sample variations are within 17%. We have used this technique to study the effects of thermal aging in the presence of a variety of metallic materials. The change in additive concentration was studied over 28 day periods in three jet fuels, at 160F, 200F, and 350F, in the presence of Fe, Cu, Ni, Al and several stainless alloys. Preliminary results indicate that the concentration of BETZ 8Q405 remaining in solution is dependent on the storage temperature and type and condition of metal surfaces in contact with the fuel.

SESSION 4: AVIATION FUELS – IV

HIGH REYNOLDS NUMBER THERMAL STABILITY (HiReTS) RIG FOR REALISTIC, RAPID EVALUATION OF DISTILLATE FUEL THERMAL OXIDATIVE STABILITY

Joanna M. Bauldreay, Richard I. Heins, Geoffrey Houlbrook, and Johanne Smith

Shell Research Limited have developed a small-scale rig to evaluate jet fuel thermal stability under realistic test conditions. Pre-production prototypes of the HiReTS (High Reynolds number Thermal Stability) rig, known during its laboratory history as the Capillary FTOT (CJFTOT), have now been produced. Fuel passes through a stainless steel capillary tube at flow rates sufficient to ensure that turbulent conditions prevail. The tube is electrically heated and PC control ensures a fixed fuel outlet temperature. More

power must be provided to maintain the fuel outlet temperature when deposits build up on the inner capillary surface. A noninvasive infrared thermometer monitors the tube outer surface during the, typically, two hour test. The more deposit produced, the higher the temperatures rise. The end-of-test result is the HiReTS or C-JFTOT number, the summation of final temperature rises at set scanning positions. C-JFTOT numbers have correlated well both with post-test carbon burnoff values and with results from large-scale rigs. 3-D displays of temperature changes provide dramatic pictures of temporal and positional differences in fuels' deposit-forming tendencies. HiReTS numbers for hydroprocessed fuels are up to an order of magnitude lower than those for specification-passing Merox fuels. Standard operating conditions were chosen to identify poor fuels, and differentiate between typical commercial fuels. Thermal stability improving additives can significantly lower HiReTS numbers and different flow/temperature/time conditions may be needed for the HiReTS to differentiate between high thermal stability fuels rather than to reject poor fuels. USAF are now evaluating a pre-production HiReTS machine, both as a possible specification test and as a research tool.

ELECTRICAL CONDUCTIVITY OF HITTS ADDITIVE PACKAGES FOR THE JP8+100 PROGRAMME

Brian Dacre and Janice I. Hetherington

The behaviour of two RITTS high temperature additive packages has been studied to examine possible interference with existing conductivity improver and also to assess their potential as conductivity improvers. The RITTS additives are shown to impart sufficient conductivity to fuels to meet certain fuel conductivity specifications without the addition of Stadis. Use of the IDTTS additives with Stadis is shown to produce values of conductivity above the fuel specification. The conductivity performance of the IITTS additives is unaffected by the presence of phenolic or sodium salt impurities in the fuel which have been shown to have a detrimental effect on the performance of Stadis. The conductivity behaviour of the individual components of the IDTTS additives is discussed. The dispersant is the main conducting component in the additive packages, but there are variations in the magnitude of the conductivity observed.

TESTING JP-8+100 PACKAGES IN EUROPEAN JET FUELS - EVALUATING AND UNDERSTANDING BENEFITS AND DRAWBACKS

Joanna M Bauldreay, William G Blundell, Richard J Heins, Geoffrey Houlbrook and Johanne Smith

The UK's Ministry of Defence (MoD) has instigated a European extension of the JP-8+100 programme, testing front-runner USAF additive packages and other additives from UK companies in European-sourced jet fuels. Shell Research Ltd have provided Jet A-I fuels and upgraded them to military specifications (JP-8 = NATO F-34) by the use of fuel system icing inhibitor and corrosion inhibitor/lubricity improver (CIILI) additives. Fundamental, analytical, small-scale and large-scale rig tests have been used to examine

how and if the additives improve thermal stability performance. A Flask Oxidation Test investigates the first stages of fuel oxidation and indicates that none of the additives has a significant impact on this step. Later stages in the fuel degradation are affected as evidenced by higher JFTOT breakpoints, lower levels of deposit in a carbon bum-off version of the JFTOT, and lower levels of deposition in Shell's new HiReTS (High Reynolds number Thermal Stability) rig. Fuels containing both CI/LI and JP-8+IOO additives produce the greatest apparent improvements in thermal stability performance. Other performance characteristics have been tested in parallel: lubricity, handling (e.g. water shedding), low temperature and storage stability. CYLI additives alone improve fuel lubricity (JP-8 better than Jet A-I) but lead to a drop in handling performance. None of the JP-8+ 100 additives significantly affects lubricity performance but results for water shedding tests are further worsened. Low temperature behaviour is insensitive to the presence of the additives while accelerated storage tests indicate that the JP- 8+ 1 00 additivated fuels produce higher levels of gums than the base fuels.

EXPERIMENTAL EVALUATION OF THE TWO-TIERED JFTOT TEMPERATURE PROVISION FOR JET A FUEL

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ABSTRACT

An experimental program is being conducted to assess the potential impact to fuel-nozzle fouling life

of using Jet A fuels which pass the JFTOT at 245°C but not at 260°C. Since the JP-8 fuel specification allows only the 260°C minimum temperature, this is an important consideration for

military aircraft which upon occasion refuel with Jet A at commercial airports. The methodology of

accelerated fuel-nozzle fouling tests and subsequent analysis follows previous projects for the US

Navy to answer similar questions on the effect of reductions in thermal stability.

Although the project

is underway, unforeseen delays precluded the presentation of actual results at this meeting. Anticipated results are presented and discussed.

STUDIES OF JET FUEL OXIDATION USING OXYGEN MONITORING AND CHEMICAL KINETIC MODELING

Steven Zabarnick, Shawn D. Whitacre, Mark S. Mick, and Jamie S. Ervin

A quartz crystal microbalance (QCM)/Parr bomb system with a headspace oxygen sensor is used to measure oxidation and deposition during thermal oxidative stressing of jet fuel. In studies of jet fuel antioxidants, we find that rapid increases in oxidation rate occur upon consumption of the antioxidant. The antioxidant appears to be consumed by reaction with alkylperoxy radicals. In studies of metal deactivator (MDA) additives, we find that MDA is consumed during thermal stressing, and this consumption results in large increases in the oxidation rate of metal containing fuels. Mechanisms of MDA consumption are hypothesized. Chemical kinetic modeling was used to simulate the autoxidation of jet fuel including the chemistry of peroxy radical inhibiting antioxidants and hydroperoxide decomposing species. Recent experimental measurements of oxygen concentration during autoxidation of jet fuel were used to "calibrate" the rate parameters of the mechanism. The model showed excellent agreement with oxygen profiles of static measurements at 140°C. At 185°C, the model predicts that peroxy radical inhibiting antioxidants and hydroperoxide decomposers both slow and/or delay oxidation, but the resulting oxygen profiles display different characteristics. We have shown that comparison of these profiles with fuel blending and fuel dilution measurements have the potential to differentiate between the two types of oxidation slowing species. The modeling predicts that the presence of both types of species in a fuel results in a synergistic slowing of the oxidation rate.

