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CRUDE OIL AND FINISHED FUEL STORAGE STABILITY: AN ANNOTATED REVIEW
1990 REVISION

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FOREWORD

The IIT Research Institute/National Institute for Petroleum and Energy Research (NIPER) and its predecessor research organizations--Petroleum Experiment Station, Bureau of Mines: Bartlesville Energy Research Center, Energy Research & Development Administration; Bartlesville Energy Technology Center, Department of Energy--have long been a leader in the field of storage and thermal stability of petroleum, petroleum products, and liquids derived from tar sands, coal, and shale.

The subject of storage stability of liquid hydrocarbons has become increasingly important as the supply of high quality conventional crude oil has declined and refiners have had to resort to increased processing severity to convert residual materials to distillate fuels. Since the degree of stability required for commercial viability may determine the severity of hydrotreatment necessary and directly affect the processing cost of the product, stability data are of continuing interest to the industry. Fortunately, much work has already been done which can serve as a foundation on which to build.

As a result of long involvement in the area of stability research at IITRI/NIPER, a comprehensive library of related reports has been compiled and a systematic compilation of information on the subject has been recorded and published at timely intervals. The last publication was the 1983 review which contained 143 literature citations and 231 tables of data.

The current update of that 1983 publication is brief and concise in both the narrative discussions and the annotated bibliography. Thus, we encourage those who base future work on these data to pursue the full copies of the relevant individual publications. Abstracts are meant to help readers determine the relevance of specific articles. To the extent possible, complete references are provided, as they were derived from the computer printout obtained from the various data bases. The lack of uniformity among the citation formatting provided from the data bases has made it necessary to provide all references in upper case print while abstracts were rewritten and reworded to avoid any possible copyright infringement.

References in each of the subject sections are listed chronologically, starting with the oldest and working up through 1990. Papers covering more than one subject were not relisted under other subject headings to avoid redundancy and a complex numbering system. An alphabetical senior (first) author listing with the page number(s) on which citations can be found is provided at the end of this publication for reader convenience.

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CRUDE OIL AND FINISHED FUEL STORAGE STABILITY: AN ANNOTATED REVIEW
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INTRODUCTION

A state-of-the-art review and assessment of storage effects on crude oil and product quality was undertaken through a literature search by computer accessing several data base sources. Pertinent citations from that literature search are tabulated for the years 1980 to the present. This 1990 revision supplements earlier reviews by Brinkman and others (125) which covered stability publications through 1979 and an update in 1983 by Goetzinger and others (7) that covered the period 1952-1982.

For purposes of organization, citations are listed in the current revision chronologically starting with the earliest 1980 publications. The citations have also been divided according to primary subject matter. Consequently 11 sections appear including:

Alternate Fuels
Gasoline
Distillate Fuel
Jet Fuel
Residual Fuel
Crude Oil
Biodegradation
Analyses
Reaction Mechanisms
Containment
Handling and Storage

Each section contains a brief narrative followed by all the citations for that category.

ALTERNATIVE FUELS

The United States currently imports about half of its crude petroleum requirements. Oil embargoes in the 1970's and 1990 make alternative domestic energy sources more attractive if not a necessity. The use of liquids derived from shale and coal has presented many storage stability problems, however. Brinkman and others (1), in 1979, studied the stability characteristics of two gasolines and six jet fuels derived from coal, tar sands or oil shale. Their conclusion was that generally, synfuels had poor relative stabilities.

Wasilk and Robinson (2), in 1981, reported that fuels meeting military specifications and possessing good storage stability characteristics could be produced from shale oil utilizing conventional refinery equipment although hydrotreating and acid/clay treating were required to meet thermal and storage stability requirements of the jet and diesel fuel. Other investigators have studied the storage stability characteristics of fuels derived from coal syncrudes (3-11,13,14) and shale liquids (1,6,7,12,15-17).

