

**5TH INTERNATIONAL CONFERENCE ON STABILITY
AND HANDLING OF LIQUID FUELS
Rotterdam, The Netherlands
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Abstract Summaries

SESSION 1: JET FUELS

COMMERCIAL JET FUEL QUALITY CONTROL

Kurt H. Strauss

The paper discusses the purpose of jet fuel quality control between the refinery and the aircraft. It describes fixed equipment, including various types of filters, and the usefulness and limitations of this equipment. Test equipment is reviewed as are various surveillance procedures. These include the Air Transport Association specification ATA 103, the FAA Advisory Circular 150/5230-4, the International Air Transport Association Guidance Material for Fuel Quality Control and Fueling Service and the Guidelines for Quality Control at Jointly Operated Fuel Systems. Some past and current quality control problems are briefly mentioned.

THE TRANSITION OF NEW TECHNOLOGY TO SOLVE TODAY'S PROBLEMS

Richard A. Kamin, Calvin J Martin, and Lynda M. Turner

Extensive research has been conducted in the development of methods to predict the degradation of F-44 in storage. The Low-Pressure Reactor (LPR) has greatly enhanced the stability prediction capabilities necessary to make informed decisions concerning aviation fuel in storage. This technique has in the past been primarily used for research purposes. The Naval Air Warfare Center, Aircraft Division, Trenton, NJ, has used this technique successfully to assist the Defense Fuel Supply Center, Cameron Station, Alexandria, VA, in stability assessments of F-44. The High-Performance Liquid Chromatography/Electrochemical Detector (HPLC/EC) antioxidant determination technique has also aided in making stability predictions by establishing the amount of inhibitor currently in the product. This paper will address two case studies in which the above new technology was used to insure the rapid detection and diagnosis of today's field and logistic problems.

ANALYTIC TESTS AND THEIR RELATION TO JET FUEL THERMAL STABILITY

Shawn P. Heneghan and Robert E. Kauffman

The evaluation of jet fuel thermal stability (TS) by simple analytic procedures has long been a goal of fuels chemists. The reason is obvious: if the analytic chemist can determine which types of material cause his test to respond, the refiners will know which materials to remove to improve stability. Complicating this quest is the lack of an acceptable quantitative TS test with

which to compare any analytic procedures. To circumvent this problem, we recently compiled the results of TS tests for 12 fuels using six separate test procedures. The results covering a range of flow and temperature conditions show that TS is not as dependent on test conditions as previously thought. Also, comparing the results from these tests with several analytic procedures shows that either a measure of the number of phenols or the total polar sulfur present in jet fuels is strongly indicative of the TS. The phenols have been measured using a cyclic voltammetry technique and the polar material by gas chromatography (atomic emission detection) following a solid phase extraction on silica gel. The polar material has been identified as mainly phenols (by mass spectrometry identification). Measures of the total acid number or peroxide concentration have little correlation with TS.

BEHAVIOUR OF CONDUCTIVITY IMPROVERS IN JET FUEL

Brian Dacre and Janice I. Hetherington

Dangerous accumulation of electrostatic charge can occur due to high-speed pumping and microfiltration of fuel. This can be avoided by increasing the electrical conductivity of the fuel using conductivity improver additives. However, marked variations occur in the conductivity response of different fuels when doped to the same level with conductivity improver. This has been attributed to interactions of the conductivity improver with other fuel additives or fuel contaminants. The present work concentrates on the effects of fuel contaminants, in particular polar compounds, on the performance of the conductivity improver. Conductivity is the fuel property of prime interest. The conductivity response of model systems of the conductivity improver STADIS 450 in dodecane has been measured and the effect on this conductivity of additions of model polar contaminants sodium naphthenate, sodium dodecyl benzene sulphonate, and sodium phenate have been measured. The sodium salts have been found to have a complex effect on the performance of STADIS 450, reducing the conductivity at low concentrations to a minimum value and then increasing the conductivity at high concentrations of sodium salts. This work has focused on characterising this minimum in the conductivity values and on understanding the reason for its occurrence. The effects on the minimum conductivity value of the following parameters are investigated: (a) time, (b) STADIS 450 concentration, (c) sodium salt concentration, (d) mixed sodium salts, (e) experimental method, (f) a phenol, (g) individual components of STADIS 450. The complex conductivity response of the STADIS 450 to sodium salt impurities is discussed in terms of possible inter-molecular interactions.

STADIS® 450 IN MEROX-SWEETENED JET FUELS

C. P. Henry

Stadis® 450 has been used in aviation fuels since 1983, and in many cases is the additive of choice due to conductivity retention of treated fuels during distribution, and other characteristics. In the past several years, manufacture of Shell ASA-3 (the other aviation-approved static dissipator additive) has been discontinued; current stores are being drawn down and for some refiners conversion from ASA-3 to Stadis® 450 is underway. In fuels sweetened by hydrogen-treating, Stadis® 450 performs very well and there are few reported difficulties. Chemically sweetened fuels sometimes contain trace materials not removed by the sweetening process.

When treated with Stadis® 450 some of these fuels have exhibited two behaviors which are being addressed: in one case, the formation of a precipitate which disarmed coalescers; in several other cases, reduced conductivity response and loss of conductivity during storage coupled with unusually large effects on the microseparator water separation properties. In late 1992, a Coordinating Research Council (CRC) Panel on Coalescer Deactivation was formed to address these problems. The results of DuPont and CRC efforts are discussed, along with actions taken and underway to eliminate these problems.

FACTORS AFFECTING THE SILVER CORROSION PERFORMANCE OF JET FUEL FROM THE MEROX PROCESS

Carl L. Viljoen, Sibbele Hietkamp, Boshoff Marais and Johannes J Venter

The Natref refinery at Sasolburg, South Africa, which is 63,6% owned by Sasol and 36,5% by Total, is producing Jet A-I fuel at a rate of 80 m³ by means of a UOP Merox process. A substantial pan of the crude oil slate is made up from crudes which have been stored for considerable times in underground mines. Since the 1970's, Natref has experienced sporadic non-conformance of its treated jet fuel to the silver corrosion (IP 227) test. Various causes and explanations for the sporadic silver corrosion occurrence have been put forward but a direct causal link has remained obscure. The paper addresses these possible causes for silver corrosion and some of the process changes which have been made to alleviate the problem. Emphasis is placed on the most recent approaches which were taken to identify the origin of the sporadic silver corrosion. An inventory of all the potential causes was made, such as bacterial action, elemental sulphur formation in storage, etc. and experiments designed to test the validity of these causes, are discussed. A statistical evaluation which was done of the historical process data over a 2-year period, failed to link the use of mine crudes directly to Ag-corrosion occurrence. However, a correlation between elemental sulphur and H₂ levels in the feed to the Merox reactor and Ag-corrosion was observed. Finally, the outcome of the experiments are discussed, as well as the conclusions which were reached from the observed results.

AUTOXIDATION OF JET FUELS; IMPLICATIONS FOR MODELING AND THERMAL STABILITY

Shawn P. Heneghan and Long P. Chin

The study and modeling of jet fuel thermal deposition is dependent on an understanding of and ability to model the oxidation chemistry. Global modeling of jet fuel oxidation is complicated by several facts. First, liquid jet fuels are hard to heat rapidly and fuels may begin to oxidize during the heat-up phase. Non-isothermal conditions can be accounted for but the evaluation of temperature versus time is difficult. Second, the jet fuels are a mixture of many compounds that may oxidize at different rates. Third, jet fuel oxidation may be auto accelerating through the decomposition of the oxidation products. Attempts to model the deposition of jet fuels in two different flowing systems showed the inadequacy of a simple two-parameter global Arrhenius oxidation rate constant. Discarding previous assumptions about the form of the global rate constants results in a four-parameter model (which accounts for autoacceleration). This paper discusses the source of the rate constant form and the meaning of each parameter. One of these parameters is associated with the pre-exponential of the autoxidation chain length. This value is

expected to vary inversely to thermal stability. We calculate the parameters for two different fuels and discuss the implication to thermal and oxidative stability of the fuels. Finally, we discuss the effect of non-Arrhenius behavior on current modeling of deposition efforts.

SESSION 2: MICROBIOLOGY

SAFE, ACCEPTABLE ANTI-MICROBIAL STRATEGIES FOR DISTILLATE FUELS

E.C.Hill

Microbiological fouling, spoilage and corrosion have for years been considered as end-user problems but they have now become endemic up-stream affecting cargoes, tank farms and terminals. Trading agreements to share storage and distribution facilities impose the need to mutually agree antimicrobial strategies which satisfy all health, safety and environmental regulations wherever that fuel is distributed and used. Also agreed must be the infection levels at which antimicrobial action is initiated. Physical decontamination methods are described and the use of biocides discussed in relation to increasing regulatory restrictions.