NUMERICAL SIMULATIONS OF JET FUEL OXIDATION AND FLUID DYNAMICS

J. S. Ervin and S. Zabarnick

A pseudo-detailed kinetics model which considers antioxidant chemistry was employed in a computational fluid dynamics code, and concentration profiles of various species along a stainless-steel tube were calculated for both nearly isothermal and non-isothermal flowing systems. Flowing experiments were performed with both a severely hydrotreated fuel and a straight-run fuel, and the predicted dissolved oxygen and hydroperoxide profiles agreed well with the measured profiles over a range of bulk fuel temperatures and flow conditions. Favorable comparison was also found between model predictions and measurements taken from the literature. The model was found to be capable of simulating a synergistic reduction in the oxidation rate that is sometimes observed among different fuel antioxidants. The present model offers an improved understanding of jet fuel oxidation, antioxidant chemistry, and the involved fluid dynamics.

SESSION 5: LONG-TERM AND STRATEGIC STORAGE

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

Takao Hara, Naoyuki Binata, Yutaka Imagawa, Isataka Kawai, Yoshiyuki Imai, Yoshihiko Kon and Tatsuo Seiki

Japan National Oil Corporation has been practicing the long-term strategic stockpiling of crude oil since 1978. The total amount of reserved crude oil now exceeds 48 million kl, corresponding to near 80 days' supply in Japan. Storage stabilities of crude oil, including formation of organic sludge, have been surveyed on four kinds of stockpiling systems (on-ground tank system, in-ground tank system, floating tank system and under-ground cavern tank system). Depositing sludge formed during stockpiling is removed periodically by the particular sludge sampler to clarify the physical and chemical properties. Depositing sludge is found to form W/O type oil-water emulsion and to be composed of crystalline n-paraffins of substantially higher carbon numbers. The amount of depositing sludge settled on the bottom of the tank has been carefully monitored during stockpiling for emergent discharging. The efficiency of operational control against sludge accumulation is evaluated for various mixing device adopted in the on-ground and in-ground tank systems. In some occasional case, a slight amount of residual sludge is recovered after crude oil washing procedure (COW) during tank cleaning inspection. The residual sludge forms quite stable W/O emulsion, water content of which reaches 33 wt%. Minimum pour point of the sludge is found to be 52.5 °C. In such case, hot water washing should be necessary in addition to the ordinary COW procedure. The mechanism of sludge formation is discussed and numerical analysis is applied to the relationship between amounts of accumulated sludge and stockpiling period. In further investigation, the coefficients of the assumed function could be expressed as variables source, storage temperature, temperature drop, of storage system, crude experienced condition on previous tank storage and so on.

ASSESSING THE POTENTIAL FOR OXIDATIVE CRUDE OIL DEGRADATION DURING LONG-TERM STORAGE

J. B. Green, J. Y. Shay, K. Q. Stirling and H. N. Giles

Alteration of crude oil composition and properties is a major concern for those involved with its long-term storage or strategic stockpiling. Significant alteration of crude oil could potentially occur via any of several pathways: microbial degradation, contamination, precipitation of slightly soluble components, or oxidative degradation. Over the course of an ongoing program for support of the U.S. Strategic Petroleum Reserve (SPR), the authors have examined each of the pathways listed above. This paper will focus on assessing the potential for oxidative degradation of crude oil. In order to assess the maximum extent of degradation likely to occur, three crude oils were subjected to a modified version of the oxygen overpressure test used to test diesel fuel storage stability (ASTM D 5304). Hot (85°C) filtration and sediment washing were employed to avoid wax precipitation. The crude was aged for 16, 40, and 90 hours under pure oxygen using conditions prescribed in the test method. Additional tests were also carried out under air and inert (N₂) atmospheres. The resulting aged crude oil samples and sediments were subjected to a variety of analyses. Aging under pure oxygen at 90°C for 90 hours produced maximum sediment levels of 2.3-23 g/L for the range of crude oils tested. Sediment levels

obtained under air or nitrogen were much lower, typically <0.3 g/L. Maximum sediment formation was directly proportional to either asphaltene or vanadium content of the crude oils examined. Both of these parameters correlate with the proportion of high molecular weight, slightly soluble crude oil components present. Sediments from oxidized crude oil exhibit atomic H/C ratios near 1.0, moderately elevated heteroatom contents compared to the respective > 1,050°F resid, and relatively low «1 wt%) levels of carbonyl and sulfoxide functional groups. Based on the results obtained, it was concluded that oxidative degradation of crude in SPR caverns is of minimal concern.

SESSION 6: FUEL BLENDING AND COMPATIBILITY

CONTROLLING RESIDUAL MARINE FUEL COMPOSITION BY TGA

John D. Bacha

Residual fuel oils are produced by blending cutter stocks with petroleum residues. Petroleum refiners' increasing adeptness at converting more of the bottom-of-the-barrel to light products can/does affect the quality of the derivative oils. All residual fuel oils exhibit some bimodal character, reflecting the volatilities and other characteristics of the light and heavy components from which they were generated. Residual fuels produced from some solvent extracted residues can exhibit extreme bimodal character (dumbbell blends). While such fuels may meet existing standard specifications, they have been found to readily foul injectors of large marine diesel engines. The compositional deficiencies of such fuels can be characterized, monitored and controlled by use of thermal gravimetric analyses.

FUEL BLENDING: HOW TO MINIMIZE RISK OF INCOMPATIBILITY

Rudolph Kassinger, Ph.D.

A sound theory for understanding the principals of residual fuel compatibility and stability has been available for decades. "The Stability of Residual Fuels -Theory and Practice of the Shell Concept' was presented in some detail at the 16th CIMAC Conference in Oslo, in June 1985 by Lewis, Johnson and Berryman. Griffith and Siegmund of Exxon Research presented an equally detailed methodology in their paper "Controlling Compatibility of Residual Fuels" which was presented to the ASTM Symposium on Marine Fuels in 1983. I have also found an excellent paper published in 1938 by Hulse and Thwaites of the Standard Oil Development Co. (now Exxon Research and Engineering Co.) on fuel stability and a sediment test procedure which was the forerunner of Exxon's Sediment by Hot Filtration Sediment test. Van Kerkvoort and Nieuwstad published an equally comprehensive paper in 1951 in the J Institute of Petroleum. This paper also discussed the theory of compatibility, and I believe this paper gives the first detailed description of the Shell Hot Filtration Sediment Test. The Shell and Exxon tests evolved into very similar procedures. A careful reading of these papers reveals that the Shell and Exxon theoretical bases for stability and compatibility are in fact very similar. The following discussion is based on the principles espoused in the referenced papers.

A COMPUTERIZED SYSTEM FOR PREDICTION OF COMPATIBILITY OF FUEL OILS

Josefa Ben-Asher, David Luria, Gregory Krenis and Gal Kirpichnikov

Two fuel oils, thermally stable per se, may form suspended solids when mixed. Consequently, the blend will cause operating problems such as excessive centrifuge loading, strainer plugging and tank sludge formation. Though it is possible to check in laboratory whether two fuels are compatible, there are difficulties in obtaining a sample of fuel oil designated for the tank. Presently, it is impossible to decide, based on the data supplied with the fuel, what can be blended with what. Hence, there is a necessity for a predictive tool. The aim of the present study was to develop a computerized system for prediction of compatibility of fuel oils. Blends have been prepared. Their properties and thermal stability have been checked in the laboratory. An artificial neural network called "Back Propagation" has been chosen for feasibility studies. The system has been trained by supervised learning method. The properties of 235 blends and their constituents have been incorporated by the network. Additional 78 blends were used in order to check the system's ability to predict compatibility between the constituents of new blends. The network predicted correctly the stability of 39, out of 42, unstable blends. It was found that fuel oil forming incompatible blend with one fuel, may produce thermally stable blends with other fuel oils. 5 new incompatible combinations of fuel oils have been discovered. It was proved that computerized neuron networks can be used for prediction of compatibility of fuel oil blends.

