

**4TH INTERNATIONAL CONFERENCE ON STABILITY
AND HANDLING OF LIQUID FUELS
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Abstract Summaries

SESSION 1: UNDERGROUND AND STRATEGIC STORAGE

PETROLEUM STOCKPILING PROJECTS - A WORLDWIDE SURVEY

Harry N. Giles

In the western world, stockpiling of petroleum dates to 1938, when the looming specter of world war prompted the British government to begin building buried tanks for reserves of aviation gasoline. Similarly, stockpiles of gasoline and middle distillate fuels were developed in Sweden beginning about 1940 and continuing throughout the decade; although, cavities excavated in rock were used for these reserves. These early projects were fairly modest in size compared with some of today's petroleum stockpiles. The advent of large-scale stockpiling is believed to date from 1956, when the British government responded to the Suez crisis by constructing solution-mined cavities in bedded salt near Chester, England for crude oil storage. A further expansion in worldwide development of petroleum stockpiles took place in 1966, when South Africa began storing crude oil in converted coal mines. In 1969, France commenced a program utilizing a converted iron mine and solution-mined cavities in salt; followed, in 1971, in Germany by construction of solution-mined cavities in salt for stockpiling of crude oil. Not until after the oil crisis of 1973-74, however, did the United States begin a strategic petroleum reserve program. Many of these projects have been expanded and now include other products and means of storage, increasing their versatility to respond to differing interruption scenarios, and contributing to greater storage security and integrity. Today, Finland, Norway, Denmark, Japan, Italy., the Netherlands, Switzerland, Morocco, South Korea, and Saudi Arabia are also known to have petroleum stockpiles. These reserves may be government-owned, company-held, or both. Stockpiles of gasoline and aviation turbine fuel apparently exist in the Soviet Union, several eastern European countries, and Iraq, but little information is available on these projects. A number of different technologies have been used for stockpiling of petroleum reserves. These include aboveground and buried tanks, floating vessels, converted mines, and specially-constructed cavities in rock. Worldwide, there is now a documented strategic storage capacity of over 150 million m³ in tanks or rock cavities ranging from under 5,000 m³ to more than five million m³. Regardless of the mode of storage or the size, three principal factors will determine the extent to which degradation in quality of stored petroleum will occur, namely: instability, incompatibility, and contamination.

SUMMATION OF EXPERIENCE GAINED IN DENMARK OVER A 25 YEAR PERIOD IN OIL STORAGE IN ABOVE- AND UNDERGROUND TANKS

John M. Rasmussen

The Association of Danish Oil Reserve Stocks (Foreningen Danske Olieberedskabslagre) was established in May 1964 by law and concerned all oil companies with stock obligations to fulfill. The purpose was to build capacity to contain strategic storage in underground tanks of gasoline and automotive gasoil. In May 1972, another law was passed - as a consequence of Denmark's membership in the EEC - to provide storage facilities in aboveground tanks to carry minimum stocks corresponding to 90 days sales of gasoline, middle distillates, and fuel oil. The strategic underground storage stocks (A) are held in depots throughout the country; whereas, the minimum storage stocks (M) are kept in three tank farms and contained in large aboveground tanks. All storage depots and tank farms are connected by pipelines, and the system has harbor facilities at certain locations for supply by tankers. The B storage (strategic) consists of approximately 450,000 m³ of gasoline and 350,000 m³ of automotive gasoil, and the M storage (minimum) holds some 1,300,000 m³ of heating gasoil and 260,000 tons of fuel oil. The petroleum products - originally all of straight run, non-cracked material - have, in principle, been in storage since purchased successively over the years. A total rotation of stocks commenced in 1988, and is planned to be completed by 1994. In recent years our quality monitoring has provided us with evidence of a deterioration in the long-term stability in some parcels of our gasoil. Hence, the decision to initiate an accelerated rotation of all our stocks of gasoil, and also of gasoline due to its relatively high lead content. The quality of gasoline and gasoil available in the marketplace today appears to require a rotation period of two to three years. Our infrastructure and overall handling capability is not designed for a rotation of products on such a scale. We have, therefore, been compelled to plan for a conversion of at least 25 percent of our present storage of petroleum products to crude oil.

SLUDGE FORMATION AND COMPOSITION IN THE U.S. STRATEGIC PETROLEUM RESERVE

John B. Green, Paul W. Woodward, Jane S. Thomson, and Johanna Y. Shay

Formation of a stable emulsion or "sludge" layer has been observed during long-term storage of crude oil in the USA and other countries. The objective of this work was to determine the composition of sludge, as well as factors affecting the rate and ultimate quantity formed from a given crude oil mixture. Sludge formation results from gravitational settling of insoluble or slightly soluble species in crude oil: waxes, brine/seawater, and inorganic particulates. Sludge also contains crude oil entrapped via settling of the above components. The composition of crude oils entrapped in sludge is similar to that of the bulk crude for storage reservoirs or caverns with adequate convective mixing. Minor sludge constituents include components carried into the sludge layer concurrent with deposited wax or brine. Some of these minor constituents, particularly those soluble in the brine, may promote sludge formation and stabilization.

THE COMPOSITION OF SLUDGE WAXES FROM UNDERGROUND CRUDE OIL STORAGE RESERVOIRS

Jane S. Thomson, Ronald D. Grigsby, Daryl A. Doughty, and Paul W. Woodward

Long term strategic storage of crude oil in underground salt domes frequently produces a bottom sludge layer, reported to contain inorganic sediment, agglomerated waxes, polar compounds, and entrained brine. "Wax" is an operationally-defined mixture produced by chilling petroleum stocks at temperatures below production levels, either directly, or in the presence of added solvent. It consists largely of higher molecular weight α -paraffins, and also includes aromatics and polar compounds. There is considerable interest in the formation of wax-crystals during transportation and storage of crude oils, because wax formation causes an increase in crude oil viscosity, and can lead to gelling of crudes and plugging of pipelines. Recent studies are reviewed.

ORIGIN AND COMPOSITION OF SLUDGE-ENTRAINED BRINES IN THE U.S. STRATEGIC PETROLEUM RESERVE

John B. Green, Shirley K.-T. Yu, and Paul W. Woodward

The composition of brines entrained in "sludge", a stable emulsion of brine, wax and crude oil formed in minor amounts over long-term storage of crude oil, was investigated. The objectives of the work included determination of the origin of brine in sludge, as well as factors responsible for the stability of the emulsion. Sludge-entrained brine originates from settling of oil field brine in as-received crude as well as from injection of fresh or brackish water during cavern operations. The contribution of brine originally present in the cavern from solution mining is negligible. The salinity of sludge entrained brine typically varies from near relative saturation at the top of the sludge layer, to g. 50% saturation at the sludge/bulk brine interface. Prominent inorganic components include bromide, sulfate, and strontium ions, in addition to the major component--sodium chloride. Organic carbon content typically approaches 0.1 wt%. Organic constituents include polyglycols, sulfoxides formed from cyclic sulfides, alkylquinolines, straight-chain fatty acids containing from 2 to 20 carbon atoms, and minor amounts of phenol, C1 -C3-alkylphenols, and other aromatic species with one or more polar functional group(s). The majority of the organic components originate from liquid-liquid extraction into brine droplets as they settle through the bulk crude oil into the sludge layer. Organic components of brine, particularly polyglycols, may stabilize the sludge emulsion and contribute to sludge buildup.

MICROBIAL ACTIVITY IN CAVERNS OF THE STRATEGIC PETROLEUM RESERVE

Rebecca S. Bryant, Karen L. Chase, and Anita K. Stepp

To determine the impact of microbial activity on the Strategic Petroleum Reserve (SPR), research has been performed at the National Institute for Petroleum and Energy Research (NIPER) to identify the actual microbial populations that are present in the SPR caverns. The ultimate goal of this research is to provide information and recommendations for the Office of the Strategic Petroleum Reserve (OSPR) to establish procedures for crude oil storage that will mitigate any potentially harmful biological activity. Sludge is known to form in most subterranean caverns used for the storage of crude oil. The formation of sludge may be

exacerbated by the presence of microorganisms in the surface water used to leach salt dome caverns and to periodically displace oil from these caverns. This surface water becomes hypersaline rather rapidly once it is injected, so that microbial activity on stored crude oil should be insignificant. Nevertheless, repeated injections of surface water for operational purposes and repeated introduction of new crude oil from various sources may result in episodic growth of microorganisms capable of metabolizing hydrocarbons. Results from microbial testing of samples are presented in this paper. Correlations of microbial activity are made with the presence of sludge and sour crude oil occurrence in these caverns. Based upon the samples received, microbial activity does not appear to contribute to sludge formation. High microbial activity was detected only in cases where fresh water persisted at the interface between the brine and oil. There are microorganisms present in many of the caverns, and there are more microorganisms present when sludge and/or sour crude oil is indicated.