CASE STUDY: USE OF ISOTHIAZOLINONE AND NITRO-MORPHOLINE BIOCIDES TO CONTROL MICROBIAL CONTAMINATION IN DIESEL AND GASOLINE STORAGE AND DISTRIBUTION SYSTEMS

Howard L. Chesneau, Frederick J. Passman, Ph D., David Daniels

Responding to feed-back from its retail outlet network, a major, vertically integrated petroleum company undertook to diagnose and remediate diesel and gasoline performance problems. Analysis of samples from tanks at refinery, distribution terminal and retail outlet sites established that uncontrolled microbial contamination was rampant throughout the distribution system. The company then developed and instituted a two-phase action plan. During Phase I, all tanks received corrective (shock) biocide treatment preceding mechanical tank cleaning and fuel polishing. An ongoing Phase II program currently includes routine sampling and analysis combined with periodic preventive biocide treatment. This paper describes the initial problem diagnosis, corrective action plan and preventive program; recommending the Phase II program as a model for all companies involved with refining, distribution or retailing gasoline.

HARMONISATION OF MICROBIAL SAMPLING AND TESTING METHODS FOR DISTILLATE FUELS

Graham C. Hill and Edward C. Hill

Increased incidence of microbial infection in distillate fuels has led to a demand for organisations such as the Institute of Petroleum to propose standards for microbiological quality, based on numbers of viable microbial colony forming units. Variations in quality requirements, and in the spoilage significance of contaminating microbes plus a tendency for temporal and spatial changes in the distribution of microbes, makes such standards difficult to implement. The problem is compounded by a diversity in the procedures employed for sampling and testing for

microbial contamination and in the interpretation of the data obtained. The following paper reviews these problems and describes the efforts of The Institute of Petroleum Microbiology Fuels Group to address these issues and in particular to bring about harmonisation of sampling and testing methods. The benefits and drawbacks of available test methods, both laboratory based and onsite, are discussed.

CATALASE MEASUREMENT: A NEW FIELD PROCEDURE FOR RAPIDLY ESTIMATING MICROBIAL LOADS IN FUELS AND WATER-BOTTOMS

Frederick J. Passman, Ph.D., Howard F. Chesneau and David A. Daniels

Low-grade microbial infections of fuel and fuel systems generally go undetected until they cause major operational problems. Three interdependent factors contribute to this: mis-diagnosis, incorrect or inadequate sampling procedures and perceived complexity of microbiological testing procedures. After discussing the first two issues, this paper describes a rapid field test for estimating microbial loads in fuels and associated water. The test, adapted from a procedure initially developed to measure microbial loads in metalworking fluids, takes advantage of the nearly universal presence of the enzyme *catalase* in the microbes that contaminated fuel systems. Samples are reacted with a peroxide-based reagent; liberating oxygen gas. The gas generates a pressure-head in a reaction tube. At fifteen minutes, a patented, electronic pressure-sensing device is used to measure that head-space pressure. The authors present both laboratory and field data from fuels and water-bottoms, demonstrating the excellent correlation between traditional viable test data (acquired after 48 -72 hours incubation) and catalase test data (acquired after 15 min. - 4 hours). We conclude by recommending procedures for developing a failure analysis data-base to enhance our industry's understanding of the relationship between uncontrolled microbial contamination and fuel performance problems.

BIOCIDAL TREATMENT AND PRESERVATION OF LIQUID FUELS

Wolfgang Siegert

Strict microbiological limit values are the result of damage caused by microorganisms in fuels. With MAR 71, a biocide based on methylenebisoxazolidine, a product is available which has been tested and approved by leading car manufacturers, the mineral oil industry, and NATO. Depending on the degree of microbiological contamination, different decontamination concepts are presented, and recommendations for the treatment of fuels which are contaminated when purchased are given. In order to avoid recontamination, planning principles for the new design of tanks are necessary. The possibility of convenient, economical and regular drainage is a key factor here. Introduction

SESSION 3: JET FUELS – II

THE EFFECT OF COPPER, MDA, AND ACCELERATED AGING ON JET FUEL THERMAL STABILITY AS MEASURED BY THE GRAVIMETRIC JFTOT

Seetar G. Pande and Dennis R. Hardy

Thermally unstable jet fuels pose operational problems. In order to adequately identify such fuels, factors that realistically impact on thermal stability were examined. Evaluation was based on a quantitative method of measuring thermal stability, viz., NRL's recently developed gravimetric JFTOT. This method gives a quantitative measurement of both the strip deposit and filterables formed. The pertinent factors examined, included the individual and interactive effects of: soluble copper, MDA (metal deactivator), and aging. The latter was accelerated to simulate field conditions of approximately six months aging at ambient temperature and pressure. The results indicate that the individual and interactive effects of copper, MDA, and accelerated aging appear to be fuel dependent. Based on the results, the three test fuels examined (one JP-8 and two JP-5s) were categorized as exhibiting very good, typical, and poor thermal stabilities, respectively. For both the very good and poor thermal stability fuels, the effect of copper in conjunction with accelerated aging did not significantly increase the total thermal deposits of the neat fuels. In contrast, for the typical thermal stability fuel, the combined effects of copper and accelerated aging, did. Furthermore, the addition of MDA *prior to* aging of the copper-doped, typical stability fuel significantly counteracted the adverse effect of copper and aging. A similar beneficial effect of MDA was not observed for the poor stability fuel. These results focus on the compositional differences among fuels and the need to elucidate these differences (Physical and chemical) for a better understanding and prediction of their performance. MECHANISM OF

DEPOSIT FORMATION ON FUEL-WETTED METAL SURFACES

Leo L. Stavinoha, Steve R. Westbrook, and Lona A. McInnis

Experiments were performed in a Single Tube Heat Exchanger (STHE) apparatus and a Hot Liquid Process Simulator (HLPS) configured and operated to meet Jet Fuel Thermal Oxidation Tester (JFTOT) ASTM D 3241 requirements. The HLPS-JFTOT heater tubes used were 1018 mild steel, 316 stainless steel (SS), 304 stainless steel (SS), and 304 SS tubes coated with aluminum, magnesium, gold, and copper. A low-sulfur Jet A fuel with a breakpoint temperature of 254°C was used to create deposits on the heater tubes at temperatures of 300°C, 340°C, and 380°C. Deposit thickness was measured by dielectric breakdown voltage and Auger ion milling. Pronounced differences between the deposit thickness measuring techniques suggested that both the Auger milling rate and the dielectric strength of the deposit may be affected by deposit morphology/composition (such as metal ions that may have become included in the bulk of the deposit). Carbon bumoff data were obtained as a means of judging the validity of DMD-derived deposit evaluations. ESCA data suggest that the thinnest deposit was on the magnesium-coated test tube. The Scanning Electron Microscope (SEM) photographs showed marked variations in the deposit morphology and the results suggested that surface composition has a significant effect on the mechanism of deposition. The most dramatic effect observed was that the bulk of deposits moved to tube locations of lower temperature as the maximum temperature of the tube was increased from 300° to 380°C, also verified in a single-tube heat exchanger. The results indicate that the deposition rate and quantity at elevated temperatures is not completely

temperature dependent, but is limited by the concentration of dissolved oxygen and/or reactive components in the fuel over a temperature range. Experiments were done for several fuels using the Single Tube Heat Exchanger (STHE) apparatus to evaluate deposit formation with fuel at measured temperatures. The STHE test tubes were 0.64 cm O.D., 304 SS test tubes, heated at 340°, 380°, 420°, 460°, 500°, and 540°C for 4 hours with a fuel flow of 10 mL/minute. The position of the fuel deposit in the tube versus the fuel temperature at various bath set temperatures very closely approximates what was observed for HPLS heater tubes. These data support the observation based on HPLS data that the depositing position on the tube is temperature dependent. Furthermore, the magnitude of the deposit is essentially the same at all three temperatures. Oxygen measurements in both MPLS and STHE tests, indicate that oxygen is depleted at temperatures below 260°C. At higher temperatures (set temperature of 420°C) for the STHE, methane generation is observed due to pyrolysis of the fuel. At pyrolysis temperatures, surface deposit formation is fuel composition dependent

EFFECT OF HIGH SURFACE AREA ACTIVATED CARBON ON THERMAL DEGRADATION OF JET FUEL

Katia Gergova, Semih Eser, Rathnamala Arumugam, and Harold H. Schobert

Different solid carbons added to jet fuel during thermal stressing cause substantial changes in pyrolytic degradation reactions. Activated carbons, especially high surface area activated carbons were found to be very effective in suppressing solid deposition on metal reactor walls during stressing at high temperatures (425 and 450°C). The high surface area activated carbon PX-21 prevented solid deposition on reactor walls even after 5h at 450°C. The differences seen in the liquid product composition when activated carbon is added indicated that the carbon surfaces affect the degradation reactions. Thermal stressing experiments were carried out on commercial petroleum-derived JPTS jet fuel. We also used n-octane and n-dodecane as model compounds in order to simplify the study of the chemical changes which take place upon activated carbon addition. In separate experiments, the presence of a hydrogen donor, decalin, together with PX-21 was also studied.