SESSION 7: GENERAL I

AN IMPROVED FUEL FILTERABILITY TEST

Erna J. Beal, Janet M. Hughes, and Dennis R Hardy

This paper describes our efforts to improve upon existing filterability test methods used in the laboratory and in various field applications. Our goal has been to better define scaling parameters especially in regard to large scale fuel handling systems such as airport and shipboard systems and to improve test method reality by investigating various types of filter media. By carefully controlling the effective cross sectional area we have minimized the effects of sample viscosity on pressure drop. When sample viscosity is thus taken into account and all the other physical variables such as flow rate, pressure and temperature are also controlled then it is possible to use pressure drop to very accurately predict solid contamination concentration in fuel samples. This paper describes the rationale behind our selection of the controlled variables and presents the data which support these changes. Thus, these improvements should now allow us to use this type of filterability test which realistically mimics actual fuel systems and their associated filtration devices as much more accurate predictors of potential field problems.

RAPID DETAILED CHEMICAL ANALYSIS OF TRANSPORTATION FUELS BY GC-FIMS

Ripudaman Malhotra, Michael J. Coggiola, Steve E. Young, Charles A. Spindt

Determination of the detailed molecular composition of transportation fuels by standard GC and GC-MS techniques is limited to gasolines only. The complexity of higher boiling fuels makes it extremely difficult to obtain reliable composition data by using these methods. Unlike many other ionization techniques, field ionization produces only the molecular ions for most compounds, and thus simplifies the analysis. However, because compounds of different classes sometimes share the same nominal mass, it is not possible to get detailed compound type analysis by FIMS alone. We have modified an HP 5971A Mass Selective Detector by replacing its standard electron impact source with a volcano-style field ionization source developed at SRI. Several samples, including gasolines, jet, and diesel fuels as well as Arabian sweet crude oil were analyzed by this GC-FIMS. The chromatography was not optimized, with typical run times being on the order of 12 min. The total ion current chromatogram showed the expected poorly resolved hump. However, examination of selected ion chromatograms clearly showed well-separated peaks for different compound types sharing the same nominal mass. This information was used to prepare tables giving the detailed composition of the fuel. These results clearly show the feasibility of using GC-FIMS for rapid and quantitative analysis of transportation fuels.

STUDIES ON THE NATURE OF GUM FORMED IN CRACKED NAPHTHAS

Jag M. Nagpal, Girish C. Joshi, Indra D. Singh and Krishan Kumar

Cracked naphthas from fluid catalytic cracking (FCC) operations are generally the major blending components in gasoline. Naphthas from thermal cracking operations also find their ways in gasoline pool in some refineries. Composition of these two generic classes of naphthas, their gum forming tendencies and nature of gum formed have been studied. The soluble and insoluble gum have been characterised for functional groups by infrared (i.r.) spectroscopy and the molecular weight profile, using gel permeation chromatography. The nature of the gum is correlated with the composition of the naphthas. Two FCC naphthas, two visbreaking naphthas and one coker naphtha were taken for the study. The FCC naphthas contain relatively higher levels of mono-olefins and conjugated diolefins with high branching. The thermal cracking naphthas have higher levels of α -olefins and are abundant in d -tri and cyco-olefins. The infrared spectra of gum produced under identical accelerated ageing conditions show that the hydroxyl functionalities in the gum from FCC and thermal cracking naphthas are of the same nature but hydrogen bonding in gums from thermal cracking naphthas are stronger. Carbonyl functionalities indicate formation of different types of esters in gum formed in naphthas from two different routes. Molecular weight of both the soluble and insoluble gums are distributed from 140 to around 2000 in both types of naphthas. However, the distribution shows that the insoluble gums contain higher amount of high molecular weight polymers as compared to the soluble ones.

AN EXPERT SYSTEM TO PREDICT FALL-OUTS FROM CRUDE OIL IN STORAGE

Jehuda Hartman and Joachim W. J Koenig

Crude oil in storage may exhibit fall-out phenomena. Heavy emulsion sludge, often formed by sea water, waxes and asphaltenes, appears at times. In other cases, heavy asphaltene rich gatch,

sometimes oxidized, and unorganics, often held in heavy emulsion, are noticed. These changes will usually have detrimental results, which frequently are followed by severe economic loss. A well established theory on the causes and affecting factors of crude fall-out does not exist today. However, extensive data and long time experience, has been collected and documented by several storing organizations. An expert system, called EQPS, to predict deterioration of oil products, is in operation a number of years in Europe. In the present paper we wish to apply EQPS established technology to the problems of crude storage. Our aim in this presentation, is to exhibit a framework for a crude expert system. The assessment is based on related factors, such as the source of the crude, its producing and transportation methods, storage conditions, climatic influences and time in storage. The logical structure and reasoning patterns, for products are very similar to those of crude. The presented demonstration module is not based on actual data and real collected experience. The framework however, could turn into a real system, by collecting the relevant knowledge base from storing entities, and compiling it into the suggested system.

UNITED STATES TANK EPA REGULATIONS, TANK INSPECTION METHODS, TANK REMEDICATION TECHNIQUES AND STRATEGIES

E. J. Guthrie

Changes in the United States EPA AUST regulations has prompted increased emphasis on tank integrity upgrades and inspections as well as new methods to coat and repair damaged tanks. API 653 Tank Standards has been the primary standard that is followed, although some States at present are not using it. Traditional pressure testing to detect leaking tanks and associated plumbing is only as effective as the test that day. It does not address corrosion problems that may exist. With increases in reported microbial attacks, internal inspection of steel tanks has become more important. Unfortunately, most tank testing requires physical tank entry. Recent advances in robotics have minimized the need for a man to enter the tank. This paper will address some of these advances and discuss various strategies in dealing with this complex issue as well as coating issues as opposed to tank removal and exchange.

TANK CLEANING STRATEGIES AND TECHNIQUES

Howard L. Chesneau

Recent increases in contamination levels at retail outlets in the United States have prompted the need for improved contaminant removal techniques. These have involved both diesel and gasoline. This paper will discuss several techniques employed to remove both contaminants and additive separations. The utilization of chemicals, tank design modifications and housekeeping all play an important role in fuel storage. Tank cleaning becomes necessary when contaminant levels reach a point where problems are being experienced. Contaminants usually enter the system through various means. The most prevalent of all contaminants is water. Water promotes biological growth, attracts particulate matter, and can pull various additives from the fuel.

SESSION 8: MIDDLE DISTILLATES

THE ACID CATALYSED FORMATION OF EXISTENT SOLUBLE GUMS AND PARTICULATE MATTER IN DIESEL FUELS

Ria Pardede and Barry D. Batts

In contrast to the many studies on the formation of particulate matter in petroleum fuels, relatively little attention has been paid to the role of soluble gum. This study reports a series of experiments in which the relative amounts of existent gum and particulate matter were determined as a LCGO fuel was aged. These experiments were part of a larger study on the influence of the diesel fuel acid fraction on fuel stability. As expected, the total insoluble (adherent plus filtered) and soluble gums increase with increasing temperature, time and amount of acid fraction (isolated from LCGO or ADO) added to the fuel. If the neat amount of gum (either total insolubles or solubles) is defined as that due directly to the added acid fraction, it can also be shown that the weight of neat soluble gum formed also increases with time, temperature and amount of acid dopant use as a spike. Whereas the total insoluble gums also behave in the same manner when the LCGO acid fraction is used as dopant, the addition of ADO acid fraction tends to decrease the amount of neat insolubles formed with ageing time. These findings cast doubt on the frequently made assumption that soluble gum is only a more soluble, lower molecular weight version of the more prevalent insoluble matter and is formed as part of the process leading to the formation of insoluble matter.