SESSION 2: MICROBIAL ASPECTS OF PETROLEUM HANDLING AND STORAGE

MICROBIOLOGICAL STUDIES RELATED TO PROLONGED STORAGE OF CRUDE OILS IN SALT CAVERNS

K. Bosecker, A. Morche, R. Naveke, D. Panzer

Crude oil and oil product storage in solution mined salt caverns has now been practiced since more than 20 years. Despite of this long period of time only few studies have been performed on the long-term behaviour of the stored oils. In 1978 studies in qualitative effects from prolonged storage of crude oil and heating oil in salt caverns have been conducted which demonstrated deleterious changes in quality years¹. Some findings from that the oils do not undergo during storing over a number of crude oil/brine interfaces in caverns e.g. sludge/emulsion formation and the presence of methane however may indicate that microbiological activity could be present at the interface. For this reason in 1988 microbiological investigations have been conducted on oil and brine samples from caverns after prolonged storage.

CORROSION IN A CRUDE OIL PIPELINE CAUSED BY BACTERIA

Wolfram Kleinitz, Hans G. Behrendt

Crude oil from eleven different production stations is transported. to the tank farm near Hannover, Germany, by way of a 6 and 8" pipeline. After 25 years of operation, internal pitting corrosion has been detected in the 8" section. A magnetic inspection log has indicated 108 pits with a decrease in wall thickness by more than 50 per cent. Bacterial analyses of the free water from various sections of the pipeline system revealed the presence of up to 10^5 hydrogen-utilizing sulphate-reducing bacteria per millilitre in some samples. Three morphologically different sulphate-reducing strains have been isolated in pure culture and examined with respect to their adaptation to conditions prevailing in the pipeline (high salt content and low temperature). The frequent occurrence of methanogenic and homoacetogenic bacteria in counting series and enrichments, besides sulphate-reducing bacteria, indicates that other metabolic types of hydrogen-utilizing bacteria may be important in the pipeline system, as well.

On the basis of the results from the chemical and microbiological investigations, a plastic liner (PE) has been installed in the 8" pipeline to prevent further corrosion in the system.

EFFECTS OF STABILIZING ADDITIVES ON THE SUSCEPTIBILITY OF DIESEL FUELS TO MICROBIAL ATTACK

J. Geva, J. Propes, J. Papier, M. Busanni, E. Zehavi and R. Fass

Three different types of Diesel fuels, with or without stabilizer additives, were tested regarding their susceptibility to microbial growth. The fuels were sampled from buses of the public transportation system during actual road service (before and after a 300 Km ride). The experiments were performed in two stages: In stage one, fresh Diesel fuels (with and without additives), before and after a 300 km ride, were submitted to the experimental system. The experiments involved incubating the different Diesel fuels in contact with microbial contaminated water (fuel/water ratio 4:1), at 26°C under static conditions, for one year. In stage two, Diesel fuels, after one year storage in drums outdoors, before and after 300 km ride, were tested in an experimental system where the fuel/water ratio was 100:1. The fuel types in stage two included the same fuel types as in stage one. In addition, a new stabilizer and a new biocide were investigated. The results indicated that the road service did not influence the susceptibility of any of the fuel types to microbial activity. However, it was found some evidence that stabilizer additives enhanced the microbial activity in the water phase of the two experimental systems, even though two commonly used biocides were included in the additives package. Diesel fuels with no stabilizer additives which contained a biocide consisting of the same active ingredients as the biocide included in one of the stabilizer additives packages, prevented microbial growth. It is assumed that incompatibility of the biocides and the stabilizer additives deactivated the biocides. The results of the study suggest that improving stability of Diesel fuels in service by the storage addition of additives might create a microbiological problem in the fueling system. Therefore, It is strongly recommended to include biocides which are effective and compatible with both the fuel and the stabilizing agents, in any additives package.

A COMPUTERIZED EXPERT SYSTEM FOR DIAGNOSIS AND CONTROL OF MICROBIAL CONTAMINATION IN JET FUEL AND DIESEL FUEL STORAGE SYSTEMS

J. Hartman, J. Geva and R. Fass

Microbial contamination of Jet fuel and Diesel Fuel in different storage situations may lead to the deterioration of some fuel properties as well as to operational problems and severe corrosion of storage tanks. The effects of microbial contamination on the properties of fuel and the effects of contaminated fuels on the distribution systems and at the end user level depends upon the fuel type and the nature of the end user. Therefore, the evaluation of fuel tests results and any recommendation for maintenance work or preventive measures to be taken depend on the type of fuel and the storage situation. Recently we have presented a computerized expert system which uses an artificial intelligence approach to deal with Jet fuel storage in large above ground storage tanks. We present here an expanded version of the system which includes the analysis of several Diesel fuel storage situations. The diagnostic procedure is based on a set of microbiological and chemical measurements in the fuel and in the water bottom of the storage tank. Analysis of the results coupled with the definition of the maintenance state of the storage tank leads to

recommendations of appropriate corrective measures to prevent future damage. A user-friendly interface can justify the program's final decisions and its intermediate findings. The system acts as an expert consultant providing judgment and explanations based upon the tests' results. The computer program written in PROLOG is implemented on an IBM- PC.

SESSION 3: INCOMPATIBILITY

A CHEMICAL AND PHYSICAL EXPLANATION OF INCOMPATIBILITY DURING REFINING OPERATIONS

James G. Speight

The incompatibility of feedstocks and products is a continuing issue during refining operations. The occurrence of sediments during thermal operations and from products during storage reduces the efficiency of a variety of processes. The polar (i.e. heteroatom) constituents of feedstocks are responsible for the formation of such sediments. This is particularly true of the higher molecular weight constituents, i.e., the asphaltenes. Petroleum asphaltenes are defined as the pentane- or heptane-insoluble fraction of crude oil. The nature of the molecular species that constitute asphaltenes has been a well-researched subject over the past three decades. For whatever reasons, it has been the general consensus of the majority of the researchers that asphaltenes are predominantly highly condensed systems that are graphitic in nature. Such models are difficult to use to explain the chemistry and physics of incompatibility. A more logical conclusion is that petroleum asphaltenes contain much smaller condensed aromatic systems that are consistent with the components in other fractions of crude oil feedstocks. Such formulae are based on the inclusion of structural entities from natural product origins which are more appropriate for the prediction of incompatibility in refining processes and in products. This presentation deals with the use of the formulae to explain various aspects of asphaltene behavior including deposition in petroleum reservoirs, sludge formation, refining/conversion to fuel oils, asphalts, and the like.

FORMATION OF ORGANIC SLUDGE IN INCOMPATIBLE FUEL OIL BLENDS

Husna Kassim and Zakaria Man

Ignition and combustion problems aside, one of the greatest factors causing operational problems in utilizing blended fuel oil is incompatibility. The present study highlighted incompatibility in fuel oil. as mainly due to improper selection of the diesel used for the viscosity blending. In blending a residual fuel oil, a distillate stock of sufficiently high aromaticity, that is high C/H ratio must be used to ensure that the asphaltenes present in the residual component remain adequately peptised in the final fuel blend. Excessive sludging is most pronounced in the low viscosity fuel blends, such as 10 cSt and 30 cSt where volumes of the paraffinic commercial diesel used are higher compared to volume used to prepare blends with higher viscosities such as 50 cSt or 80 cSt. The formation of sludge in incompatible fuel oil. blends are governed by four factors, namely the dilution, compositional, asphaltenes solubility and other special compounds. These factors influenced 67%, 9%, 9% and 2% of the sludge formation while the last 13% could not be explained using the present set of data. The problem of sludging due to incompatibility could be alleviated by using a more aromatic fuel oil diluent or adding a high aromatic diesel to

the commercial diesel currently used for blending. Types of diesels that could be used are heavy catalytically cracked cycle oil, cycle oil slurry, or vacuum gas oil. The present study showed 35% to be a sufficient quantity of light cycle oil to be added to the commercial diesel to produce satisfactorily sludge-free fuel oil products at any viscosity.

SESSION 4: THERMAL STABILITY OF AVIATION TURBINE FUELS

THERMAL OXIDATION STABILITY OF AVIATION TURBINE FUEL: A SURVEY

Robert N. Hazlett, Robert E. Morris

Three serious operational problems have been experienced with jet fuel thermal stability over the past 35 years. Two of these problems were associated with combustor nozzle fouling and the third involved deposition on interior surfaces of the main engine control. These difficulties have been alleviated by modifying engines, developing and upgrading fuel specifications and test equipment, changing refinery processes, and defining the chemistry of fuel instability. Among physical factors affecting thermal stability, temperature is the most important. Studies of temperature effects in many different test rigs have all found increases in deposition as temperature rises, at least up to about 350°C. The rates of increase, however, as represented by energies of activation are widely different in various devices. Pressure in the test rig is not a major factor if it is maintained at a value in excess of that needed to prevent vapor formation at the test temperature. Fuel flow velocity appears to affect deposition, the latter increasing at low velocities. The character of a heated surface in contact with jet fuel exhibits a significant effect on deposition rate and this is an active area of current research. Chemical processes are intimately involved in thermal stability. Autoxidation is a significant process and removal of dissolved oxygen makes all fuels, except some sulfur containing ones, much more stable. Hydroperoxides are the key intermediates in the autoxidation scheme. Compounds containing oxygen, sulfur, nitrogen and metals are major participants in deposit formation. Copper is the most active metal, exhibiting effects at 15-50 parts/billion. The very small extent (<0.1 ppm) of conversion of jet fuel into harmful insolubles in an aircraft fuel system makes the tracking of susceptible molecules very difficult even with sophisticated analytical instruments. Antioxidants, metal deactivators, dispersants and passivators have some merit in improving thermal stability but they should be used with caution.