DEVELOPMENT OF OXYGEN SCAVENGER ADDITIVES FOR JET FUELS

Bruce D. Beaver, Romila Demunshi, Vaqar Sharief, Dake Tian, and Yun Teng

Our current research program is in response to the U. S. Air Force's FY93 New Initiative entitled "Advanced Fuel Composition and Use." The critical goal of this initiative is to develop aircraft fuels which can operate at supercritical conditions. This is a vital objective since future aircraft designs will transfer much higher heat loads into the fuel as compared with current heat loads. In this paper it is argued that the thermal stability of most jet fuels would be dramatically improved by the efficient in-flight removal of a fuel's dissolved oxygen. It is proposed herein to stabilize the bulk fuel by the addition of an additive which will be judiciously designed and programmed to react with oxygen and produce an innocuous product. It is envisioned that a thermally activated reaction will occur, between the oxygen scavenging additive and dissolved oxygen, in a controlled and directed manner. Consequently, formation of insoluble thermal degradation products will be limited. It is believed that successful completion of this project will result in the

development of a new type of jet fuel additive which will enable current conventional jet fuels to obtain sufficient thermal stability to function in significantly higher temperature regimes. In addition, it is postulated that the successful development of thermally activated oxygen scavengers will also provide the sub-critical thermal stability necessary for future development of endothermic fuels.

DEVELOPMENT OF THERMAL STABILITY ADDITIVE PACKAGES FOR JP-8

Steven D. Anderson, William E. Harrison III, Tim Edwards, Robert W. Morris and Dale T. Shouse

Advanced military aircraft use fuel as the primary heat sink: to cool engine and airframe components. As the fuel is thermally stressed, thermal oxidative reactions take place that result in the formation of deposits. These deposits degrade aircraft performance and ultimately lead to premature servicing of the affected components. The frequency of these incidents, coupled with the projected cooling requirements for future systems, demonstrates that current thermal stability limits are inadequate. In response to this situation, the United States Air Force (USAF) has embarked on a program to improve thermal stability using specially formulated additive packages. Results indicate that additives offer significant thermal stability improvement. This paper describes the USAF program to develop and deploy an improved JP-8 for fleet-wide use by 1998.

STUDIES OF JET FUEL ADDITIVES USING THE QUARTZ CRYSTAL MICROBALANCE AND PRESSURE MONITORING AT 140 C

Steven Zabarnick and Rebecca R Grinstead

The quartz crystal microbalance (QCM) and pressure monitoring are used for the evaluation of jet fuel additives for the improvement of jet fuel thermal stability. The mechanisms of additive behavior are determined by measuring the time dependent deposition with the QCM and oxidation by pressure measurements. Studies at various additive concentrations permits the determination of optimum additive concentrations. Additive packages made of mixtures of antioxidants, detergent/dispersants, and metal deactivators are shown to yield good improvements in thermal stability over a wide range of jet fuel types.

EFFECT OF ADDITIVES ON THE FORMATION OF INSOLUBLES IN A JET FUEL

Steven D. Anderson, E. Grant Jones, Larry P. Goss, and Walter J. Balster

Dynamic near-isothermal techniques have proven to be valuable in assessing the tendency of aviation fuels to form surface and bulk insolubles under thermal stress. These methods are applied in this study to the investigation of the neat Jet-A fuel POSF-2827 and changes introduced by a series of four candidate additives. In each case fuel is stressed while flowing through a heat exchanger under near-isothermal conditions at 185°C. The average surface deposition rate as a function of stress duration and the quantity of both surface and bulk insolubles have been determined after complete consumption of the dissolved oxygen. The additives, introduced individually, include a common antioxidant, a metal deactivator, a

dispersant, and a combination detergent/dispersant. Of the four additives, only the dispersant-types are found to improve fuel thermal stability.

SESSION 4: LONG-TERM & STRATEGIC STORAGE

STRATEGIC STORAGE PROGRAMME FOR DEVELOPING COUNTRIES -TO BE OR NOT TO BE?

Bernhard W. Morse

In the industrialised world agreements between countries or legislation will dictate that there shall be strategic fuel storage of "X" amount of days. What about the developing countries, the third world? For the most part they have no storage regulations. Should they consider a strategic fuel storage programme? If so, how can they go about it? What are the obstacles? Many have neither the technical expertise nor the monies. This paper will explore how developing countries can have a strategic oil storage programme - How they can plan, justify, finance, execute and operate such a storage without having a major impact on their countries

USE OF ASTM D5304 IN ASSESSING UNSTABLE DIESEL FUEL

Lynda M. Turner, Calvin J. Martin, Erna J. Beal, and Dennis R. Hardy

The storage stability, or the length of time a fuel can be stored, is of great concern to diesel fuel users. This paper reports on the use of the new ASTM accelerated test for storage stability by oxygen overpressure (D5304) to predict future storage life span of 63,000,000 gallons of a diesel fuel for U.S. Naval vessel use. This paper demonstrates the use of ASTM D 5304 at storage times of 16, 40 and 96 hours to accurately determine the length of time that this large quantity of diesel fuel could be stored at ambient temperatures before the maximum allowable amount of particulate contamination was reached.

METAL-DEACTIVATING ADDITIVES FOR LIQUID FUELS

Margarita Boneva, Slavi K. Ivanov, A. Terebenina, Olga I. Todorova

The metal-deactivating and the antioxidant properties of 1-phenyl-3-methylpyrazolone- 5 derivatives have been investigated both in the model reaction of low temperature oxidation of ethylbenzene and in gasoline oxidation. The study of the ability of these derivatives to reduce the catalytic effect of copper naphthenate demonstrates that they are promising as metal deactivating additives for light fuels. Some of the pyrazolone compounds appear to be of special interest for the long-term storage of liquid fuels due to their action as multifunctional inhibitors.

SESSION 5: PREDICTIVE SYSTEMS & METHODS

A RAPID COLORIMETRIC METHOD FOR PREDICTING THE STORAGE STABILITY OF MIDDLE DISTILLATE FUELS

Sheila J Marshman

Present methods used to predict the storage stability of distillate fuels such as ASTM D2274, ASTM D4625, DEF STAN 05-50 Method 40 and in-house methods are very time consuming, taking a minimum of 16 hours. In addition, some of these methods under- or over-predict the

storage stability of the test fuel. A rapid colorimetric test for identifying cracked, straight run or hydrofined fuels was reported at the previous Conference. Further work has shown that while a visual appraisal is acceptable for refinery-fresh fuels, colour development may be masked by other coloured compounds in older fuels. Use of a spectrometric finish to the method has extended the scope of the method to include older fuels. The test can be correlated with total sediment from ASTM D4625 (13 weeks at 43°C) over a sediment range of 0-60mg/L. A correlation of 0.94 was obtained for 40 fuels.