THE RELATIONSHIP BETWEEN CONDUCTIVITY AND LUBRICITY IN "NEW" EUROPEAN ON ROAD DIESEL FUELS

Simon C. P. Ashton, Wendy M. Thomson, Sophia Dixon

From 1st October 1996 European automotive diesel has been limited to a maximum sulfur content of 0.05% wt. The various processing techniques used to achieve this remove not only sulfur but also nitrogen, oxygen and polyaromatic compounds. It is known that these species provide the fuel with intrinsic natural lubricity, conductivity and protection against peroxide formation. Removal of these compounds from diesel has a well recognised effect on fuel lubricity. It also, however, has an impact on fuel conductivity which may have serious implications when distributing fuel particularly if switchloading with gasoline. The properties of a number of unadulterated fuels meeting the current European specification, EN590, were analysed. The relationship between conductivity and lubricity was considered as well as the effects of additives commonly used in retail fuels on these properties. It was shown that fuels with poor lubricity have poor conductivity. The majority of refinery additives have little effect on conductivity, though some do provide lubricity improvement. To ensure that the required levels of lubricity and conductivity are achieved it is necessary to use appropriate additives designed specifically to provide these properties to the fuel. Analysis of forecourt fuels showed that in most cases the requirements of adequate lubricity were addressed but this was not necessarily the case with fuel conductivity.

THE EFFECTS OF MODERATE TO SEVERE HYDRO TREATING ON DIESEL FUEL PROPERTIES AND PERFORMANCE

J. B. Green, K. Q. Stirling, D. L. Ripley, and J. Vanderveen

Hydrotreating is currently the most viable refining process for lowering sulfur and aromatic contents of diesel streams to conform with environmental regulations. Although the individual aromatic ring saturation and desulfurization reactions occurring during hydrotreating are relatively straightforward, some of the overall changes in stream composition and properties are not. A major objective of this work was to correlate properties and composition as a function of stream origin and hydro treating severity. The initial sample pool included seven straight run distillates (SR), eight light cycle oils (LCO), one coker distillate, and three finished diesel fuels. Individual streams or blends of two or three streams were hydrotreated to various levels of total aromatics nominally 10, 20, and 30 percent. Compositions of feeds and products were determined by high resolution mass spectrometry (HRMS) and other methods. Properties investigated included storage stability, lubricity, cetane number, cetane index, viscosity, boiling point distribution, flash point, and specific gravity. In general, hydrotreating improved storage stability and cetane number/index, but lowered lubricity, viscosity, boiling point, and flash point. However, in some cases, notably SR and severely hydrotreated LCO, storage stability and peroxide formation were significantly worse after hydrotreating. Negative effects of hydrotreating on storage stability and lubricity were largely attributed to removal of minor polar constituents which act as antioxidants and coatings on metal surfaces. Removal of beneficial constituents appeared to be less if raw SR/LCO/coker streams were blended and then hydrotreated, rather than hydrotreated separately and then blended.

EFFECT OF INCREASINGLY SEVERE HYDRO TREATING ON STABILITY-RELATED PROPERTIES OF NO.2 DIESEL FUEL

J. Andrew Waynick

This paper reports the effect of increasingly severe hydrotreating on the compositional and stability-related properties of four No.2 diesel fuels ranging in sulfur level from 222 ppm to 11 ppm. The effect of the most commonly used phenylene diamine antioxidant on fuel properties was also determined. Denitration was essentially complete when the fuel sulfur level had been reduced to 86 ppm. At 222 ppm sulfur (similar to current U.S. low sulfur diesel fuels), fewer multi-ring but similar total aromatics were present compared with the high sulfur feed. With further sulfur removal, total aromatics were reduced as well, due to removal of mono-ring aromatics. Storage stability was excellent for all four fuels. Hydroperoxide susceptibility appeared adequate to excellent under conditions similar to commercial transport and storage. Phenylene diamine (PDA) antioxidant appeared to be directionally detrimental to storage stability for diesel fuels with sulfur levels as low as 86 ppm. However, storage stability was still acceptable, due to the excellent stability of the non-additized diesel fuels. Tests currently used in many refinery, pipeline, and end-user specifications did not detect the adverse effect of PDA antioxidants on storage stability. Additional information concerning diesel fuel instability chemistry was also demonstrated.

DIESEL FUEL THERMAL STABILITY AT 300°F

John D. Bacha and David G. Lesnini

Thermal stability is an important attribute of diesel fuel quality because of the fuel's design function as a heat transfer fluid. A recent investigation led us to conclude that poor thermal stability, as measured by 300°F laboratory tests, was responsible for premature fuel filter plugging experienced by certain diesel fuel users. The investigation focused on three sets of fuels: random samples of fuels from major suppliers of a particular California fungible fuel terminal, hand-blends of these, and "naturally-blended" terminal tank samples. The results demonstrate that mingling fuels with reasonably good thermal stability can yield blends with poor thermal stability. The degradation of thermal stability on blending is attributed to interactions between insolubles precursors in the fuel and added 2-ethylhexyl nitrate diesel ignition improver.

THERMO-CHEMICAL AND THERMO-OXIDATIVE STABILITY OF DIESEL FUELS CONTAINING COMPONENTS OF LIGHT CATALYTIC GAS OIL

Zh. D. Kalitchin, Slavi. K Ivanov, Margarita I.Boneva, Atanas Ivanov, Konstantin Kanariev, Petko T.Georgiev, Setrak K.Tanielyan

The influence of Light Catalytic Gas Oil on the tendency to total insolubles formation of conventional Diesel Fuels with higher sulfur content (up to 0.2 %) is investigated. They are of special interest for a long term storage and exploitation for military purposes. The experiments are carried out under different conditions: diffusion, diffusion-kinetic and kinetic. Special attention is paid to the suppressing of total insolubles formation by commercial stability additives. It is shown that metal surfaces substantially affect the fuel stability. The addition of Light Catalytic Gas Oil deteriorates the tendency to total insolubles formation of Diesel Fuels. Several criteria are selected for prognostication of the storage terms of Diesel Fuels on the basis of the existing standards in Russia and U.S.A.

STUDIES ON GUM FORMATION TENDENCIES OF MIDDLE DISTILLATE DIESEL FUELS

Yogendra K. Sharma, Indra D. Singh, Kalika P. Bhatt & Krishna M. Agrawal

The rapid growth in transportation fuel demand is compelling greater use of severe processing like catalytic cracking, visbreaking, coking etc, which results increased contents of olefines & aromatics and consequently less stable processed fuels. Total gum formation in coker kerosene (191- 454°C), straight run gas oil (156-477°C) available from an Indian refinery and their blends were determined using UOP-413 method and correlated with their composition. Effect of hydrocarbon type composition, bromine no. sulphur and nitrogen content, maleic anhydride and diene value and also of boiling range on formation of sediment and adherent gum in these blends was investigated. Composition has been observed to play an important role in the degradation of these distillate fuels.