AN INVESTIGATION OF THE DEGRADATION OF AVIATION FUEL THERMAL OXIDATION STABILITY DURING TRANSIT

Richard A. Kamin and Clarence J. Nowack

The United States Navy has experienced an increase in the number of incidents involving the degradation of the thermal oxidation stability of JP-5 fuel (F-44) occurring during transit and storage. The cause of this degradation has been postulated to be either trace contamination and/or chemical compositional changes within the fuel. Due to both the uncertainty of the cause of degradation and the subjectivity of the current Jet Fuel Thermal Oxidation Test (JFTOT), varying options exist on how to deal with these fuels. This paper discusses the Navy's multifaceted investigation into this problem. Emphasis will be placed on 1) the testing used to

identify the severity and potential cause of the degradation, 2) the relationship between the JFTOT test results of an off-specification fuel and the fuel's potential effects on aircraft hardware, and 3) the potential role of Metal Deactivator Additive (MDA) in the upgrading of an off-specification fuel.

COMPARISON OF ACCELERATED PREDICTIVE TECHNIQUES TO MEASURE THE OXIDATIVE TENDENCIES OF AVIATION FUELS

Lynda M. Turner and Clarence J. Nowack

Extensive research has been conducted in the development of a method to accurately predict the degradation behavior of JP-5 in storage. Until recently, the only method universally accepted in the fuel research community was the 65°C bottle storage method. Recent research has been directed in the development of three different "reactors" used for predicting oxidation rates. The basic principle of these "reactors" is similar with the difference being in the way oxygen is introduced into the sample. Two hydroprocessed JP-5 samples were analyzed by all three techniques and compared to the bottle storage method. This paper will present the results and propose that oxidation prediction may be made used as an alternate method as opposed to the labor-intensive bottle storage technique.

RESULTS AND EVALUATION OF A JET FUEL THERMAL STABILITY FLOW DEVICE WHICH EMPLOYS DIRECT GRAVIMETRIC ANALYSIS OF BOTH SURFACE AND FUEL INSOLUBLE DEPOSITS

Erna J. Beal and Dennis R. Hardy, Jack C. Burnett

The purpose of this paper is to precisely define the basic parameters of the current ASTM D3241 standard test method/apparatus and to examine how these parameters affect thermal oxidation deposition. By reproducing these defined parameters, it is possible to construct a new device that allows for direct determination of deposit weight by weighing the test substrate before and after the test. The usefulness of these gravimetric results in defining jet fuel thermal stability will be explored.

THE EFFECT OF TEMPERATURE ON JET FUEL THERMAL STABILITY USING A FLOW DEVICE WHICH EMPLOYS DIRECT GRAVIMETRIC ANALYSIS OF BOTH SURFACE AND FUEL INSOLUBLE DEPOSITS

Dennis R. Hardy and Erna J. Beal, Jack C. Burnett

The successful use of a new thermal stability flow device which employs direct gravimetric analysis of both surface deposits and filterable fuel insolubles at 260° C has been previously described. In this work several of the aviation fuels evaluated at 260° C by this new technique are selected for further study at temperatures up to 360° C. In addition, the effect of oxygen and of surface metallurgy on thermal stability has been examined. Based on the gravimetric results it is possible to propose: a theoretical model for fuel thermal stability which invokes both chemical and physical aspects in a much more general and useful way than previously proposed models.

QUANTITATION OF FUEL DEPOSITION ON HOT METAL SURFACES

L.L. Stavinoha, S.R. Westbrook, D.W. Naegeli, S.I. Lestz

Experiments were performed in a Hot Liquid Process Simulator (HLPS) configured and operated such that it performed under conditions similar to Jet Fuel Internal Oxidation Tester (JFTOT) ASTM D 3241 requirements. The JFTOT heater tubes used were 1018 mild steel, 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, 340 and 380°C. Deposit thickness was measured by dielectric breakdown voltage and Auger ion milling. Auger ion milling of the deposits showed the order of deposition to be copper > Mild Steel > gold > aluminum > magnesium. The dielectric strength method indicated deposit thickness ranking of Mild Steel > 304 SS > gold > magnesium = aluminum = copper. The 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 burn-off data have been obtained as a means of judging the validity of DMD derived deposit evaluations. ESCA data had suggested that the thinnest deposit was on the magnesium coated test tube. The 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. Aside from variations in the thickness of deposits due to metallurgy, 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 is highly temperature dependent and may be limited by the concentration of dissolved oxygen or reactive components in the fuel. The overall results show that the surface temperature and composition play an important role in deposition.

AN AUTOMATED DEVICE FOR QUANTITATIVE MEASUREMENTS OF JFTOT TUBE DEPOSITS BY INTERFEROMETRY

Robert E. Morris and Robert L. Wagner, Clark S. Mitchell

The aspect of the JFTOT test procedure that is subject to the greatest variability is the evaluation of heater tube deposits. It has been shown that the visual rating method is very subjective and is not quantitative. While the TOR eliminates operator subjectivity, the values obtained are not always a true representation of the quantity of tube deposit. Total carbon can be determined by combustion from stainless steel tubes, but it is generally not reliable on aluminum heater tubes. A method based on light interferometry has been found to correlate well with combustion data. A computer controlled device was constructed which acquires the data and calculates deposit volumes.

DIFFERENTIAL SCANNING CALORIMETRY- A NEW TECHNIQUE FOR FUEL THERMAL OXIDATIVE STABILITY STUDIES

Dennis L. Ripley, Robert D. Chirico, and William V. Steele, Richard A. Kamin

A new technique using differential scanning calorimetry has potential as a unique tool for examining the thermal oxidative stability of all fuels, and jet fuels in particular. The technique

makes use of a commercially available differential scanning calorimeter, used extensively within the pharmaceutical industry for drug quality-control testing. The development of the new research tool has been made possible by the design and construction of high-temperature (1300° F), high-pressure (1450 psia) cells. In contrast to the relatively large samples required in conventional jet fuel thermal oxidation tester (JFTOT) tests, this technique requires only 50-microliter samples. The basis of the technique has been the realization that when a fuel is heated through the temperature region 250° F to 450° F in the presence of oxygen, chemical reactions occur that produce an excess enthalpy (heat). Research at NIPER on a range of jet and diesel fuel samples has led to the definition of a relationship between the total enthalpy of these reactions and the JFTOT break point of the fuel. This paper discusses the development of this relationship, its extension to other fuel systems, and the use of the differential scanning calorimeter technique in research to find problem compound types within those present in jet fuel samples. In addition, the development of techniques to obtain the kinetics of the initial oxidation reactions that lead to the production of deposits in jet fuels when heat stressed (input parameters for Computational Fluid Dynamics calculations) are discussed.

SESSION 5: STABILITY OF PRODUCTS OTHER THAN AVIATION TURBINE FUEL

STORAGE STABILITY OF MIDDLE DISTILLATE FUELS: A WORLDWIDE SURVEY

Sheila J Marshman and Joanna F Pedley

Middle distillate fuels consisting wholly or partly of cracked products can degrade during storage producing significant quantities of organic insolubles and darkening in colour. A mechanism to account for the formation of a large part of the insolubles produced in ambient storage by such fuels was described at the last conference. A world-wide survey of commercial marine gas oils and refinery product streams was undertaken to investigate the relationship between the fuel chemistry and the nature and quantity of sediment found in the fuel. The concentration of phenalenes/phenalenones and the filter blocking tendency (FBT) of each fuel was determined and any sediment found was characterised. Phenalene species were found in fuels world-wide, confirming the general applicability of the mechanism. There was good correlation between the presence of the phenalene species in the fuels and the presence of the typical 'storage stability sediment'. No phenalenes or phenalenones were found in straight run distillate fractions, which typically contained low levels of sediment, and no detectable 'storage stability sediment'.

MOTOR GASOLINE STABILITY REQUIREMENTS: RESULTS OF A FIVE YEAR TEST PROGRAM

L.L. Stavinoha, J.N. Bowden, and M.E. LePera

This report presents results of a five-year program whose primary goal was the development of improved methods for evaluating motor gasoline stability. Several existing and potential predictive tests were applied to both individual refinery components of gasoline, selected laboratory blends, and commercial gasolines for which ASTM D 525 induction periods ranged from 75 to >5000 minutes. Darkroom storage was conducted at 43°C, 54°C, and ambient temperatures for various time periods with ambient storage ultimately reaching 4 years for many

of the samples. Results confirm the findings of earlier researchers that ASTM D 525 is not viable as a predictive device by virtue of a low coefficient of determination between induction period and gum formed in storage at 43°C for periods up to 1 year. It is recognized, however, that ASTM D 525 is not likely to be abandoned as a specification stability test. Based upon the data generated under the four phases of this storage stability program including supporting data obtained from literature sources and current surveillance information on both military and industry practices, the method recommended for evaluating stability of commercial/military motor gasoline is the ASTM D 873 Method using a 6-hour aging existent gum maximum limit of 5 mg/100 mL. The ability of this test to distinguish between stable and unstable low induction period fuels and/or components is discussed in both terms of gum and engine induction system deposits. Due to the page restrictions, this report attempts to summarize the more important aspects of this program which will be covered in detail by a technical publication distributed by the National Technical Information Center.