SESSION 6: TEST RIGS & SIMULATORS

THERMAL STABILITY AND FILTERABILITY OF JET FUELS CONTAINING PDR ADDITIVES IN SMALL-SCALE TESTS AND REALISTIC RIG SIMULATIONS

Joanna M. Bauldreay, Richard H. Clark, and Richard J. Heins

Specification, small-scale and realistic fuel simulation tests have addressed concerns about the impact of pipeline drag reducer (PDR) flow modifying additives on jet fuel handling and performance. A typical PDR additive tended to block filters which were similar to those used in the specification Jet Fuel Thermal Oxidation Tester (JFTOT) and other thermal stability test apparatus. Blockages reduced flow rates and PDR concentrations downstream of the filters. Consequently, two PDR additives (A & B) were tested in JFTOT apparatus without the usual in-line pre-filters as part of a Ministry of Defence (MoD) co-ordinated Round Robin exercise. Some fuel/PDR additive combinations caused decreases in JFTOT breakpoints. Effects were additive-(type, concentration and degree of shear) and fuel-dependent; most failures were caused by filter blockages and not by a failing lacquer rating. In further work at Thornton, the thermal stability characteristics of similar fuel/additive combinations have been examined in non-specification tests. In Flask Oxidation Tests, PDR additives caused no significant increase in the liquid phase oxidation rates of the fuels. Additives were tested in the Single Tube Heat Transfer Rig (STHTR) which duplicates many of the conditions of a heat exchanger element in an engine's fuel supply system. B produced an average two-fold decrease in thermal stability in a Merox fuel; A had no significant effect. In hydrotreated fuel, B reduced the thermal stability up to five-fold. A had little effect below 205°C, while at higher temperatures there may have been a marginal improvement in thermal stability. Again, certain jet fuel/PDR combinations were seen to reduce thermal stability.

SYSTEM EVALUATION OF IMPROVED THERMAL STABILITY JET FUELS

Kenneth E. Binns, Gordon L. Dieterle, and Ted Williams

A single-pass, single-tube heat exchanger device called the Phoenix rig and a single-pass, dual-heat exchanger system called the Extended Duration Thermal Stability Test system are specific devices/systems developed for evaluating jet fuel thermal stability. They have been used extensively in the evaluation of various jet fuels and thermal stability additives. The test results have indicated that additives can substantially improve the thermal stability of conventional jet fuels. Relationships of oxygen consumption, residence time, bulk, and wetted wall temperatures on coking deposits that form in the heated tubes have also been investigated.

IMPROVEMENT OF TEST METHODOLOGY FOR EVALUATING DIESEL FUEL STABILITY

Marcel Gutman, Leonid Tartakovsky, Yosef Kirzhner, Yoram Zvirin, David Luria, Arthur Weiss, and Max Shuftan

The storage stability of diesel fuel has been extensively investigated for many years under laboratory conditions. Although continuous efforts have been made to improve testing techniques, there does not yet exist a generally accepted correlation between laboratory methods (such as chemical analysis of the fuel) and actual diesel engine tests. A testing method was developed by the Technion Internal Combustion Engines Laboratory (TICEL), in order to address this problem. The test procedure was designed to simulate diesel engine operation under field conditions. It is based on running a laboratory-modified single cylinder diesel engine for 50 h under cycling operating conditions. The overall rating of each test is based on individual evaluation of the deposits and residue formation in the fuel filter, nozzle body and needle, piston head, piston rings, exhaust valve, and combustion chamber (six parameters). Two methods for analyzing the test results were used: objective, based on measured data, and subjective, based on visual evaluation results of these deposits by a group of experts. Only the residual level in the fuel filter was evaluated quantitatively by measured results. In order to achieve higher accuracy of the method, the test procedure was improved by introducing the measured results of nozzle fouling as an additional objective evaluating (seventh) parameter. This factor is evaluated on the basis of the change in the air flow rate through the nozzle before and after the complete engine test. Other improvements in the method include the use of the nozzle assembly photograph in the test evaluation, and representation of all seven parameters on a continuous scale instead of the discrete scale used anteriorly, in order to achieve higher accuracy. This paper also contains the results obtained by application of this improved fuel stability test for a diesel fuel stored for a five-year period.

SESSION 7: DEPOSIT & INSOLUBLES MEASUREMENTS

THICKNESS MEASUREMENT OF JFTOT TUBE DEPOSITS BY ELLIPSOMETRY

Clive Baker, Peter David, Spence E Taylor, Andy J Woodward

Thickness measurement of Jet Fuel Thermal Oxidation Test (JFTOT) tube deposits has long been a desirable goal to characterise better the thermal stability of jet fuels. The current visual rating method used for specification purposes suffers from the drawback of operator subjectivity and provides little information on the thickness and volume of deposits, parameters which are far more meaningful for characterising fuels for users and suppliers. Ellipsometry has been identified as a suitable technique for measuring the thickness of JFTOT tubes. Such a system would be robust and non-destructive; cover the important thickness range with regard to visual ratings; provide quick and easy absolute measurement of thickness; enable single spot and profiling measurements; and there would be no restriction on minimum deposit thickness.

WEIGHING BY STOPWATCH· SORTING OUT THE VARIABLES IN FILTER BLOCKING TENDENCY

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

This paper first reviews the work reported in the early 1960's on the major variable governing rate of flow of a liquid through a membrane filter - viscosity. Ignoring this major variable leads to both confusing interpretation of filter blocking tendency (FBT) experiments in the laboratory and also for FBT standard tests which cannot adequately or correctly assess FBT from fuel to fuel. Next, the paper will establish a protocol for correctly assessing any given liquid FBT by first calibrating given porosity membrane filters for viscosity and then for solids content. The technique can then be used to measure not only existent solids in various liquid samples but also solids formed during typical accelerated tests such as the gravimetric JFTOT test (for aviation fuels) or ASTM D5304 (for diesel fuels) using only a stopwatch and graduated cylinder. Accuracy and precision of this weighing technique will be compared with direct gravimetric determinations.

MONITORING THE FORMATION OF SOLUBLE DEPOSIT PRECURSORS IN FUELS WITH LIGHT SCATTERING PHOTOMETRY

Robert E. Morris, Dennis R. Hardy, Seetar Pande and Margaret A Wechter

The reactions that can take place in hydrocarbon fuels often manifest themselves as an increase in the propensity to form thermally induced insoluble reaction products. This is not a one-step process but the result of a multitude of intermediate processes. These intermediate processes will produce a range of soluble products that differ considerably in structure and functionality from the fuel itself. Since these soluble "precursors" can, upon further thermal stress, lead to insoluble products, a method for following their formation could form the basis of a useful predictive measurement. It would also serve as a research tool for following the discrimination between soluble and insoluble product formation. Light scattering photometry was evaluated as a means of monitoring the formation of large soluble product molecules as they are formed in fuels. Changes in light scattering properties were measured after thermal stressing in the presence of dissolved copper and a metal deactivator additive. These results correlated well with the amounts of soluble and insoluble products formed. Fuel changes were detected by light scattering before detectable quantities of insoluble products were produced.

AN IMPROVED REFERENCE FUEL SYSTEM: PART 2 - A STUDY OF ADHERENT AND FILTERABLE INSOLUBLES FORMATION AS FUNCTIONS OF TRIMETHYLPYRROLE CONCENTRATION IN DODECANE

Edmund W. White and Michael D. Klinkhammer

At the 4th International Conference on the Stability and Handling of Liquid Fuels, a trimethylpyrrole (TMP)/dodecane reference fuel system for use with ASTM Test Method 02274 was presented. It was concluded that the TMP/dodecane system would have sufficient reproducibility of total insolubles values to serve as a reference fuel system. In this paper, the filterable and adherent insolubles from the same data base are examined. Like the total

insolubles, the FY 91 results for both adherent and filterable were less scattered than the FY 90 data. Both adherent and filterable insolubles were found to be adequately represented as linear functions of the initial TMP concentration. Further, the data support a hypothesis that filterable insolubles do not form in the 16 hours of stress unless the initial TMP concentration is greater than about 25 mg/100 mL. A plot of the FY 91 ratio of adherent insolubles to filterable insolubles as a function of the initial TMP concentration approaches 0.6 at TMP concentrations in excess of 75 mg/100 mL.

REVISED PROCEDURE FOR THE MEASUREMENT OF PARTICULATE MATTER IN NAVAL JP5 AVIATION TURBINE FUEL (F44; AVCAT) USING THE CONTAMINATED FUEL DETECTOR (CFD)

Grier G McVea and Alan J Power

USA Military Specification MIL-D-22612 provides a procedure for measurement of particulate levels in Naval aviation gas turbine engine JPS fuel (E44: RAN A VCAD using the contaminated fuel detector (CFD). Evaluation of this procedure within the specification has revealed significant shortcomings in the application of the theoretical principles upon which the method is based. CFD measurements have been compared to gravimetric results from ASTM D2276, which provides accurate determination of concentrations of particulate matter in JPS. Inaccuracies evident in the CFD readings have been found to relate to the high sensitivity of the CFD to variations in fuel particulate extinction coefficients (ECs) (relating to fuel sediment colour) and to an error in the application of light transmittance theory in the recommended method. This report demonstrates that accurate CFD determination of JP5 particulate concentrations depends on spectrophotometric measurement of a narrow range of ECs of particulate matter. A range of fuel sediments derived from Australian naval ship and shore fuel storages was studied. It was observed that the CFD plot, which is in light transmittance mode, in theory provides a curved line graph against the gravimetric test results, whereas MIL-D-22612 describes a straight line graph. It was concluded that this must be an approximation. However, conversion of light transmittance data derived from the CFD into the reciprocal logarithm to give light absorbance data was shown to give a straight line graph which corresponded well with the gravimetric results. This relationship depended on construction of the graph on the basis of a narrow range of known particulate ECs. The conversion to absorbance gave improved correlation for JPS particulate measurements with gravimetric procedures, using the CFD.