A BIT OF HISTORY - THE DEVELOPMENT OF STORAGE STABILITY TESTS FOR MIDDLE DISTILLATE FUELS SINCE WORLD WAR II

Edmund W. White

After World War II, refiners in need of a viable outlet for by-product middle distillate stocks from cracking operations found that such stocks could be blended to a limited degree into burner fuels, distillate diesel fuels, and similar products. However, when long term storage was required, the buyer had to be certain the fuel would be usable at the end of the storage period. This led to extensive studies of the stability of such fuels and to the development of accelerated stability tests which ultimately evolved into AS1M, IP, ISO and other standard test methods. This paper summarizes those developments and examines their limitations. This encompasses work by the U. S. Bureau of Mines and by the U. S. Navy in the 1950's, and the standardization of AS1M Test Methods 02274 (the 95°C/16 hour test), 04625 (the 43°C test), and 05304 (the oxygen overpressure method).

STABILITY OF DIESEL FUELS WITH IMPROVED LOW TEMPERATURE CHARACTERISTICS.

Sl.K. Ivanov, Zh. D. Kalitchin, A. Ivanov, K. Kanariev, M. I. Boneva, P. T. Georgiev, and S. K. Tanielyan,

Diesel fuels with low sulfur content (below 0.05 %) belonging to the so called "green fuels", are preferred for exploitation in the big cities, but the interest towards the conventional fuels with higher sulfur content (up to 0.1 - 0.2 %) has not ceased. These types of fuels are characterised by increased storage terms and are used for military purposes. Studying the processes of total insolubles formation in Diesel Fuels, with higher content of sulfur compounds, it is possible to throw light on the mechanism of their formation in an inert atmosphere as well as in the presence of oxygen. In the present paper the total insolubles formed after tests of accelerated oxidation, are studied with the help of gel-permeation chromatography, NMR, IR and other physical methods. The tests are performed in different conditions: diffusion, diffusion-kinetic and kinetic and the effect of metal surfaces is investigated. The obtained data make it possible to evaluate the ways for improvement of the low temperature characteristics of motor diesel fuels for military purposes.

IMPROVEMENT IN DIESEL FUEL QUALITY THROUGH ADDITIVES

S.Nandi, V.K. Sharma, R. Manoharan, P. Bhatnagar, B.R. Tyagi, S.P. Srivastava and A.K. Bhatnagar

Out of a number of quality requirements for high speed diesel (HSD), stability characteristics is considered to be an important criterion for HSD blended with cracked streams. Stability behaviour of an Indian HSD and its blends with a cracked stream (Visbreaker gas oil-VB GO) as such and in presence of three stabilizing additives has been studied with a view to maximize the HSD production. Test methods UOP-413 (16Hrs.) and three months storage IP-378 (modified) have been followed. It has been found that blending of VBGO to HSD adversely affect the stability. However, by using a suitable stabilizing additive, VBGO in concentration range of 2-4% can be accommodated in HSD pool and finished blend meet the Indian HSD specification IS: 1460-1995. Attempt has also been made to examine the relationship between UOP-413 and IP-

378 (modified) test data and between 45 days and 90 days data of IP-378 (modified) test by linear regression analysis technique. The correlation coefficient in the range of 0.96-0.98 has been found, showing very high degree of reliability in predicting the total sediment value of IP-378 (modified) test either from UOP-413 or 45 days test data of IP-378 (modified) test. Considering the better acceptability of IP-378 test limit, more stringent pass limit of 0.8 mg/100 ml of HSD has been proposed for UOP-413, as against the specified limit of 1.6 mg/100 ml of HSD.

SESSION 9: MICROBIOLOGY

MICROBIAL DETERIORATION OF HYDROCARBONS

Klaus Bosecker

A wide range of bacteria, yeasts and filamentous fungi utilise hydrocarbons as their sole energy and carbon source. Microbial degradation of hydrocarbons has economic implications when spoilage of crude oil and petroleum products occurs, e.g. fuels, hydraulic oils, lubricating oils and machine tool coolants. As a consequence of microbial activity an oil product changes chemically and functionally and some components may disappear entirely. Metabolic products may cause severe corrosion or may be used as substrates by other microorganisms, e.g. sulphate-reducing bacteria whose products can in turn also cause damage. The biomass can clog pores and pipes. As spoilage can occur only in the presence of free water, good housekeeping is a prerequisite for preventing microbial degradation of hydrocarbons. The growth of anaerobic bacteria (e.g. sulphate-reducing bacteria) can be inhibited by introducing oxygen into the system. Coatings can be used to protect metals from corrosion.

ABILITY OF FUEL AND WATER SOLUBLE BIOCIDES TO PREVENT MICROBIAL SUCCESSION CHANGES TO OXYGENATED GASOLINE AND SYNTHETIC TANK WATER BOTTOM CHEMISTRY IN LABORATORY MICROCOSMS

Frederick J. Passman, Beverly L. McFarland, and Martin J. Hillyer

Biodeterioration has a cost impact that is only beginning to be recognized and quantified. The ability of two biocides to prevent microbial succession changes to oxygenated gasoline was followed for seven-months in replicated microcosms. Three concentrations of each biocide were evaluated representing the maximum allowable dose, the manufacturer's recommended dose, and the lowest effect dose. Fuel and water phase samples were taken at day 0, 0.25, 1, 3 and 7 months and analyzed for gasoline hydrocarbons and pH, TDS, alkalinity, dissolved oxygen, nitrite and nitrate nitrogen, respectively. Gasoline and aqueous phases were characterized with respect to total heterotrophs, total aerobes, total anaerobes, acid producing and sulfate reducing bacteria, and catalase activity. Both biocides initially provided protection against changes in gasoline quality and minimization of rag layer development. However, by one month, we observed significant performance differences between the two products. Sulfate reducing bacteria were the most difficult to control of the microbial groups investigated. Threshold concentrations of microorganisms that correlate with negative fuel impacts will be discussed as well as the impacts of biocides on corrosion rate and fuel filterability.

A NEW ON-SITE QUANTITATIVE TEST FOR MICROORGANISMS IN FUEL

E. C. Hill, G. C. Hill and D. Collins

Traditional viable count technology for determining microbial numbers in aqueous samples, involves incubation and assesses microbial numbers as colony forming units (cfu), i.e. visible nodules of microbial growth. Methods fall into two categories, 'shake' plates in which samples are dispersed in nutritive molten agar which is solidified by cooling and then incubated or by spreading samples onto solid nutritive agar plates. Neither method is suitable for non-aqueous samples. Microbes are recovered from these by membrane filtration and the membrane is then placed on top of a nutritive agar plate. Alternatively the sample is emulsified in water before a conventional viable count procedure. The increasing demand for reliable viable counts on fuel samples has led to a membrane filtration procedure, IP385/95, and to an emulsification procedure AFNOR M07070/92. The former is unsuitable for on site use and although the latter can be coupled to a Dip-slide test it inherits the errors of this procedure and lacks sensitivity. The methodology described in this paper was a direct response to the need for a sensitive, quantitative on-site microbiological test for fuel but the technology can be applied to any aqueous and nonaqueous sample. It allows the "shake" plate concept to be used in the laboratory or on-site. In principle a nutritive solution is gelled with thixotropic and/or pseudo-plastic agents instead of agar. An aqueous or non-aqueous sample can be dispersed in the gel by shaking and the gel is allowed to re-set as a flat horizontal layer. During incubation microbes develop into visible colonies comparable to colony formation in 'shake' plates. In the preferred configuration for fuel testing c.16ml of gel is dispensed into screw capped rectangular glass containers c. 65ml capacity. The size of the sample is selected according to the sensitivity required but the volume of gel must be kept in proportion; 0.25ml of fuel is normally tested. During incubation a sensitive redox indicator is reduced to a coloured formazan within the microbial colonies and assists enumeration. The accuracy is similar to a shake plate. Very large numbers of microbes produce coloured formazan within a few hours - a real time test. The gel composition described has been formulated so that fuel samples emulsify and completely disperse but it is also suitable for aqueous samples. The formulation has been used to test diesel fuel and aviation kerosene; the results are comparable to the methods IP385/95 and AFNOR M07070/92.