COMPARISON OF MIDDLE DISTILLATE FUEL STABILITY TEST METHODS AND THEIR IMPACT ON EVALUATING STABILIZER PERFORMANCE

Bruce E. Wright and Dwight K. Reid

Numerous test methods are used to predict the storage stability of various middle distillate fuel blends. When results from the 43°C (110°F), long-term storage test (ASTM D4625) were compared with results of accelerated tests, in which fuels are severely stressed [temperature > 92°C (200°F)], correlations were not found. However, acceptable correlations were observed between results from some of the moderately accelerated test methods [49°C (120°F) to 80°C (180°F)] and the 43°C storage test. Additionally, stabilizer additive performance was determined to vary depending on the test method used. Some additives appeared to exert a positive stabilization effect on fuels when evaluated in the most severe tests, but were ineffective when evaluated in the low temperature storage test. Other additives provided some benefit in fuels under low stress conditions, but were virtually ineffective on fuel stability when evaluated in the most accelerated tests. Differences in fuel degradation mechanisms associated with test method conditions, and the reactivity of additive chemistries at varying temperatures, is believed to account for the observed performance discrepancies. These findings suggest the need for the industry to re-evaluate current standard test methods used for monitoring storage stability, and also for predicting additive performance in middle distillate fuels. Test results that more closely reflect actual field performance will ensure use of the most effective treatment package for stabilizing distillate fuels.

LONG TERM STABILITY OF RESIDUAL FUEL OILS OBTAINED BY VISBREAKING OF SHORT RESIDUE

Indra D. Singh and Mehendra P. Kapoor

Long term stability, under ambient conditions, of visbroken residues (150°C+) , obtained through Soaker visbreaking of petroleum short residue on pilot plant under different operating severities , were studied in terms of sediment yield and viscosity. The effect of storage time and compositional data of residue (150°C +) as well as structural parameters of asphaltenes on

sediment yield are reported. Qualitative characterization of sediment was done employing infrared spectroscopy. While an increasing trend in sediment yield is obtained with asphaltene and olefin content of residues (150°C), a decreasing trend with asphaltenes is shown. Further, the sediment yield is found to increase with pyrrolic compounds in the residue (150°C+). The comparison of IR spectra of sediment as such and their THY-insoluble portion reveals that latter still contain aliphatic groups predominantly naphthalenes condensed with aromatic clusters.

SESSION 6: HANDLING CONSIDERATIONS IN FUEL INSTABILITY

RELIABLE FUEL

Ubaidallah S. Alghamdi

SAMAREC, Saudi Arabian Marketing and Refining Company, is responsible for the refining, marketing, transportation, storage, and distribution of all petroleum products in the Kingdom of Saudi Arabia. There are seven refineries in the Kingdom and about twenty 'bulk plants in different locations. Petroleum products are transported to these different locations by several means (i.e. trucks, pipelines, railway, and by tankers). This paper will give an overview of the refining systems and products specifications. It will also describe the storage and handling systems and how quality problems are prevented, especially for jet fuel and diesel fuel while in storage and during handling. Quality problems could be related to design, construction materials, operations, and handling. Experience of some of these problems will be discussed and recommendations will be presented. It is of great importance that management function is directed to ensure total quality and reliability and conformance of petroleum products to established specification standards in order to minimize/eliminate costly corrective actions required for off-specification products. Dedication, well trained personnel, and well established procedures are very important tools to ensure that total quality and reliability objectives of petroleum products are met, from the point of production through consumption.

THE EFFECTS OF FUEL COMPONENTS ON THE BEHAVIOUR OF CONDUCTIVITY IMPROVERS IN JET FUEL

B Dacre and W G Abi Aoun

The aims of this work are a) to investigate the way in which fuel additives and naturally-occurring fuel components affect the performance of the conductivity improvers and b) to understand the nature of the intermolecular interactions involved. Solutions have been studied by monitoring the electrical conductivity of solutions of conductivity improvers chiefly in the pure alkanes heptane and dodecane. The parameters studied were a) the conductivity response to additions of other additives or compounds of similar structure, these include antioxidant, icing inhibitor and corrosion inhibitor and b) the conductivity response to additions of compound types similar to those which are naturally-occurring, these include aromatics, organo- nitrogen, sulphur and oxygen compounds. Interpretation of data has to take account of adsorption processes occurring in the measuring cells. The results demonstrate that strong proton donor-acceptor interactions correlate with antagonistic effects on the performance of the conductivity improver. Such effects may be important at extremely low concentrations of strong proton donor molecules.

AUTOMOTIVE DIESEL FUEL FILTER QUALIFICATION METHODOLOGY

Gary B. Bessee, Steven R. Westbrook and Leo L. Stavinoha

This paper discusses the development of a methodology to evaluate military vehicle fuel filters that would become part of a proposed military fuel filter specification. For this study, 13 different fuel filters used on military and commercial vehicles were tested using a multipass fuel filter test stand. Each filter type was tested in triplicate. Test parameters measured included differential pressure across the filter, particulate contamination in both the influent and effluent fuel (measured gravimetrically), filter load capacity, and filter efficiency. Particle size distribution in both influent and effluent fuel was also measured for some of the filters. The filter test results varied widely. Average efficiencies ranged from 65 to 98 percent, and average load capacities ranged from 5 to 80 grams. Analysis of the results illustrated the need for better specification and control of filters used in Army fuel systems. The filtering media in some of the filters tended to separate or channel at widely varying pressure drops. Some of the higher efficiency filters tested were also found to allow a significant number of large diameter particles to pass. A rating system was designed that incorporated filter load capacity and filter efficiency. The product of these two parameters was plotted for each of the filters tested, and a rating scale was determined. The results based on this rating scheme were compared to results obtained by ranking the filters according to other commonly used rating schemes. No two of the rating schemes ranked the filters in the same way. Summaries of a government/industry meeting to discuss the military's fuel filtration needs and a proposed specification are also provided.

SESSION 7: THEORETICAL AND CHEMICAL ASPECTS OF FUEL INSTABILITY

MIDDLE DISTILLATE FUEL INSTABILITY AND HETEROATOM REACTIONS

George W. Mushrush, Dennis R. Hardy, Robert E. Pellenbarg, Robert N. Hazlett

Instability problems in middle distillate fuels have been correlated with the presence of polar heteroatomic species. This observed degradation- can be manifested by the formation of deposits on filters, in nozzles and on combustor surfaces. Heteroatoms (oxygen, nitrogen, sulfur) and ash have been found to comprise up to 4 0% of such deposits. Trace levels of certain organo-sulfur compounds, especially sulfonic acids, have been found to influence dramatically the deposit formation process. Findings that free radical inhibitors were ineffective in controlling stability of middle distillate fuels posed the question: is free radical chemistry the key to distillate fuel instability with respect to deposit formation? The effectiveness of organic amines in countering fuel degradation suggests that acid/base chemistry is also involved in the formation of deposits. A model study of organo-sulfur compounds and hydroperoxides in both middle distillate fuels and hydrocarbon solvent is reported.

SYNERGISTIC EFFECTS IN MIDDLE DISTILLATE STORAGE STABILITY

Kathleen A. Stirling, John B. Green and Dennis L. Ripley

Synergistic actions are those which combine to make a total effect that is greater than the sum of the individual effects. These actions can be either beneficial or detrimental. In middle distillate storage stability, synergistic effects can be measured as increases or decreases in sediment. As part of a study of light cycle oil (LCO), several factors thought to influence storage stability were examined for possible synergistic effects. The effect of existing sediment on the rate of formation of new sediment was studied. Several samples of the same LCO were stored at the same time. Samples were removed, filtered, and returned to the oven over a period of several weeks. The cumulative sediment in those samples was compared to that of samples not subjected to periodic sediment removal. The presence of sediment appeared to slightly retard the quantity of sediment formed over a given time. Interactions between components spanning the middle distillate range were examined by distilling an LCO into four fractions (<240° C, 240-330° C, 330-360° C, and >360° C) and testing the stability of each fraction. The cumulative sediment formed from the four fractions, 1.7 ± 0.2 mg/100 ml, was significantly less than that of the whole fuel, 5.4 ± 0.1 mg/100 mL. Thus, a significant proportion of sediment formation in the whole fuel probably involves reactions between components with appreciably different volatilities. A slate of LCOs and straight-run middle distillates was separated into compound classes using liquid chromatographic techniques. Potential interactions between the various polar compound classes during storage were examined by aging blends of neutral components plus one or more polar classes. Generally, the weighted sum of sediments formed by each individual polar class (blended only with neutrals) was within experimental error of the sediment formed by the whole fuel. Thus, synergistic effects between compound classes were minimal.