SESSION 8: GASOLINES

EFFECT OF METAL OXIDES AND TANKS' DIEPOSITS ON THE OXIDATIVE STABILITY OF GASOLINE

Slavi K. Ivanov, Margarita I. Boneva, Zhetcho D. Kalitchin, Petko T. Georgiev and Setrak K. Tanielyan

The present investigation is devoted to assessment of the influence of species isolated from fuel tanks and tank bottoms on the oxidative stability of gasoline. The aim of the paper is to be evaluated quantitatively the effect of rust and tank deposits on the oxidation processes and the storage terms of motor gasoline containing catalytic cracking fraction on the basis of a method developed by us earlier. As a result of the theoretical model and the experiments is found that the

deposits decrease the chemical stability of gasoline containing 50 % fraction from catalytic cracking, while the rust has no significant influence on this parameter. Correction coefficients are calculated and introduced, taking into account the influence of deposits and rust on the predicted storage terms.

IMPROVING STORAGE STABILITY OF GASOLINE USING ELEVATED ANTIOXIDANT CONCENTRATIONS

Seth Sommer, David Luria, Jacob Sufrin, Arthur Weiss, Max Shuftan, Itamar Lavie.

The purpose of this study was to examine the feasibility of increasing storage-stability of gasoline by blending it with elevated concentrations of standard antioxidants, normally added at low concentrations to gasolines. It was thought that, by raising the concentration of these additives in the gasoline from 25 ppm to 100 ppm, the storage stability of the fuel can be improved. In this study, two types of antioxidants (an aromatic diamine type and an alkylphenol type), and a mixture of the two, were added at different concentrations to two different gasoline blends. The various blends were stored in drums, simulating tank storage conditions, for a period of 25 months. Samples were drawn at varying intervals over the test duration and tested for Existent Gum, Potential Gum, Induction Period and other properties (according to standard ASTM test procedures). It was found that raising the concentrations of the aromatic amine antioxidant adversely effected the storage stability of the gasoline blends, whereas elevated concentrations of the alkylphenol antioxidant indeed improved the gasoline's stability.

THE EFFECT OF SOME METALS ON THE OXIDATIVE AND STORAGE STABILITY OF GASOLINE

Zhetcho D. Kalitchin, Margarita I. Boneva, Slavi K. Ivanov, Petko T. Georgiev, and Setrak K. Tanielyan

The catalytic action of transitional metal compounds on the oxidation of organic substrates with atmospheric oxygen has received considerable attention in the literature. The effect of metal surface (Fe and Zn) on the oxidation processes and storage terms of motor gasoline containing fraction from catalytic cracking have been investigated. Both metals are chosen because they are the main construction material of the fuel tanks. On the basis of the kinetic data the correction coefficient k_m evaluating the influence of metals on the oxidation processes of gasoline has been determined. This correction coefficient is included in the calculation for prediction of the real storage terms of gasoline.

GUM FORMATION TENDENCIES OF OLEFINIC STRUCTURES IN GASOLINE AND SYNERGISTIC EFFECT OF SULPHUR COMPOUNDS

J M Nagpal, G C Joshi, D S Aswal

The high octane gasoline pool contains varying amounts of cracked naphthas as an important ingredient in formulating high-octane lead-free gasoline. The cracked naphthas are largely from Fluidised Catalytic Cracking (FCC) units and to lesser extend from thermal cracking units. While the role of olefinic unsaturation in gum formation during storage of gasoline has been

extensively studied, there is little published work on contribution of individual olefin types in storage stability and gum formation tendency of gasoline containing these compound types. In the present work we report our results on storage stability and gum formation tendency of different olefin types present in cracked naphthas through model compound matrix. It is found that cyclic olefins and cyclic/diolefins are the most prolific gum formers. We have also studied the role of sulfur compounds present in the gasolines on gum formation tendency of olefins. While thiols enhance gum formation from all olefinic types, sulfides and disulfides interact depending on the structure of olefins. These can have either an accelerating, or inhibiting effect on gum formation.

SESSION 9: HEAVY OILS AND REFINERY PROCESSING

INTERCOMPATIBILITY OF RESIDUAL FUEL BLENDS

Josefa Ben-Asher, Gregory Krenis and David Luria

It is a well-known fact that two fuel oils, thermally stable by themselves, may produce sludge of asphaltenic nature when blended together. Settling out of asphaltenes from the fuel medium will result in strainer and burner plugging, causing serious operational difficulties in industrial and marine fuel systems. It was the aim of the present study to establish criteria for the phenomenon of incompatibility. The parameters which influence thermal stability of the blend were assessed, and an attempt was made to predict possible separation of asphaltens from fuel oil mixtures. *Fuel* oils originating from Brasil, France, Honk-Kong, Greece, U.S.A., Japan as well as locally (Israel) produced residual fuels were mixed. Thermal stability of the blend was determined by ASTM 0-4740 method. In some cases, total sediment was measured by ASTM 0-4870. Blends of fuels were stored at 50°C to assess the effect of elevated temperatures on thermal stability. It was found that most of the blends were compatible though composed of fuels originating from different refineries. Density, Pour Point, Sulfur content and Xylene Number served as useful tools for predicting the thermal stability of residual fuel blends.

COMPATIBILITY AND STABILITY OF RESIDUAL FUELS

R. Kassinger

Much of the heavy viscous so-called "bunker" fuel oil of the present day contains residual products from cracking operations. This material varies widely in character with the nature of the crude oil from which it is derived and the method and degree of cracking to which it has been submitted. Cracked residues are not always completely soluble in petroleum distillates or uncracked residues, thus complicating the problem of preparing merchantable blends. They usually contain solid or semisolid particles which are not objectionable if dispersed, but which sometimes agglomerate in the form of troublesome sludges or deposits if the fuels are subjected to unfavorable conditions of storage and use. The solubility problem at one time was most serious, when it was frequently necessary to blend cracked residues with paraffinic gas oils. Difficulties of this particular kind are less frequent today, since the oil industry is plentifully supplied with cracked distillates for blending purposes. However, the solubility problem in lesser degrees still exists, even though it may not be recognized as such. The problem of minimizing

the precipitation of residues and sludges is still frequently troublesome, and even the best informed technologists are not always able to predict whether or not a given oil will cause difficulty." While I fully concur with these words and concepts, I must admit I did not write them. They were published in 1938, in a paper which described the Exxon Sediment by Hot Filtration (SHF) Test. There are a number of other papers, published about 50 years ago which describe procedures for predicting whether two fuel components will be compatible, i.e., will produce a stable fuel when blended. The actual concepts of fuel composition, stability and compatibility of which I speak today are relatively unchanged from these very early papers. Among the most thorough and influential papers on the subject in my opinion, were those published by Shell and Exxon.

THE U.S. DEPARTMENT OF ENERGY'S OIL PROCESSING PROGRAM

Arthur M. Hartstein

The U.S. Department of Energy's (DOE) Office of Gas and Petroleum Technology (OGPT) has been engaged in a strategic planning activity in response to the changing needs of the oil and gas industry and DOE's expanding role to address these needs. The Oil Processing sub-program is an important element of the OGPT program and is the topic of this paper. The major components of the Oil Processing Strategic Plan are described including the Mission, Situation Analysis, Vision of the Future, Strategic Goals, Strategic Barriers, and Objectives and Strategies.