SESSION 10: ALTERNATIVE FUELS

STABILITY AND HANDLING OF SASOL SEMI-SYNTHETIC JET FUEL

Piet Roets, J.I. (Johan) Botha, Clifford A. Moses and-Leo L. Stavinoha

Jet fuel made from shale and coal by various methods employing hydrogen treatment and polymerization (as used in the Sasol Fischer-Tropsch gas/syncrude process) usually results in hydrocarbon fuel with very high thermal stability and negligible levels of sulphur and aromatics. Early work during the 1980's on both shale- and coal- derived jet fuel identified two drawbacks to the potential commercial use of these fuels. These were the fuel's poor lubricity properties and the shrinkage of seals previously wetted by crude oil-derived fuels. Additional concerns expressed at the time were the fuel's additive response and its capacitance, or dielectric constant, when used in density correlations. In order to produce a more acceptable fuel for use in commercial aircraft operating out of Johannesburg International Airport, Sasol will blend a synthetic jet fuel component with crude oil-derived jet fuel to increase the blend's aromatic

content. This will improve both the elastomer compatibility and the lubricity of the fuel. These and other properties of the synthetic jet fuel component and the semi-synthetic jet fuel blend are discussed in this paper. Other properties studied included the fuel's gum and peroxide formation tendencies which were evaluated for both the neat and additised fuel using accelerated stability tests to confirm antioxidant additive response in the fuel. The compatibility of elastomeric materials used in fuel handling equipment, such as the hoses on ground equipment and pump seals in aircraft components, with the semi-synthetic jet fuel was also confirmed. Finally biocide additive efficacy in the synthetic fuels was determined. It was found that the Sasol synthetic jet fuel is an excellent blending component to blend Sasol semi-synthetic Jet A-I.

EVALUATION OF THE STABILITY, LUBRICITY, AND COLD FLOW PROPERTIES OF BIODIESEL FUEL

J. Andrew Waynick

The stability, lubricity, and cold flow properties of fuels containing a commercially available methyl soyate biodiesel fuel were evaluated. The stability of the neat biodiesel fuel was significantly inferior to that of a typical, additive-free L8 No.2 diesel fuel. In fuel blends containing varying concentrations of biodiesel, total insolubles formed during ASTM D4625 and ASTM D2274 were greater for blends of intermediate compositions than for either LS F02 or neat biodiesel. The instability of biodiesel appeared to be primarily due to a peroxidation mechanism similar to that known to occur in fats and oils. Conventional distillate stability additives did not effectively control instability in fuel blends containing biodiesel. A hindered phenol antioxidant was the most effective additive for controlling instability. A phenylene diamine antioxidant was not effective in controlling insolubles formation in fuel blends containing biodiesel, even though other tests indicated that the additive was controlling the peroxidation. The presence of steel significantly decreased the stability of fuels containing biodiesel, and commonly used corrosion inhibitors and metal deactivators made the situation much worse. Biodiesel imparts excellent lubricity to fuel blends that contain as little as 2% of it. Although cold flow properties of biodiesel were inferior to that of a conventional, additive-free L8 No.2 diesel fuel, a typical cold flow improver additive was able to improve CFPP in a fuel blend containing 20% biodiesel. Although higher cold flow improver additive concentrations were required in the 20% biodiesel blend, maximum additive effectiveness in the 20% biodiesel blend was superior to that achieved in the LS F02. Some information on stability test method reliability is also given.

OXIDATION STABILITY OF FATTY ACID METHYL ESTERS USED AS DIESEL FUEL SUBSTITUTE

P. Hodl, M. T. Rodo-Cima, H. Schindlbauer, N. Simkovsky and W. Tuechler

The oxidation stability of fatty acid methyl esters (FAME) used as diesel fuel substitute is an important feature, which describes the storage possibilities. Due to their very different chemical structure and resulting higher reactivity as compared to petroleum middle distillates FAME are more subjected to oxidation processes as well as auto oxidation. The unsaturated components of the biogenic fuel are mainly responsible for this higher reactivity. The oxidation process leads to undesirable properties, like higher viscosity due to polymerisation or enhanced corrosive effects, caused by short chained free acids. Within this work a few general test methods for the

determination of the oxidation stability should be highlighted as well as two very specific ones. These two methods, a modified IP- 306 method and the Baader Test", of which the IP-306 should be included within the European Standard Specification for FAME used as Diesel Fuel Substitute, will be correlated and compared. The FAME used in these investigations were of different age and origin, and we will show, that, besides other properties of the oil, the production process of the FAME has an important influence on the oxidation stability.

SESSION 11: GENERAL II

STORAGE STABILITY OF REFORMULATED GASOLINES (RFG)

Leo L. Stavinoha, Mario E. LePera, Regina L. Gray, Lindsey H. Hicks, and Linda Turner

The Defence Fuel Supply Center (DFSC) is procuring reformulated gasoline (RFG) for storage aboard Military Prepositioned Ships (MPS). For DFSC's procurement of RFG, a time period extending to four years after time of acceptance is anticipated, with an average storage temperature assumption of approximately 20°C. The oxidation stability of the RFG using the standard induction period method (ASTM D 525) has been specified at a minimum of 480 minutes. Additionally, use of oxidation inhibitors over the range of 5 to 15 pounds per 1,000 barrels (Pfb) of gasoline, and an approved metal deactivator at 1 to 3 PTB of gasoline are being required. An approved corrosion inhibitor may be added but is not required. While these additives have been previously developed and used over the past many years for conventional gasoline, their effectiveness in RFG has not been established. DFSC-supplied RFG and TFLRF(SwRI) formulated RFG blends (containing either MTBE, TAME, or ETBE) using a moderately stable gasoline blending stock, made unstable by the addition of dimethylhexadiene (DMHD) were evaluated for stability characteristics using test methods ASTM D 525 (Induction Test Method) and ASTM D 873 (Accelerated Gum Test Method) and the following additives: antioxidants (a phenylenediamine, a hindered phenol, and a SO/50 blend); metal deactivator; corrosion inhibitor; deposit control additive. This data supports the suggestion that these additives were not antagonistically affected by the presence of any of the three ethers and formed a basis for recommending additive treatment rates. Based on previous Army evaluations, the washed gum limit was set at 5 mg/100mL as a maximum storage stability procurement guide for the D 873 8-hr test. In general, as a fuel ages, it develops higher intake valve deposit (IVD) capabilities which are measured indirectly by ASTM D 381 washed gum values and FTM 791 C, Method 500.1 ISD appearance and mass values. When DFSC deposit control additive was added to base fuels in this program, they gave relatively low D 381 washed gum and were somewhat ineffective at 80 PTB for fuels which were probably dirtier than the reference fuel used to obtain the initial EPA qualification for this additive. In practice, the deposit control additive treat rate should be determined by D 381 testing for washed gum and ISD testing (both visual and mass of deposit) with neat and deposit control additive treated fuel.