STORAGE STABILITY OF MIDDLE DISTILLATE FUELS: DEGRADATION CHEMISTRY OF CATALYTICALLY CRACKED GAS OIL BLENDS

Sheila J Marshman

Several previous papers have described a mechanism for the formation of organic insolubles during the ambient storage of middle distillate fuels containing catalytically cracked stocks. The mechanism involves the acid catalysed condensation reactions between indoles and oxidation products of phenalenes such as the phenalenones. A number of fuel components and blends from UK and European refineries have therefore been analysed for a number of reactive species before and after accelerated ageing at 43°C. These species include mercaptans, acid content, phenalenes, phenalenones and indoles, and an attempt has been made to relate these concentrations to the insolubles content of the fuels after ageing.

STORAGE STABILITY AND HYDROTREATING CHEMISTRY OF PHENOLIC COMPOUNDS PRESENT IN MID-DISTILLATE

John B. Green, Kathleen Q. Stirling, and Dennis L. Ripley

Light cycle oils (LCO) from commercial-scale processes were fractionated into acidic, basic and neutral types using nonaqueous ion exchange liquid chromatography. Accelerated storage stability testing of those fractions showed the acid fraction to contain the bulk of the sediment and color-forming species present in LCO. Further fractionation of the whole acid concentrates into compound classes, in conjunction with stability testing to determine the relative contribution of each acidic class to sediment formation, showed an appreciable contribution from phenolic compounds toward the instability of most LCOs. Chemical modification of whole LCOs was also used to determine the relative impact of phenolic compounds on storage stability. GC/MS analysis of phenolic concentrates before and after accelerated aging revealed dramatic decreases in alkylphenol, indanol and alkylindanol, and 2-naphthol concentrations after aging. Changes in concentrations of alkylnaphthols, phenylphenols and alkylphenylphenols, fluorenols and alkylfluorenols, and naphthylphenols/phenylnaphthols were generally smaller in magnitude and more variable among the individual isomers detected. GC/MS analysis of raw and hydrotreated coal-derived mid-distillates (200-325° C) obtained at medium (1 000 SCF H₂/bbl) to high (3000 SCF H₂/bbl) severities showed the rate of removal for alkylphenols to depend on the position and chain length of the alkyl group(s) on the aromatic ring. Also, significant amounts of 2-phenyl- and 2-cyclohexylphenols were produced via partial hydrogenation of cyclic ethers. These and other results indicate that: (1) phenolic compounds will be reduced in concentration but not eliminated at hydrogenation severities required to achieve proposed environmental regulations for sulfur and aromatic content of diesel fuels, (2) the distribution of phenolic compounds in low-medium severity products will be shifted to 2-alkyl- and 2-phenyl-substituted isomers, and (3) high severity hydrogenation removes the bulk of the Q-alkyl isomers with potential antioxidant properties, thereby increasing the oxidation susceptibility of the fuel.

FIELD IONIZATION MASS SPECTROMETRIC ANALYSIS OF SEDIMENTS: CHEMISTRY OF INSOLUBLES FORMATION

Ripudaman Malhotra, Rohert N. Hazlett

We have previously shown that pyrolysis-field ionization mass spectrometry (Py-FIMS) is very useful in characterizing the insolubles formed during storage of fuels. We have analyzed filtered and adherent insolubles from several diesel fuels that were aged under a variety of conditions including ambient storage, storage at 800C, doping with strong acids, thiols, and/or stressing under oxygen overpressure. During the FIMS analysis about 60% of the insolubles were devolatilized. The spectra showed very similar profiles, which indicates that accelerated aging with these dopants or oxygen overpressure does not drastically alter the chemistry of natural ageing. Depending on the fuel, the spectra consisted of either three or four clusters of peaks. Py-FIMS of the soluble precursors of sediments (SMORS) also gave a very similar pattern with four clusters of peaks. In this case, the sample was completely vaporized during analysis and the amount of the tetramer cluster was greater than that of the lower MW clusters. Comparison of

the specific peaks within a given cluster shows substantially greater amounts of oxidized (dehydrogenated) species in the spectra of the insolubles.

STUDY OF FUEL DEGRADATION PROCESSES BY UV USER TECHNIQUE

I. Rotel, J. Zahavi, N. Por, Y. Ben-Asher

The study of degradation of fuels by excimer laser irradiation was carried out in order to find a method for replacing conventional time-consuming processes. Irradiation was carried out on drops of diesel fuels producing deposits on microscopic slides which were darker, heavier and denser for the more unstable type of diesel fuel. Analysis of the diesel fuels, after irradiation revealed increase in the gum and peroxide content. Irradiation of pure compounds was carried out in order to understand the mechanisms involved in the irradiation of the complex hydrocarbon mixture, comprising the diesel fuel fraction. Precipitation and darkening of the product was observed after irradiation of aromatic compounds and carbonyl groups were formed as a result of irradiation of paraffinic compounds.

THE EFFECT OF SULFUR CONTAINING COMPOUNDS ON THE STABILITY OF DIESEL FUELS

A. Zuhdan Fathoni, B. D. Batts, R. F. Sprecher, G. Veloski

A high-resolution low voltage mass spectrometric study has been carried out on the sulfur containing fractions of fresh diesel fuel and on samples aged at 43°C in borosilicate bottles (ASTM D 4625 test) for periods of 6.5, 13, 19.5 and 26 weeks and at 80°C for periods of 0.5, 1, 1.5, 2, 3, and 4 weeks. Homologous series of benzo- and dibenzothiophenes are the principal sulfur containing components of these fractions and of the fresh diesel fuel. Trace amounts of oxygen and sulfur containing compounds were detected. The concentrations of all species present with aging were monitored and the role of each compound in the gum forming process assessed.

MECHANISTIC ASPECTS OF OXIDATION PROCESSES INVOLVED IN COLOUR AND SEDIMENT FORMATION DURING AGEING OF LCO CONTAINING FUELS

Frederic Tort and Bernard Waegel, Christian Bernasconi and Laurent Germanaud

While studying the coloration and sediment formation, which occurs during the ageing of LCO containing fuels, we succeeded in isolating various coloured and non-coloured precipitates which can interconvert one in each other. We will present our results on their structural identification, as well as mechanistic considerations allowing to explain their formation which essentially involves an oxidation of particularly oxidizable aromatic hydrocarbons like phenalene or fluorene. These oxidized aromatic hydrocarbons now feature a carbonyl group and can further undergo an acid catalyzed condensation with other nucleophilic aromatic derivatives like indoles. Several mono and disubstituted tautomeric forms could be identified and characterized both by spectroscopic methods (NMR) and chemical reactions. The mechanism of these processes will be discussed. It will be shown that the phenalenyl radical intermediate, which could be

spectroscopically identified, is most likely to play a decisive role during the Initial oxidation stage preceding the formation of condensation products. We will also provide answers to the question of the origin of such - more or less oxidized • phenalene derivatives in LCO containing fuels. As a conclusion, It will be shown that the stability of LCO containing fuels is likely to be related with some common features of these products and that their study could provide some useful indications concerning the stability of much heavier products like bitumens.

DEGRADATION PHENOMENA OF HEAVY PETROLEUM PRODUCTS ASSOCIATED WITH OXYGEN DIFFUSION PROCESSES

Nahum Por

During laboratory investigations on viscosity increases of stored residual fuels it has been observed that temperature and especially exposure to air (oxygen) have been dominant factors in viscosity increases of stored samples. In some cases viscosity increases were uniform throughout the bulk of the fuel, but in others the viscosity of the upper layers increased, viscosities of middle layers changed to a lesser degree, while in the bottom layers they were not affected at all. Such viscosity layering was more pronounced in viscous fuels, while for the lower viscosity fuels, the increase of viscosities during storage was uniform throughout the bulk of the fuel. In addition, also the reactivity of the fuel, i.e. its susceptibility to free radical formation, was observed to have a similar effect. An oxygen diffusion process was recognized to be of Interest and has been consequently studied.