SESSION 10: MIDDLE DISTILLATE FUELS – I

MECHANISMS FOR AGEING OF MIDDLE DISTILLATES MANUFACTURED FROM CRUDE OILS

Peter Derst

European middle distillate marketers and manufacturers have recently seen a surprising increase of ageing phenomena, mainly in the new eastern provinces of Germany after installation of new home heating oil units. Some of these phenomena remain unexplained, so that the "Committee Product Application-Fuels" of the DGMK (German Society for Petroleum and Coal Science and Technology) agreed to foster a research study with respect to ageing of middle distillates manufactured from mineral oils. As step I a literature search was authorized, as it was felt that since over 50 years of work had been done on the subject without culminating in an overall deterioration and degradation theory yet. The available literature from international sources is massive. 320 papers/books have been reviewed and it is hoped that the most important publications have been covered. A step II may follow in future looking into the verification of the most promising theories via laboratory testing and possibly providing better methodology to predict the most common ageing through its parameters - and finally recommending prevention methods. What has been found by the search is a majority of papers dealing with the results of ageing processes taken from real life cases and trying to resimulate them in the laboratory while reducing the reaction time. Relatively few papers try to explain chemical/physical reaction mechanisms on which an ageing theory could be built. Differentiation into chemical, physical and biological causes become necessary. An obvious problem with testing distillates and presented by many papers is the isolation of a blend component often found harmful for a

finished product, from the rest of the fuel components, thus omitting preventative forces or activating/accelerating agents from the findings. Many tests with Light Cat Cycle Oil (LCO) are typical examples. This isolation can explain the many contradictive findings in literature, which this paper will document in detail. The most promising theory requires a set of conditions/chemicals to be met/present to kick off the ageing process and progress it until one of the components is consumed. On their own many of the "danger chemicals" may not be harmful at all, unless they are being matched by their corresponding mates. The paper will provide details on these "danger chemicals" found in literature. Finally, the most promising reaction kinetic models found in the literature will be critically reviewed.

EVALUATION OF COMMERCIAL STABILITY ADDITIVES IN MIDDLE DISTILLATE FUELS

Ten commercial distillate stability additives were evaluated to determine their effect on the stability and chemistry of two distillate fuels. The two fuels were light catalytic cycle oil (LCCO) and a diesel fuel blend containing 15% of the same LCCO. Additives were evaluated for their ability to improve stability as measured by three test procedures. Also, their effect on fuel composition was measured. All additives were essentially sulfur-free nitrogen-containing compounds. Most of the nitrogen in each additive was basic nitrogen. Additive effectiveness did not correlate with total or basic nitrogen content. Additives that were blends of stabilizer, dispersant, and metal deactivator did not show a clear performance improvement when compared to additives of a simpler composition. The most cost-effective additive in improving stability was N,N-dimethylcyclohexylamine, with only one other additive giving comparable performance. One additive decreased stability. All additives were found to inhibit the formation of SMORS, species reputed to be sediment precursors. Also, all additives promoted increased levels of phenalenones that were formed in aged LCCO. The effect on SMORS and phenalenones are consistent with current theories of distillate instability chemistry.

THE EFFECT OF ALIPHATIC OLEFINS ON THE STABILITY OF DIESEL FUEL

Adiwar and B. D. Batts

The effect of aliphatic olefins on the storage stability of a number of distillates was observed and characterised, mainly by determining the amounts of total insolubles formed during accelerated ageing. It was observed that the aliphatic olefins in light cycle oil (LCO), a product of catalytic cracking, accelerated the degradation process in accordance with general expectations and in straight run diesel (SRD) and hydrotreated diesel (HTD), aliphatic olefins were shown to have no effect on stability. However, contrary to expectations, the aliphatic olefins inhibited the degradation process of light waxy gas oil (LWGO). The effect of aliphatic isomers on the degradation of LCO is in the order of terminal olefins < internal olefins < branched chain olefins. The effect of aliphatic olefinic isomers on L WOO is, on the other hand, in the order of terminal olefin > internal olefins > branched chain olefins. Three possible mechanisms to explain the effect of aliphatic olefins on the LCO and L WOO samples are proposed.

CHEMISTRY OF SEDIMENT FORMATION AND ADDITIVE RESPONSE IN CRACKED MIDDLE DISTILLATES

Yogendra K. Sharma, Indra D. Singh, Krishna M. Agrawal and Girish C. Saxena

The current trend in middle distillate maximization is to blend significant proportions of cracked stocks. This blending enhances instability of the product which creates application problems. In order to reduce/prevent sediment formation it is essential to understand the chemistry of sediment formation. Further knowledge of sediment precursors in cracked middle distillates facilitates in screening of the suitable additives and in studying their response in prevention of sediment formation. The present paper discusses the characterization of sediment precursors, separated through - methanol extraction, employing derivatization technique and FTIR spectroscopy. The effect of few commercial additives on the stability of cracked fuels both under accelerated conditions and ambient storage have also been studied. The study indicated that performance of an additive in cracked middle distillate fuels depends on fuel composition, additive structure and fuel storage conditions. From the comparison of FTIR spectra, it has been concluded that methanol extracts the sediment precursors.

SESSION 11: MIDDLE DISTILLATE FUELS – II

A STUDY OF THE SAFETY OF THE ASTM D5304 OXYGEN OVERPRESSURE STABILITY TEST

Edmund W. White and Keith W. Flohr

While the test method for assessing distillate fuel storage stability by oxygen overpressure was being evaluated as a potential ASTM standard, a question of its safety was raised, specifically whether the juxtaposition of liquid fuel and oxygen at elevated pressure could lead to explosive self ignition. As a consequence, the authors conducted a literature search followed by a small experimental program. The results of those studies show that the temperature and pressure used in Test Method D5304 are probably safely below the conditions that would lead to auto ignition of normal middle distillate fuels. However, middle distillate fuels of unknown or unusual sources, or containing additives, e.g., ignition improvers, should be screened before evaluating their stability by Test Method D5304.

A COMPARISON OF LOW AND HIGH SULFUR MIDDLE DISTILLATE FUELS IN THE UNITED STATES

J. Andrew Waynick and Susan M. Taskila

Sixty-nine low sulfur (LS) and twenty-six high sulfur (HS) No.2 diesel fuel samples were collected from twenty-four marketers throughout the United States in early 1994. Fuel samples were tested for chemical composition, physical properties, and stability. All data was statistically analyzed, and a multi-variable regression analysis was performed to determine predictive equations for stability and cold flow test results. The statistical analysis indicated that other than sulfur and nitrogen levels, the main compositional difference between LS and HS diesel fuels was a partial saturation of poly-aromatics to mono-aromatics in LS fuel. Storage stability via ASTM D4625 was improved in LS fuels compared to HS fuels, and poly-aromatics were identified as important contributors to insolubles formation. Hydroperoxide susceptibility of LS

and HS fuels was equivalent and acceptable under conditions of ambient fuel transport and storage. However, under progressively severe thermal and oxidative stress, LS fuels appeared increasingly less stable than HS fuels. Under the most stressful conditions used, average hydroperoxide formation rates for LS and HS fuels had regression equations that differed only by a constant factor. Compositional variables that contributed to secondary and benzylic carbons were found to strongly increase hydroperoxide formation. Examination of the test data also indicated that LS diesel fuels might be less responsive to cold flow improvers than HS diesel fuels.

CHARACTERIZATION OF SOLUBLE MACROMOLECULAR OXIDATIVELY REACTIVE SPECIES (SMORS) FROM MIDDLE DISTILLATE DIESEL FUELS: THEIR ORIGIN AND ROLE IN INSTABILITY

Margaret A. Wechter and Dennis R. Hardy

Compositional characterization of a solid phase material isolated by extraction from filtered liquid phase diesel fuels is reported. This solid phase material (SMORS) is shown to be the product of reactive fuel constituents and intermediate to the formation of fuel insoluble sludge. The composition of this material changes during blending processes and tends to become more oxygen rich and thus more polar. Elemental analysis, average molecular weight and pyrolysis mass spectral data are presented for SMORS from a number of representative blended fuels and their blending stocks. SMORS has been shown to be made up of oxidized trimers, tetramers and possibly higher n-mers of nitrogen containing precursors originally present in the fuel. It is not possible to determine the SMORS precursors in field aged fuel (such as those in this study) since these precursors are essentially depleted from the fuel by the time very small amounts of SMORS have been formed.