SUMMARY FINDINGS OF THE PROPERTY/COMPOSITIONAL RESULTS OF A WORLDWIDE COMMERCIAL MARINE DISTILLATE FUEL SURVEY

Robert M. Giannini, Regina Gray, Lindsey Hicks, Neil Lynn, and Richard Struck

The Defense Fuel Supply Center, U.S. Navy and U.S. Army jointly managed the conduct of a survey of commercial distillate marine fuels and ground vehicle distillate fuels from forty-one locations around the world, including the continental United States. The type of samples sought were diesel fuels, 100-percent distillate (containing no residual) that are available in the commercial marketplace. Fuel sample collection was initiated in June 1996, and completed in October 1996. Over 2700 analytical results were obtained from the survey. This paper summarizes the extensive analytical data obtained including an interpretation of the results.

SURVEY OF DIESEL FUELS AND AVIATION KEROSENES FROM U. S. MILITARY INSTALLATIONS

Steven R. Westbrook and Maurice E. LePera

In support of the Department of Defense goal to streamline procurements, the Army recently decided to discontinue use of VV-F-800D as the purchase specification for diesel fuel being supplied to continental United States military installations. The Army will instead issue a commercial item description for direct fuel deliveries under the Post/Camp/Station (PCS) contract bulletin program. In parallel, the Defense Fuel Supply Center and the U.S. Army Mobility Technology Center-Belvoir (at Ft. Belvoir, VA) initiated a fuel survey with the primary objective to assess the general quality and lubricity characteristics of low sulfur diesel fuels being supplied to military installations under the PCS system. Under this project, diesel fuel delivery samples were obtained from selected military installations and analyzed according to a predetermined protocol. The results obtained from various tests show that the average, low-sulfur diesel fuel meets military requirements for DF-2 with the exception of lubricity performance. Proposed fuel lubricity requirements for military, ground vehicle, diesel fuels are presented.

RECENT DEVELOPMENTS IN THE PRODUCTION OF STABLE FUEL OIL FROM H-OIL PROCESS BOTTOMS

James J. Colyar, Refa O. Koseoglu, and Alain Quignard

The H-Oil Process, a commercial ebullated-bed process licensed by HRI, Inc a subsidiary of IFP Enterprises, is used to convert and upgrade heavy petroleum residue. In the H-Oil Process, typically 50 to 75 percent of the vacuum residue in the feedstock is converted to distillates. The remaining, unconverted atmospheric or vacuum residue can be utilized in traditional bottoms outlets such as coker feed, resid FCCU feed, feed to a hydrogen generation unit or fluxed with distillates and sold as a No.6 fuel oil. Many new H-Oil Licensees, with existing markets for fuel oil, have designated that the unconverted bottoms be used to produce a heavy fuel oil product. The use of heavier, more sour crudes, coupled with more stringent specifications for saleable fuel oil has made the production of stable, high quality fuel oil a difficult challenge. With six operating or planned commercial H-Oil Plants producing heavy fuel oil from the unconverted bottoms, HRI/IFP has taken the lead and initiated a high level of research and development in the area of fuel oil blending. The results of this R&D are discussed in this paper and have greatly

increased the understanding of and subsequent utility of the blended fuel oil product from the H-Oil Process.

THE ELIMINATION OF COLOR IN KEROSENE FRACTION DERIVED FROM DURI AND MINAS CRUDE OIL MIXTURE BY EXPOSURE TO LIGHT

Adiwar, Maizar Rahmani and Humala P. Sihombini

Kerosene derived from a mixture of Duri and Minas crude oils 70:30 changes color during storage. The color develops rapidly, few hours after distillation. Ageing of distillates obtained by a narrow cut TBP distillation of the crude mixture in the range of kerosene showed that the color precursors in the kerosene were distributed in all the distillates. Sun light treatment on the colored kerosene showed that the treatment can eliminate or reduce the color considerably. Sun light treatment on the fresh kerosene developed color at the beginning, but then after reaching peak the color began to disappear. Light treatment using an incandescent lamp showed similar results, but the effect occurred more slowly. It seems that the colorless color precursors in the fresh kerosene distillate changes into colored compounds during the storage which is then converted into colorless compounds after being exposed to light. Apart from the change or the elimination of the color, the data of the kerosene characteristics showed that most of the properties of the untreated and treated kerosene were very similar.

DEVELOPMENT OF FIELD ANALYTICAL PROCEDURES FOR BETZ DEARBORN SPEC.AIDTM 8Q462, A JET FUEL THERMAL STABILITY ADDITIVE

W. L. Parker and Nancy R. Calvert

The United States Air Force proposes to change the specification for jet fuels to include a thermal stability additive. This change in specification requires a method for rapid determination of the presence of the additives. Field usable analytical procedures to determine the presence of the additive above a threshold concentration and others capable of providing semi-quantitative determination of the concentration of Betz Dearborn's SPEC-AID TM 8Q462 have been developed and will be discussed.

SESSION 12: POSTER PRESENTATIONS

A COMPARISON OF JET FUEL THERMAL OXIDATION TEST VISUAL TUBE RATINGS WITH DEPOSIT MEASUREMENT BY ELLIPSOMETRY

Kevin A. Bower, Peter S. Brook and Jonathan O. Whitby

A new analytical technique for measuring deposit thickness and/or volume on JFTOT tubes, called Ellipsometric Tube Analysis, has been developed. A study of over 500 samples, produced by testing operational fuels from a range of sources world-wide, has identified the representative deposit volume and thickness conditions corresponding to VTRs 0-73. The results suggest that ellipsometry has the potential to be used in the jet fuel specification for rating JFTOT tubes. Detailed analysis shows that abnormal deposits are no thicker than normal ones of a similar visual rating and the work calls into question the need for aviation turbine fuels producing abnormal JFTOT tube ratings to be automatic specification failures. This type of evaluation now allows JFTOT break points to be correlated with a quantitative measurement of deposition.

DEVELOPMENT OF AN ELLIPSOMETRIC JFTOT TUBE ANALYSER (ETA)

Peter David, Robin Mogford, Peter Paduschek, Spencer E Taylor, Andy J Woodward

Problems associated with the current visual rating of JFTOT tube deposits used for specification purposes are well known. The method suffers from operator subjectivity, the main cause of differences in visual rating of tubes between laboratories. The visual rating method also provides no information on the thickness and volume of deposit which are far more meaningful for characterising fuels, especially for aircraft and engine manufacturers. Ellipsometry was identified in the BP Oil laboratories as a suitable technique for measuring accurately the thickness/volume of JFTOT tube deposits (as described at the 5th International Conference on the Stability and Handling of Liquid Fuels). A dedicated ellipsometric JFTOT tube analyser (ETA) has now been developed through collaborations between BP, the UK MOD and the Munich-based company Plasmos GmbH, who built the instrument. The strengths of ETA lie in the ease of the measurement, and the fact that absolute measurements are produced, without the need for calibration. Three-dimensional deposit profiles along and around the whole length of the JFTOT tube test section can be generated giving information on deposit thickness and total deposit volume. ETA thus provides the capability to provide a more meaningful interpretation of deposit assessment for research and quality assurance purposes.