SESSION 8: ASSESSMENT OF FUEL INSTABILITY

COMPARISON OF STABILITY RESULTS FOR DISTILLATE FUELS EXPOSED TO DIFFERENT STRESS REGIMES

Robert N. Hazlett, Erna J. Beal, Michael D. Klinkhammer, John A. Schreifels

Two blends of 20% light cycle oil in straight run stock were stressed at ambient conditions, at 43°C (three different time periods), and with 800 kPa oxygen overpressure. The latter procedure included testing at three conditions - 43°C/3 weeks, 65°C/4 days, and 90°C/16 hours. The yields of total insolubles in these various tests were reasonably consistent. The blends were doped with 0.001 M dodecyl benzene sulfonic acid and with 0.01 M R-t-butyl thiophenol. Deposits formed rapidly from the sulfonic acid doped blends and the total insolubles were consistent for the various test regimes. One blend containing the thiophenol exhibited a predictable pattern for instability but the second blend formed less insolubles at low temperatures than expected. The insolubles, both adherent (AI) and filterable (FI), were characterized by several chemical analysis techniques. Field ionization mass spectrometry (FIMS) and X-ray photoelectron spectroscopy (XPS) showed that sulfonic acid was incorporated into the insolubles from the fuel doped with sulfonic acid. Non-aqueous titrations also demonstrated that strong acid was present in the sediments. Titration of the blends containing the thiophenol found evidence for partial conversion to strong acid. FIMS analysis demonstrated that \square -t-butyl benzene sulfonic acid was present in the insoluble material thus showing that the multi-step oxidation of a thiophenol can

proceed under accelerated storage conditions. The thiophenol oxidation to sulfonic acid was a small fraction of overall thiophenol disappearance and even this fraction was significantly smaller at low stress temperatures. The thiophenol appears to stimulate insolubles by two processes; acting as an acid catalyst after conversion to sulfonic acid and by a free radical mechanism, possibly by addition of the thiyl radical to olefins.

PREDICTION OF THE STORAGE STABILITY OF MIDDLE DISTILLATE FUELS USING A RAPID COLORIMETRIC METHOD

Sheila J Marshman

Various methods are currently used to predict the storage stability of distillate fuels, including ASTM D2274, D4625, the oxygen overpressure test and others which may be 'in house' methods or used in specifications. The most rapid of these tests are carried out over 16 hours and all use elevated temperatures to accelerate degradation reactions. A rapid colorimetric test had been developed which will identify cracked, straight run or hydrofined fuels and may be used to give an indication of the sample's storage stability within 30 minutes. A number of gas oil blends of fuel components from U K and European refineries were analysed using the colorimetric test and the results compared with results from ASTM D4625 testing (13 weeks at 43°C). By assigning a rating to each fuel based on its response to the colorimetric test, a reasonable correlation was obtained between this rating and the sediment levels from the ASTM D4625 tests. A good correlation was also obtained between the rating assigned and the final ASTM D 1500 colour obtained from the accelerated storage test. The colorimetric test is considered to be a useful 'go/no go' indicator for storage stability.

AN IMPROVED ASTM D2274 REFERENCE FUEL SYSTEM

M. D. Klinkhammer and E. W. White

The poor reproducibility of ASTM D2274, Oxidation stability of Distillate Fuel Oil (Accelerated Method), results from factors such as changes in samples during shipment, equipment differences, and procedure interpretation differences by different analysts. At DTRC, a system of reference fuels is being developed for use in checking apparatus, training analysts, quality control (as blind samples), and laboratory accreditation programs. Initial efforts were based on 1,2,5-trimethylpyrrole (TMP) in a base blend of commercial purity dodecane, dodecene, and t-amylbenzene. The system gave repeatable and predictable levels of total insolubles in the D2274 procedure. Subsequently, the t-amylbenzene became unavailable in the commercial grade and the reagent grade was considered too expensive for general use. Therefore, a system based only on TMP in dodecane has been under development. Four analysts were used in each year's series of tests, but all analysts were not the same each year. Initial TMP concentrations up to 150 mg/100 mL have been studied, but most tests were conducted at concentrations below 50 mg/100 mL, where total insolubles levels below the Navy's specification level for NATO F-76 distillate fuel are obtained. We concluded that TMP-in-dodecane can be used with sufficient reproducibility to serve as a reference fuel system, if fresh TMP is used and if rigorous control over the equipment and procedure of D2274 is maintained.

THE USE OF SOLUBLE MACROMOLECULAR OXIDATIVELY REACTIVE SPECIES (SMORS) TO PREDICT STORAGE STABILITY OF MID DISTILLATE DIESEL FUELS

Margaret A. Wechter and Dennis R. Hardy

A previous report (1) has described the isolation of a methanol extractable, hexane insoluble fraction from catalytically cracked light cycle oil blending stocks. This material could be correlated in a linear fashion with insolubles (sludge) formed in oxidative storage tests over a wide range of cycle oil stabilities as defined by accelerated tests. This work has now been extended to typical 20% v /v blends of cycle oils with straight run distillate streams. Six cycle oils (which span a wide range of stability as defined by accelerated tests) blended with low acid number straight run stocks were examined. The resulting blends also exhibited a wide range of instability. Isolation of the species (SMORS) postulated to be responsible for the formation of sludge during aging was effected as described previously (1). The solid material thus isolated is found to correlate linearly with the tendency of the fuel to form insolubles during aging using an accelerated stability test. This strongly suggests that a predictive test for fuel stability based on quantitative determination of these reactive precursors could be developed for field use.

BENCH TEST METHODOLOGY FOR DIESEL INJECTOR FOULING

L.L. Stavinoha, D.M. Yost, and S.J. Lestz

Compared to conventional compression ignition (CI) engine operation with the fuel being delivered at approximately 149°C (300°F), adiabatic engine operation can deliver the fuel at 260°C (500°F). Hypergolic CI engine combustion systems now in theoretical design stages will deliver fuel at 427° to 538°C (800° to 1000°F). The ability of a fuel to resist formation of deposits on internal injector system surfaces is a form of thermal oxidative stability for which test methodology will be required. This Injector Fouling Bench Test (IFBT) methodology will assist in defining fuel contribution to injector fouling and control of fuel quality in procurement specifications. The major observations in this program have included: 1) 40-hour cyclic IFBT tests employing both Bosch APE113 and Detroit Diesel (DD) N70 injectors are viable procedures for evaluating fuel effects on injector fouling. Cyclic operation appears to be superior to steady-state operation. Eighty-hour cyclic tests are more discriminating than 40-hour tests using the Bosch APE 1 1 3 injector bench test which is less severe than the DD IFBT 2) JFTOT tests of fuels provide directional information on thermal stability-related deposits and filter plugging but show limited correlation with IFBT DD N70 ratings and none with IFBT Bosch APE113 injector ratings. Deposition on injector pintles were more realistically rated by optical microscopy and SEM than conventional visual and bench rating methods. 3) High sulfur (from DBDS) fuel readily causes sticking of Detroit Diesel injectors. 4) Injector sticking is an important mode of injector fouling and is thought to be related to fuel insoluble material formation from fuel unstable components. This methodology is being utilized in high temperature fuel studies (such as unstable fuel pre-treatment evaluation for advanced integrated propulsion system engines requiring thermally stable fuel) which also include evaluation of engine fuel combustion effects on injector fouling.

PREDICTION OF RESIDUAL FUEL OIL STABILITY DURING STORAGE, HANDLING AND USE - ASSESSMENT OF TEST METHODS

J. Ben-Asher and N. Por

Economic demand to extract maximum distillates from the bottom of a barrel increased profusely the occurrence of problems during storage, handling and use of residual fuel oils. Operating problems result from fuel oil being a colloidal system in equilibrium. Sensitivity of fuel oil to thermal stress may cause disintegration of asphaltenes from fuel medium and subsequently tank sludge formation or strainer and burner plugging. Conventional residual fuel oil specifications were found to be inadequate to predict problems due to thermal or chemical instability. Hence the need for better discriminating tools to be put at disposal of consumers. Efficacy of various test methods to predict operating problems has been evaluated. It was found that ASTM D-4740 Test is capable of predicting thermal sensitivity of fuel oils with very good precision. All fuel oils rated 4 to 5 caused operating problems to end users. These residual fuels failed in the IP-375 Hot Filtration Test as well. An attempt has been made to find correlation between aromatic reserve of fuel oils and their sensitivity to thermal stress. Contrary to the current belief some residual fuel oils had low aromatic reserve while exhibiting excellent thermal stability. The ability of the accelerated oxidation test to predict chemical instability has been evaluated. The study has been carried out on light fuel oil samples that were actually consumed by the market. Results were compared with artificial fuel oil blends.

SESSION 9: USE OF ADDITIVES IN CONTROLLING FUEL INSTABILITY

INTERACTIONS OF A METAL DEACTIVATOR WITH METAL SURFACES AT ELEVATED TEMPERATURES

John A. Schreifels and Loc Gwynn, Robert E. Morris

The behavior of the metal deactivator additive (MDA) in thermally accelerated test procedures have raised questions whether, besides chelation of soluble metal, it functions by somehow altering the surface activity of heated metal surfaces. Previous studies of metal surfaces exposed to MDA under a variety of conditions by this laboratory and others have shown the presence of the additive on the surface. MDA could be present on the surface either as a chemisorbed monolayer (chemisorbed) or as multiple physically bound layers (physisorbed). In fuel systems and simulators, physisorbed materials will be removed and only chemisorbed species will play a role in the reactions occurring on the surface. The extent to which MDA can chemisorb to metal surfaces has been investigated with thermal desorption spectroscopy. MDA has been found to be present in both physisorbed and chemisorbed states on a 304 stainless steel substrate. All the physisorbed MDA desorbed near room temperature, leaving only the chemisorbed MDA. While not strongly chemisorbed to the stainless steel, the data indicate that the desorption energy of chemisorbed MDA was slightly less on an oxidized stainless steel surface, than on a cleaned surface.