SESSION 12: NEW FUELS & ENVIRONMENTAL MANDATES

THE EFFECT OF INCREASED REFINING ON THE LUBRICITY OF DIESEL FUEL

Paul I. Lacey and Steven R. Westbrook

The United States and Europe are mandating increasingly severe diesel fuel specifications, particularly with respect to sulfur content, and in some areas, aromatics content. This trend is directed towards reducing vehicle exhaust emissions and is generally beneficial to fuel quality, ignition ratings, and stability. However, laboratory studies, as well as recent field experience in Sweden and the United States, indicate a possible reduction in the ability of fuels to lubricate sliding components within the fuel injection system. These factors, combined with the trend toward increasing injection pressure in modern engine design, are likely to result in reduced durability and failure of the equipment to meet long-term emissions compliance. The Belvoir Fuels and Lubricants Research Facility (BFLRF) developed an accelerated wear test that predicts the effects of fuel lubricity on injection system durability. This test now has been widely used by fuel, additive, and equipment manufacturers. Several thousand fuel samples have been evaluated to date, and collectively, they form one of the largest data bases on fuel lubricity currently in existence. This range of data permits a good overview of the commercially available fuels and

confirms a general decrease in fuel lubricity due to increasing refining severity. The results indicate that no high-sulfur fuel (>0.12 wt%) had poor lubricity, while a number of low sulfur fuels (<0.05 wt%) did produce unacceptable wear. The lubricity of many severely refined fuels is probably being restored using relatively high concentrations of additive.

STABILISER ADDITIVE PERFORMANCE IN DIESEL FUELS AND GAS OILS MEETING NEW ENVIRONMENTAL TARGETS

Russell J. Batt, Cyrus P. Henry, Paul R. Whitesmith

Stabiliser additives have for many years been used to inhibit sediment and gum formation in middle distillates, both to meet national specifications and to allow maximum refinery flexibility. The greater emphasis increasingly placed on air quality requires the production of fuels which not only meet the technical requirements of the end user but which also minimise exhaust pollutant levels. Clean air legislation has targeted sulphur and aromatic contents as a method of reducing noxious emissions. Both can be reduced at the refinery by hydrogen treatment but such processes can have implications for fuel stability. The effects of hydrogen treatment processes on traditionally measured fuel parameters are evaluated and the suitability of these methods for predicting field stability discussed. Potential new problems resulting from increased processing and the resultant removal of natural antioxidants are identified, and the ability of stabiliser and antioxidant additives to resolve these difficulties demonstrated.

US DIESEL FUEL REFORMULATION: ADDITIVE TECHNOLOGY IN RESPONSE TO CHANGING FUEL PROPERTIES

J. Paul Street, Charles L. Muth and Beth W. Porlier

Rules promulgated by the US Environmental Protection Agency have forced US refiners and importers to radically change their product. While gasoline has held most of the attention, the regulations covering mid-distillates are also extensive, beginning with particulate and emissions standards in the mid-1980's and ending with the reformulation rules that began in October 1993. The assessment of sulfur and aromatic content as deleterious resulted in the final rules for on highway fuels which specify a 0.05 wt. % limit on sulfur content and a fuel cetane index ~ 40 to control aromatics. Fuels not meeting the on-highway requirements are required to be dyed blue (later changed to red) for easy identification. Most refineries have built or converted hydrotreaters to meet low-sulfur demands. Deep hydrotreating, besides reducing sulfur may change many of the physical/performance properties of the new fuel. Issues and concerns have been raised regarding lubricity, conductivity, corrosion protection, fuel detergency, and low temperature handling properties of the on-highway fuel. Cetane number and stability could be predicted to improve. In practice, however, very slight cetane improvement (approximately 1 cetane number) is being realized. Color stability is greatly improved by hydrotreating, but the same improvement in sediment control has not been uniformly observed. While sludge formation is generally reduced, the inherent solvency of the hydrotreated fuel may also be reduced and sediments may still form. Fuel stability additives can effectively control the residual propensity for sediment formation. Hydrotreating also reduces fuel lubricity, conductivity and corrosion protection. This paper will discuss the additive technology that is effective in meeting the industry needs mentioned above resulting from the October, 1993 US diesel reformulation.

THE EFFECTS OF DYEING DIESEL FUEL "BLUE"

Erna J. Beal, Lynda M. Turner, Dennis R. Hardy and Calvin J. Martin

The recent requirement that a blue dye be added to all high sulfur, off-highway diesel fuels raised many concerns among diesel fuel users about the detrimental effects on the fuel of the addition of the blue dye. In order to assess the immediate effect of the blue dye on contamination, the Naval Research Laboratory examined 6 F-76 fuels and all 15 possible 50:50 combinations of these fuels. All fuels were filtered before dyeing to set existing contamination levels to 0 mgs/L. Each fuel was dyed with 30ppm, w/v, of blue dye and allowed to stand for 24 hours in the dark at ambient laboratory conditions. A modified D5452, "Test Method for Particulate Contamination in Aviation Fuels by Laboratory Filtration" was used to gravimetrically determine the amount of filterable contamination formed in the fuels. The results of these tests, which show that the blue dye caused an immediate detrimental effect in all 6 fuels and 15 fuel combinations, will be given.

LUBRICITY CHARACTERISTICS OF LOW SULFUR, LOW AROMATIC CONTENT NAVAL DISTILLATE FUEL

Richard Strucko, Robert M Giannini, Bryan D. Shaver, and Paul I. Lacey

California-type diesel fuels are restricted to a maximum sulfur content of 0.05 wt% and a maximum aromatics content of 10 vol% because of environmental regulations. However, there have been instances where these fuels have exhibited low-lubricity characteristics in over-the road diesel engine operations. The U.S. Navy may be required to use this type of fuel in the near future when operating in California coastal waters. The Navy, therefore, has initiated a program to determine the effects that the increased refining severity employed to achieve the lower sulfur and aromatic limits will have on lubricity, and hence, durability of fuel handling and diesel fuel injection equipment. Fuels conforming to Military Specification MIL-F-1688H, Fuel Naval Distillate (NATO F-76) were obtained from five refineries worldwide. This fuel is the primary fuel used in all U.S. Navy surface ships. Lubricity evaluations will employ the Ball-On-Cylinder Lubricity Evaluator, AS1M D 5001 and the U.S. Army Scuffing Load Wear Test method. A modification to the above tests may be required to account for the uniquely high salt and moisture concentration in Navy fuels before lubricity evaluations of a forty-two sample test fuel matrix will begin.

SESSION 13: POSTER SESSION

THERMAL STABILITY OF DIESEL FUELS BY QUANTITATIVE GRAVIMETRIC JFTOT

Erna J. Beal and Dennis R. Hardy

The gravimetric jet fuel total oxidation tester (*JFTOT*) was developed several years ago to provide *JFTOT* conditions which measure quantitatively the solid/deposit products formed in aviation fuels. The gravimetric *JFTOT* has now been used to measure these products in a small set of typical diesel fuels. These baseline data are compared to a much larger data base of jet fuels and also several pure compounds. Results from the diesels indicate that the gravimetric *JFTOT* is a useful concept for ranking fuels for their thermal stability. The diesels ranged from

quite low (better than jet) to quite high (an order of magnitude greater than jet fuel) in their deposit forming tendencies. Properly ranked fuels can be used in device tests such as diesel injectors and gas turbine nozzles to assess deposition. In addition, diesels with appropriate viscosities may be able to be used as aviation fuels provided the gravimetric *JFTOT* gives a low deposition rating.

STABILITY OF LIGHT STRAIGHT RUN DIESEL FUEL DURING LONG TERM UNDERGROUND STORAGE IN SMALL SIZE STEEL TANKS

Joseph Geva, Judith Propes, Yakov Sufrin, Arthur Weiss, Max Schuftan, Zvi Lavy and Rephael Fass

Three batches of Light Straight Run Diesel Fuel (LSRDF), dyed by a green marker, were stored for five years in precleaned 50,000L, steel, cylindrical, underground storage tanks, with or without biocide and a stabilizer additives package. During this period, the fuels were kept dormant and no draining operations were performed. A close follow up on the chemical properties, biocide content and the level of microbial contamination, in the stored fuels, was done throughout the storage experiment. The chemical properties of the untreated fuel remained unchanged but the microbial contamination in 'bottom-bottom' samples gradually increased during the first year and remained high for the next four years. In contrast, no microbial activity was found in the treated fuel tanks. However, in the fuel treated only by biocide, the dye green marker gradually diminished while 'acidic' odor emitted, however the fuel stayed within chemical specifications range. Fuel treated with stabilizer additives package kept its chemical properties unchanged for the five years storage. The results indicated that untreated LSRDF can be stored for at least five years without any significant microbial or chemical damage, provided good starting condition and no turnover taken place. The biocide treated effectively hindered microbial activity but enhanced a slight oxidation activity in the fuel. Stabilizer additive addition prevented this minor oxidation, while keeping the fuel and the storage tank free from microbial contamination.