THE AUTOXIDATION OF PHENALENE

Jia Ping Guo and Bruce Beaver

It is generally agreed that the "Pedley mechanism" (J. F. Pedley, R. W. Hiley, and R. A. Hancock, *Fuel*, 68: 27, 1989) is an excellent hypothesis which can partially rationalize the oxidative degradation of many diesel fuels. The first step of the Pedley mechanism involves the autoxidation of phenalene to form phenalenone. In this paper we will report our mechanistic investigation into the details of this process and comment on the importance of our results with respect to understanding the oxidative degradation of middle distillates in general.

FOLLOW-UP STUDY OF AN OCCUPATIONAL HEALTH PROBLEM WHEN HANDLING JET FUEL AFTER INITIATE ACTIONS

Hans Kling, Per-Ake Skoog

In connection with the Swedish Air Force fuel change in 1991-1992 from Rb77 (JP-4) to Ff75 (JP-8), occupational health problems in the form of unpleasant odour, fatigue, headaches, irritated, blocked or stuffed nose and skin irritations increased. A previous study revealed that there was a connection between these health problems and certain sulfur-organic compounds in the jet fuel. Measures have now been taken to reduce such compounds. The occupational health problems have now been studied and the results show a significant decrease concerning such problems though a high frequency of occupational health problems still remains, among them fatigue, irritated, blocked or stuffed nose and skin irritation. Preliminary international reports draw attention to liver changes in connection with the handling of jet fuel, resulting in uneasiness among personnel who handle such daily over a long period of time. Exposed and unexposed groups from our previous study have now undergone blood tests to ascertain possible liver

changes. Preliminary results show liver changes in the exposed group. Measured exposure to Ff75 indicates low levels, considerably under the occupational exposure limit.

MICROBIAL SUCCESSION AND ITS IMPACT ON OXYGENATED GASOLINE IN LABORATORY MICROCOSMS

Beverly L. McFarland, Frederick J. Passman, and Martin J. Hillyer

Fuel biodeterioration costs are not well quantified. Incidents of serious biodeterioration are generally considered to be rare. Based on numerous field observations the authors had reason to believe that the actual incidences of gasoline and gasoline-system biodeterioration exceeds the recognized and reported incident rates substantially. The first step in improved biodeterioration diagnostics is a clear definition of the commercial impact of uncontrolled microbial contamination in gasoline over water. In this presentation, the authors describe a series of microcosm studies designed to evaluate the impact of a contaminant microbial community on fuel and bottom-water properties in replicate microcosms. Triplicate challenged and unchallenged microcosms were run, using oxygenated, regular unleaded gasoline over water supplemented with a commercial sea-salt preparation (3 ppt). Microbial activity in the challenged microcosms mediated a number of significant gross, physical and chemical fuel and bottom-water property changes relative to unchallenged microcosms. Most noteworthy was the average 67-% loss of oxygenates and the marked shift from isoparaffin and normal paraffin hydrocarbons to and alkyl isoparaffins. Moreover, mild-steel corrosion rates, and filter plugging occurred at least twice as fast, in challenged microcosms were four to five times greater than rates in unchallenged microcosms.

KIT FOR DETERMINATION OF HYDROGEN SULFIDE IN LIQUIDS

Rex A. Neihof and Harty N. Giles

A recently patented test kit has been successfully used for the determination of hydrogen sulfide concentrations in a variety of oils or aqueous liquids. The kit consists of a sample bottle provided with a screw cap carrying a colorimetric hydrogen sulfide indicator. The indicator is protected from contact with the liquid sample by a vapor-permeable silicone membrane. After a few minutes shaking of the sample in a closed bottle, the hydrogen sulfide content is estimated by comparison of the indicator color with a set of standard colors. The method is remarkably free of interferences from other constituents in the liquid sample. Examples of the use of this method for analysis of hydrogen sulfide in crude petroleum and aqueous solutions of surfactants are presented.

LIQUID-PHASE OXIDATION KINETICS FOR A PARAFFIN BLEND

James M. Pickard and E. Grant Jones

Kinetics of O₂ depletion in an air-saturated (74.7 ppm O₂) paraffin blend (Exxsol D-80) were conducted with a Near-Isothermal Flowing Test Rig (NIFTR) using passivated heat-exchanger tubing over the range 408 - 438 K. Hydroperoxide formation was monitored by cyclic voltammetry. Autoxidation data are consistent with an initiation mechanism involving hydroperoxide dissociation; the kinetic data are independent of the initial O₂ concentration. Data analysis yielded the following rate parameters: $\log(k_j/s^{-1}) = (15.2 \pm 1.6) - (33.1 \pm 3.1)/e$,

$\log[k_j v / (k_j / 2k_v)]^{1/2} M^{-1/2} s^{-1/2} = (9.5 \pm 0.2) - (26.3 \pm 0.4)/e$, and $\log[(k_j v / 2k_v)]^{1/2} M^{-1/2} s^{-1/2} = (3.3 \pm 1.3) - (12.5 \pm 2.6)/e$ (where k_j , $k_j v$, and k_v are rate constants for initiation, propagation, and termination, respectively, $e = 2.303RT$ kcal mol⁻¹, R is the ideal-gas-law constant, and T is absolute temperature). Results are discussed with reference to kinetic parameters reported for conventional aviation fuels and normal paraffins.

EXPERIENCE IN USE OF AUTOMATIC HEAVY FUEL OIL STABILITY ANALYZER

Olli Pilvio, Lars-Ake Larsson, Juha Vilhunen

Stability-or long-term storage life is an important factor demanding of heavy fuel oils refined in the thermal cracking/visbreaking production units. The stability figure for heavy fuel oils indicates the precipitation tendency of asphaltene molecules in the oil. The stability figure is usually determined by the manual precipitation spot test method using visual detection. However, this manual method is tedious and takes up to an hour to perform: An automatic stability analyzer performs the same stability procedure as the manual method only in few minutes. In this study we compared nearly one hundred stability figures of visbreaker products determined both manually and automatically. The results obtained by the analyzer correlated well with the those by the manual method.

TESTS TO EVALUATE AND PREDICT DIESEL AND GASOLINE ENGINE FUEL SYSTEM DEPOSITS

Leo L. Stavinoha and Paul I. Lacey

Diesel and gasoline fuels have varying degrees of depositing potential in engines. Some additives have the ability to reduce deposit potential to acceptable levels. The current fuel deposit related engine and laboratory test techniques are briefly reviewed in this paper. Data developed with deposit enhancing additives to demonstrate deposit control is also presented. Approaches for relative ranking of additive deposit controlling properties of gasolines are demonstrated.

THE MEASUREMENT OF ANTIOXIDANT PERFORMANCE IN AVIATION TURBINE FUEL USING THE QUARTZ CRYSTAL MICROBALANCE AND NEAR ISOTHERMAL FLOWING TEST RIG

Steven Zabarnick, E. Grant Jones and Steven Anderson

Antioxidants are widely used in aviation turbine fuel to inhibit hydrocarbon oxidation during transport and storage. However, the approved antioxidant formulations vary among the major turbine fuel specifications. In an attempt to rationalize the antioxidant formulations and establish a common list based on efficacy, the performance of currently approved antioxidants was measured using the Quartz Crystal Microbalance (QCM) and the Near Isothermal Flowing Test Rig (NIFTR). The QCM is a static system that employs a polarographic oxygen probe to measure the depletion of headspace oxygen in real time. The NIFTR employs a gas chromatographic technique to measure the dissolved oxygen concentration in the fuel as it passes through a heated tube. The ability of an antioxidant to delay oxygen consumption is a measure of performance. Results for the various hindered phenolic and amine antioxidants will be presented.