THE INFLUENCE OF AVIATION FUEL REFINING PROCEDURES, LUBRICITY ADDITIVES AND SURFACE COATINGS UPON WEAR SCAR GENERATION

ABSTRACT

Michael A. Stropki, Grier G. McVea and Richard K. Solly

The lubricity of hydrogenated and unhydrogenated aviation fuel (JP-8) with stainless steel, chrome, and titanium nitride (TiN) surfaces has been determined by means of wear scars generated with the Ball on Cylinder Lubricity Evaluator (BOCLE) apparatus. Wear scar data and surface analysis results are a function of the surface coating and finish, the environment (air vs nitrogen), and the load. Surface interactions evaluated included standard cylinder in contact with individual balls sputtered with chrome and TiN coatings. Results are presented with respect to data generated under standard BOCLE conditions. The effect of dilinoleic acid lubricity additives in these systems has also been investigated. The results are discussed in relation to the mechanisms of wear on the BOCLE apparatus compared with general wear patterns found in aircraft fuel pumps.

JET FUEL THERMAL STABILITY AND METAL DEACTIVATOR ADDITIVE

Cyrus P. Henry

Great efforts have been carried out in many laboratories during the past several years to better understand the role of metal deactivator additive in the ASTM D 3241 JFTOT Test Method, as a consequence of data presented in a paper by Clark at the 3rd International Conference in London during September 1988. These data suggested a metal passivation mechanism to account for substantial thermal stability improvements observed with metal deactivator additive, which could result in D 3241 benefits not observed in aircraft fuel systems when hot metal parts are already coated with deposits. We obtained field samples of jet fuels which failed to meet the normal test criteria at a D 3241 heater tube temperature of 260°C, and evaluated effects of metal deactivator. Data were also obtained using an interrupted methodology where heater tube deposits were developed with unstable base fuel, then the test continued with the fuel containing metal deactivator additive. Copper concentrations were also determined. Results show that a very low concentration of metal deactivator additive is effective - about 0.5 mg/L is usually sufficient. The interrupted run technique shows the additive functions even when deposits are already present. However, most unstable fuels obtained were found to contain 1.5 to 50 ppb of dissolved copper, suggesting that in many cases metal deactivator additive is merely chelating dissolved copper and reducing its catalytic activity in promoting oxidation.

PERFORMANCE CHARACTERISTICS OF A NITROPARAFFIN-BASED FUEL PRESERVATIVE

Frederick J. Passman, Ph.D. and John L. Pohlman

The authors report the re-examination of the functional, toxicological and system compatibility properties of a U.S. Environmental Protection Agency registered biocide. The biocide is a 90 percent active blend of 4-(2-nitrobutyl)morpholine and 4,4'-(2-ethyl-2-nitrotrimethylene)dimorpholine (NMEND). NMEND has a water:fuel partition coefficient of 0.26 ± 0.094 . Speed of kill and persistence data demonstrate product efficacy of 125-250 ppm in

No. 2 diesel fuel and associated freshwater and sweater bottoms. The authors report that 250 ppm (v/v) biocide inhibited viable counts of a mixed bacterial and fungal contaminant population by > 99.9 percent, after four hours exposure. This level of kill required 72 hours to achieve when contaminated fuel-water systems were treated with 1225 ppm NMEND. Once initial kills occurred, treated fuel-water systems remained free of detectable bacteria and fungi for 12 weeks, at which time testing was discontinued. Initially tested in fuel: freshwater systems, the blend was equally effective in fuel: seawater systems. NMEND passed all of the criteria of ASTM D-1655 and D-4054, which address specifications for aviation turbine fuels and additive compatibility with aviation turbine fuel and aircraft fuel system materials. Toxicological and environmental data supported the authors' conclusion that NMEND represents a useful addition to the relatively short list of antimicrobials approved for treating distillate fuels.

ROAD TESTED STABILITY OF STORED DIESEL FUELS

E. Zahavi, M. Busany, J. Ben-Asher and N. Por

Diesel fuels containing insoluble sediments caused problems to diesel powered vehicles by clogging fuel filters. In diesel engines gas oil serves also as an injector coolant. Part of the distillate fuel is heated, recycled to the fuel tank, cooled and then heated again. The succession of heating and cooling cycles may cause deterioration of thermally unstable diesel fuel. The efficacy of two multifunctional additives has been evaluated under service conditions. Two different straight run diesel fuels and blend containing LCO have been stored with and without additives during two years in vented drums. Daimler Benz buses were fueled with the stored diesel fuels. Samples for analysis were taken at the beginning and at the end of seven hours road service. Though a broad range of properties has been estimated, filterability, oxidation stability and color were chosen as parameters for evaluation. It was found that while stability of various stored diesel fuels was not impaired by successive heating and cooling during road service, filterability of the diesel fuels deteriorated in the presence of additives. Some diesel fuels examined in this study did not benefit from the presence of additive during storage. It seems that different fuels need different, specially tailored additives to ensure stability during storage. Additives to enhance filterability of stored diesel fuels wait to be formulated.

DISPERSANT EFFECTS ON DIESEL FUEL FILTERABILITY- REVISITED

Papers presented at the 2nd International Conference in San Antonio, July - August 1986 by Hiley and Pedley, and by Solly and Arfelli suggested that dispersants might lead to reduced filterability of diesel fuels. Efforts were initiated to consider the generality of these findings. Studies have utilized the Diesel Filtration Test discussed by Hiley in another paper at the same Conference, and a modified ASTM D 2276 Test Method for Particulate Contaminant in Aviation Fuel. The latter test is utilized at many locations to monitor the quality of diesel fuel in standby storage. The relative performance of various dispersant types was explored, along with variation in base fuel stability and dispersant concentration. Finally, the relative benefits of stabilizer packages containing dispersants were examined. Results show a broad range of benefits, and in some cases, reduced filterability resulted from dispersants. Overall, however, data suggest the

above noted papers do not represent a balanced view of the benefits which are achieved from improved dispersants in most fuels.

THE DECOMPOSITION OF AN INDOLE HYDROPEROXIDE WITH NUCLEOPHILES (POTENTIAL DIESEL FUEL COLOR STABILIZERS)

Bruce Beaver and Rajeswari Sridharan

The formation of color in diesel fuels is currently an intractable problem. We have initiated a model compound study directed at delineating the feasibility of development of additives to minimize color body formation in diesel fuels. Experimental results from this study will be presented and evaluated with respect to development of potential color stabilizers.

SESSION 10: POSTER SESSION

DEVELOPMENT OF A JET FUEL THERMAL STABILITY FLOW RIG WHICH EMPLOYS DIRECT GRAVIMETRIC ANALYSIS OF BOTH SURFACE AND FUEL INSOLUBLE DEPOSITS

Jack C. Burnett, Erna J. Beal and Dennis R. Hardy

The single, most undesirable feature of the current JFTOT now in use for over 25 years is the lack of a simple, direct quantitative assessment of the product of interest. Heater tube deposit "weights" in the JFTOT are now able to be obtained by three separate techniques all of which exhibit remarkable agreement. These are combustion of the deposits, interferometry (a volume measurement), and dielectric constant (a thickness measurement). All three of these techniques suffer from a variety of drawbacks including expense, destruction of the sample, long analysis times, and/or unavailability of equipment. This paper describes the development of a liquid flow reactor which emulates the JFTOT apparatus conditions but which is constructed of simple off-the-shelf components. This new gravimetric fuel thermal oxidation tester allows the determination of deposit weights directly, simply and non-destructively. The rig is quite compact and offers vastly improved flexibility of conditions including a wide range of test temperatures, pressures, flows and reactant types. It is also ideally constructed for the attachment of ancillary analytical devices.

JET FUEL THERMAL STABILITY RESEARCH AT USAF WRIGHT LABORATORY

Tim Edwards

This paper describes some of the ongoing jet fuel thermal stability research at the USAF Wright Laboratory. The experimental devices discussed include a single-tube heat exchanger rig, a fuel vaporization test, and various static tests. Development of thermally stable jet fuels is recognized as a critical research area because an aircraft's fuel is the only practical heat sink for increasing on-board heat loads. The use of the fuel as a heat sink is limited by thermal degradation of the

fuel and fouling of the fuel system. When the demand for fuel as a heat sink exceeds the fuel demand of the engine, fuel is recirculated back to the tank. In effect, this can result in using part of the fuel load strictly as a heat sink - unavailable for consumption by the engine. This problem will be exacerbated due to the lower fuel flows associated with the introduction of more fuel efficient engines. To reduce the penalties associated with carrying excess fuel for thermal management purposes, the Air Force has embarked on a program to develop high temperature thermally stable (HiTTS) fuels. Two fuels are currently under development. The objective of the HiTTS 100 (JP- 8+ 100) program is to develop an additive package to increase the thermal stability of JP-8 from its nominal operation limit at the fuel nozzles of 163°C (325 °F) to 218°C (425 °F) and thereby increase the available heat sink by 50%. The objective of the longer-term HiTTS 900 (JP-900) program is to develop a new fuel with a thermal stability of 482 °C (900 °F) thereby increasing the heat sink by 500%. There are many tangible benefits to these programs. An increase in the allowable fuel temperature translates to decreased fuel recirculation and reduced or eliminated requirements for fuel carried strictly for cooling purposes. Reducing the amount of excess fuel reduces the take-off gross weight and size of a fixed-mission aircraft or increases the range or payload of a fixed-size aircraft. In addition, preliminary lab tests have shown that enhanced stability JP-8 will also reduce fuel deposit related maintenance as well. A variety of tests are being used to evaluate the thermal stability of fuels in the various environments encountered in an aircraft fuel system. This paper will briefly describe some of these tests and give references for more information.