STORAGE STABILITY OF LIGHT CYCLE OIL: STUDIES FOR THE ROOT SUBSTANCE OF INSOLUBLE SEDIMENT FORMATION

Katsunori Motohashi, Kingo Nakazono, and Masami Oki

The storage stabilities of a raw and pretreated light cycle oils (LCOs) have been studied under the condition of AS1M D2274-88. The raw LCO was pretreated by five methods; 10% sulfuric acid-extraction, 10% sodium hydroxide-extraction, methanol-extraction, active clay treatment, and catalytic hydrotreating. The raw and pretreated LCOs were aged at 95°C for 144 hours while oxygen was bubbled. The pretreatment except 10% sulfuric acid-extraction showed the decreasing sediments. After removing the sediments by filtration, the changes of component of the residual oils before and after aging, were analyzed by GC/MS, GC/AED and GC/NPD. Remarkable changes were observed in nitrogen compounds such as anilines and indoles, sulfur compounds such as thiophenols, and oxygen compounds such as phenol and its derivatives. It was clarified that the sediment formation was caused by the mutual interactions among

heteroatom-containing compounds mentioned above. In addition, unstable hydrocarbons were suggested to behave as key-compounds for sediment formation.

AUTOMATIC STABILITY ANALYZER OF HEAVY FUEL OILS

Olli Pilvio

NESTE has a long history in development of production process and in the improvement of product quality by increasing automated quality adjustment and control. The objective has been to raise production efficiency and to ensure the maintenance of quality levels when using different crude oil grades, and to make economically such products that meet the requirements of the market.

EFFECT OF COAL CONCENTRATION ON STABILITY OF DISTILLATE FRACTIONS FROM COPROCESSING

P. M. Rahimi, J. F. Kelly, R. J. Torres-Ordonez and U. Lenz

Naphtha, light gas oil and heavy gas oil fractions obtained coprocessing 5 wt % and 30 wt % maf Forestburg subbituminous coal and Cold Lake vacuum bottoms were characterized for physical and chemical properties. These primary distillate fractions which were obtained in a non-catalytic process were stored at 43°C for up to 16 weeks in air to determine their storage stability before being processed to produce commercial synthetic crude oil. The initial results obtained from accelerated stability test (D2274) and total acid number (D974) predicted that the distillate fractions obtained using 30 wt % coal were less stable than the distillates obtained using 5 wt % coal. A 16-week aging test at 43°C confirmed the initial prediction. Very little or no filterable sediment was formed during 16 weeks in bottles containing low coal and high coal naphtha fractions. Sediment formation increased as the boiling point of the fraction increased and the coal concentration of the initial feedstock from which the distillates were obtained increased. The formation of adherent gum was more noticeable and increased substantially with time. Although more adherent gum is formed in high coal naphtha, considerably less adherent gum is formed in high coal light gas oil. The heavy gas oil fraction obtained in the high coal run produced more adherent gum than the corresponding fraction from low coal after 16 weeks. The initial existing gum in high coal naphtha was nearly double that of the low coal naphtha and increased slightly with time. Substantially more existing gum was found in high coal light gas oil than the low coal light gas oil and increased during the 16 week test. Overall, distillates from the high coal run produced more gum and the total gum (mg/100 mL) for all samples tested increased with time.

UTILIZATION OF THE SPENT CAUSTICS GENERATED IN THE PETROLEUM REFINERIES IN THE CRUDE DISTILLATION UNIT

G. N. Sarkar

Generally, 2 to 3 mg caustic per Litre of Crude Oil is used in the desalting Unit to take care of the acid generated from the Calcium and magnesium chlorides present in the crude Oil. Another 7-8 mg caustic is again added per litre of crude Oil to take care of the residual chlorides left over

after desalting in the atmospheric distillation column. The spent caustics from the refineries contains a considerable amount of free sodium Hydroxide along with the pollutants like Sulphides, Phenolics and Mercaptides. The various distillation cuts contain considerable amounts of Phenols, thiophenols, Mercaptans etc. and can sustain with the finished streams from them with the stipulated specification. In the present work it is shown that the addition of this spent caustic in the crude oil will not only save the consumption of fresh caustic but will also solve the disposal problem which is major concern for pollution and at the same time will not deteriorate the products as well as equipments.

ANALYSIS OF SULFUR-ORGANIC COMPOUNDS IN JET FUEL BY CHROMATOGRAPHIC SNIFFING AND GAS CHROMATOGRAPHY WITH ATOMIC EMISSION DETECTOR

Per-Alee Skoog

When the Swedish Air Force changed fuel from Jet B to Jet A-I during 1991-1992~ a working environmental problem was reported from the military air force bases. The symptoms were unpleasant odour, head ache and indisposition. This problem arose from some batches of the new fuel, Jet A-I. In order to investigate the compounds in the fuel which gave rise to this problem a chromatographic sniffing technique (sensory analysis) was used. The identification of the compounds from the sniffing analysis was done with a atomic emission detector for gas chromatography. The problem stemmed from relatively volatile sulfur-organic compounds. An interesting question is if these compounds also are strongly involved in the fuel system deposit formation. This presentation shows this new analysis technique and the complex pattern of sulfurorganic compounds related to fuels from different refinery processes.

AUTOMATED DEPOSIT-MEASURING DEVICE (ADMD)

Leo L. Stavinoha and Lona A. McInnis

The Automated Deposit-Measuring Device (ADMD) was developed and fabricated for the evaluation of lacquer-type fuel and lubricant deposits on Jet Fuel Thermal Oxidation Test (JFTOT), ASTM D 3241, heater test tubes. The ADMD employs commercially available components that provide enhanced speed and accuracy of data acquisition as well as improved maintainability, as compared to the prototype Deposit-Measuring Device (DMD) developed in an Army/Navy program. Application of power to the ADMD automatically brings up an operator selection menu on the vacuum fluorescent display. One of five modes of operation can be selected, including both short and long JFTOT tube length and transference of data from random access memory (RAM) to a personal computer (PC) diskette, if the ADMD is already attached to a PC. Maximum breakdown voltage for the DMD is 1,500 volts, compared to 1,372 volts in the ADMD. This difference in voltage will affect maximum measurable volume of deposit, causing the ADMD to sometimes yield a smaller total volume than the DMD. This fact is a problem only with the thicker deposits. The repeatability of the ADMD is at least as reliable as that of the DMD. Comparison of the ADMD values with the old and current values of the DMD reveals a compatibility between the two devices. The correlation between the volume of deposit of the ADMD and carbon bumoff is superior to the correlation between the volume of deposit of the

DMD and carbon bumoff. The ADMD is a viable and reliable instrument for measuring deposit on JFTOT standard and long test tubes. This report describes the ADMD features and compares correlations to DMD data and carbon bumoff data. Advantages and limitations of ADMD-derived data are demonstrated and discussed.

INVESTIGATION OF SENSITIVITY TO MICROBIAL INFECTION OF DIESEL FUEL AT THE REFINERY STAGE

Eric Swttrup Thomsen and Simone Petersen

In the practice of a company dealing with microbial problems of infected fuels it was possible to use associations of microorganisms in research. These associations of "wild" microorganisms appeared succesful in the environment of ship's fuel tanks, causing severe problems at the consumer level. Fresh "raw" diesel fuel was inoculated with the cultures to investigate the sensitivity of the fuel to microbial infection at the refinery stage. The fuel samples received from Danish refineries were specified as free of any additives or biocides. Before inoculation the samples were tested for presence of inhibiting substances or infection. Samples of "raw" fuel was added 1/10, 1/100 and 1/1000 of infected fuel, incubated at 27°C and observed for 14 days. Other samples were incubated at 5 °c and combinations of periods at 50 and 27 °c. In the absence of water or nutrients the inoculum did not appear to survive and colonize the "raw" fuel, although one sample did produce microbial growth in an order of magnitude corresponding to common definitions of fuel infections. The ability of the two relevant associations of "wild" microorganisms to infect the "raw" diesel fuel was not clearly demonstrated at this point.

PREDICTING STABILIIY AT THE REFINERY USING SMORS

Margaret A. Wechter and Dennis R. Hardy

Previous work has described the relationship between the methanol extractable, hexane insoluble material isolated from aged fuel stocks and storage instability. A predictive test for stability which uses this relationship has been suggested for field use. This paper presents results derived from refinery fresh fuel stocks upon being subjected to a standard storage stability test (ASTM D 5304) and subsequent isolation and quantification of SMORS from the filtered product. Additional evidence which links the extractable material (SMORS) with insoluble sediment formed during long term storage is also presented. The authors suggest a predictive test for fuel stability which might be used as early as the refinery and which might serve as a basis for recommending storage terms for fuel stocks.