THE EVOLUTION OF DIESEL FUEL TESTING AND TREATMENT

George H. Kitchen

A thirty-year period of testing and treating Middle-Distillate Fuels is discussed. The advantages and disadvantages of Chemical Treatment vs. Filtration are investigated on the basis of laboratory data compared with field observations. Accelerated aging of fuel by bench thermal stressing is evaluated by comparing results with actual field storage. Weathering of fuel by thermal, biological, and mechanical (filtering and pumping) means is explored.

STATUS OF: (1) DIESEL FUEL OIL GROUP (DFOG) FOR UTILITIES, AND (2) ANALYTICAL METHODOLOGY DEVELOPMENT ACTIVITIES

John R. Knemeyer, Nonna L. Bihl, Steven R. Westbrook and Leo L. Stavinoha

The Diesel Fuel Oil Group (DFOG) was formed to provide electric utility personnel with a forum to discuss problems associated with long-term storage of No. 2 diesel fuel oil. Some utilities, especially nuclear, face unique regulatory restrictions dealing with contamination limits, types of analyses to perform, and sampling frequency and techniques. The regulations are not necessarily uniform throughout the industry even when issued by the same agency. Therefore, utilities are often dealing with the same problems in different ways. The primary objectives of DFOG are: 1. To acquire and exchange information on procurement, storage, handling, and testing of diesel fuel oil. 2. To discuss licensing issues related to diesel fuel oil and disseminate information on applicable codes, standards and regulations. 3. To establish working groups as needed to address specific issues and report findings and recommend actions as appropriate to the DFOG membership. 4. To serve as a technical information resource on issues relevant to

diesel fuel oil. 5. To establish a forum for companies providing diesel fuel oil related products and services to the electric industry wherein they may interface with utility representatives for the exchange of technical information. Methodology to assess middle distillate fuel stability and cleanliness is being developed by Section E-V of Technical Division E on Burner, Diesel and Turbine Fuel Oils, which is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants. Section E-V on Fuel Stability and Cleanliness was organized in 1979 with a scope of activities defined as follows: "The Section shall prompt, oversee, and participate in the development of methods for predicting and monitoring the stability, cleanliness and microbiological contamination of fuels under the jurisdiction of Technical Division E (on Burner, Diesel and Turbine Fuel Oils)." DFOG is closely cooperating with and assisting Section E-V to determine what diesel fuel oil quality assurance related test methods are needed, can be standardized, and will be accepted by the petroleum industry and those it serves. Current status and future developments in analytical methodology for procurement requirements and surveillance monitoring related to storage and handling of diesel fuel oil in emergency and safety related systems are reviewed in this paper.

A PROGRAM FOR UTILITIES & REFINERIES TO MAINTAIN GAS TURBINE & JET FUELS IN REFINERY-FRESH CONDITION

Dr. I. Kukin

Great emphasis has been placed on maintaining standby fuels in refinery- fresh condition for instantaneous use when required. A program has been worked out with utilities and refineries for periodic sampling of the fuels, utilizing several test methods including the DuPont Oxidation Stability Test. Based upon the condition of the fuels at each storage location, they can be inhibited to prevent further oxidation or deterioration. At the same time, the tanks are sampled for the presence of any corrosion products or bacterial contamination. This program, if properly supervised and maintained, can provide utilities, refineries, government and private fuel storage locations with readily available distillate fuels for routine or emergency use.

APPLYING THE T-TEST PROCEDURE TO CHOOSE JET FUEL PRODUCTION PROCESSES AND ADDITIVES

David Luria, Jacob Sufrin, Nahum Por, Robert L. Mason, and Leo L. Stavinoha

Two alternative methods of producing jet fuels were examined by Israeli oil-producing companies. A test program was employed to compare the quality of the fuels obtained from both processes. The samples chosen for the program were taken from two crude oil sources. All samples were stressed and aged under two oxidation conditions at 65° and 100°C, for test periods up to 32 and 24 weeks, respectively. Various physical and chemical characteristics of the samples were analyzed during the aging at specific time periods. The significance of each fuel property tested for each crude source and temperature group was examined by a T-Test. Fuel properties evaluated included acid number, existent gum, microseparometer, peroxide number, Ball on Cylinder Lubricity Evaluator (BOCLE) wear scar diameter, Saybolt Color, and Jet Fuel Thermal Oxidation Tester (JFfOT). The results were used to demonstrate the utility of the T-Test for two different applications: first, to select the production process that yields the most stable fuel and secondly, to simplify the choice between two lubricity improving additives. In the latter

case, both the lubricity (indicated by BOCLE) and the degradation in the Water Separometer Index (indicated by MICROSEP) should be considered during accelerated aging tests. Using this approach, an expanded data set could be used to evaluate product stability, which was evidenced by changes in JFTOT, gum, color, and microseparometer values during aging.

BIOCIDE TREATMENT FOR CONTROL OF MICROBIAL CONTAMINATION AND FUEL QUALITY PROBLEMS

Terry M. Williams, Thomas K. Haack, Jo Ann Robbins, Ronald W. Gropp

Microbial contamination of storage tanks results in a variety of fuel quality problems. A biocide treatment program is required to maintain control over the growth of bacteria and fungi throughout the storage system. Laboratory tests with a mixed isothiazolone biocide in #2 diesel fuel demonstrated that low levels (3 ppm active ingredient) provided complete kill of both bacteria and fungi within 24 hours. Long-term preservative studies revealed that 1.5 ppm of isothiazolone provided complete control against microbial contamination for 8 weeks (including three fuel transfers). The efficacy in long-term / multiple transfer studies was related to the partitioning and stability characteristics of the biocide. Computer modelling studies demonstrated that although a lethal dose of biocide partitioned to the water phase, a large percentage remained in the fuel after 10 transfers. The performance of the mixed isothiazolone biocide under various field conditions was illustrated in three case histories. A total of five diesel fuel storage tanks were contaminated with various levels of bacteria (10^4 to 10^7 /ml) prior to treatment. Bacterial counts 48 hours after dosing were ≤ 10 /ml. The last two case histories highlight the importance of a comprehensive service program for the design and implementation of successful fuel storage system biocide treatment and for effectively controlling microbial contamination in the long term.

ASSESSING DISTILLATE FUEL STORAGE STABILITY BY OXYGEN OVERPRESSURE AT HIGHER TEMPERATURES

Erna J. Beal, Dennis A. Hardy, Jack C. Burnett

The continuing need for an accelerated stability test which is capable of reliably assessing the long-term storage stability of middle-distillate fuels has led to the development of the oxygen overpressure method. Oxygen is forced into solution in the fuel at a pressure of 100 psig and the fuel is then stressed under conditions of accelerated storage at temperatures from 43° to 100°C. The method makes use of gravimetric determination of the total insolubles formed. This rapid and precise method is predictive for up to three years at ambient conditions. Work at 43°C for up to 4 weeks at 100 psia and at 80°C for up to 64 hours at 100 psia shows very good correlation with bottle test done at 43°C. This paper will present results of tests run at 90°C for 16 hours at 100 psig on 22 military (NATO F-76) fuels and 26 commercial marine fuels from a worldwide survey. The good correlation between these results and other standard stability tests will be shown. We will also present comparative results for a series of fuels run at four different labs using this higher temperature method.

NEW TECHNOLOGY FOR THE DECONTAMINATION OF CRUDE AND RESIDUAL STORAGE FACILITIES

Howard L. Chesneau

The need for new technologies for decontamination and cleanup has never been more apparent as we approach the 21st Century. Environmental issues are likely to be the burning problem in the coming years. In the 1970's, engineers in Lockheed's "skunk works" sought to overcome the problems associated with traditional methods of surface preparation. Both the environmental hazards inherent in the use of volatile chemical solvents and the dangers of grit entrapment using sand blasting, had become increasingly troublesome. After years of effort and some \$5 million in research Lockheed's results produced the patented process now incorporated in the CO₂ Cleanblast (tm) system. The system delivers a high-velocity stream of solid CO₂ pellets (dry ice) to clean or strip a substrate. By adjusting the pellet parameters, the size, hardness, velocity, and quantity, it is possible to clean a wide spectrum of surfaces. Upon impact these pellets sublime, or change from a solid to a gas, and simply return to their natural state in the atmosphere. The material removed falls from the cleaned surface without any additions to the volume of waste. The advantage of this is obvious, a dramatic reduction in waste removal and a superior clean.