Other studies that have included investigation of the storage stability characteristics of fuels derived from alternate syncrudes will be found in subsequent sections that address specific products such as jet fuels, distillate fuels, etc. To avoid repeated entries of the same citation and the resulting complication of sequential numbering, each publication was entered only once and a serious effort was made to place the citation in the most appropriate category.

ALTERNATIVE FUEL CITATIONS

1. BRINKMAN, DENNIS W., WHISMAN, M. L., AND JOHN N. BOWDEN. STABILITY CHARACTERISTICS OF HYDROCARBON FUELS FROM ALTERNATIVE SOURCES. DOE/BETC/RI-78/23. MARCH 1979.

   Two gasolines and six jet fuels derived from coal, tar sands or oil shale were tested for storage stability at 43.3° and 93.3° C. Two petroleum-based gasolines and one jet fuel were also evaluated for comparative purposes. Petroleum-based gasolines had moderate gum levels at the end of the storage period. Most of the jet fuels appeared to be stable after 16 weeks of storage. The coal-derived gasoline had the highest gum content. Generally, the synfuels had poor relative stabilities.

2. WASILK, N. J., ROBINSON, E. T.; STANDARD OIL CO. COMMERCIAL-SCALE REFINING OF PARAHO CRUDE SHALE OIL INTO MILITARY SPECIFICATION FUELS. ACS SYMP. SER., 163(OIL SHALE, TAR SANDS, RELAT. MATER.), 223-35, 1981.

   Fuels meeting military specifications and possessing good storage stability characteristics can be produced from shale oil, utilizing conventional refinery equipment. The processing scheme utilized in this study required settling and a guard bed to protect the hydrotreating catalyst; hydrotreating to remove heteroatoms; increase the H/C ratio and improve the 650° F minus liquid yield of shale oil; and acid and clay treating to meet thermal and storage stability requirements of the jet and diesel fuel.

3. BRINKMAN, DENNIS W.; BARTLESVILLE ENERGY TECHNOL. CENT. BOWDEN, JOHN N.; SOUTHWEST RES INST. STABILITY OF SOME COAL AND TAR SANDS SYNCRUDE FRACTIONS. FUEL, 61(11), 1141-8, 1982.

   Naphtha and middle and heavy distillates from solvent-refined coal liquefaction, two naphthas from Exxon donor-solvent liquefaction of Illinois No. 6 coal and Wyodak coal, and gas oil, naphtha, and kerosine fractions from tar sands extraction were characterized for physical and chemical properties. Selected samples of synthetic crudes were stored at 43° C for 32 weeks in air. The tar sands materials most closely resembled the properties of conventional petroleum-based materials, whereas the coal-derived liquids from the SRC-II process demonstrated the need for considerable upgrading. Heavier fractions underwent polymerization to produce gums, whereas lighter fractions deteriorated via oxidation.

4. WELLER, S. W., KENNEDY, L. A., SHAW, D. T.; STATE UNIV. NEW YORK, BUFFALO, NY. EVALUATION OF COMBUSTION AND CLEANUP OF SRC-II COAL-DERIVED LIQUID FUEL. REPORT, NYERDA-82-09; ORDER NO. PB83-147355, 35 PP. AVAIL. NTIS. GOV. REP. ANNOUNCE. INDEX (U. S.) 1983, 83(8), 1853, 1982.

An exploratory study was described for long-term stability and combustion characteristics of a coal-derived liq. fuel oil, especially in relation to the effects of long-term aging on physical characteristics, the characterization of potential NOx and SOx and the combustion products' interaction with hot gas cleanup hardware. SRC-II may absorb excessive amounts of oxygen and aging SRC-II at 50° C produces a steady increase in viscosity.

5. HILFMAN, L.; UOP, INC., DES PLAINES, IL. UPGRADING OF COAL LIQUIDS: COAL-LIQUID STABILITY STUDY. FINAL REPORT. DOE/ET/10131-T10, 244 P. AUG 1983.

The storage stability of a freshly processed coal-derived liquid, hydrotreated products therefrom, a petroleum crude and a blend of the coal liquid and petroleum crude oil were evaluated at 43.3° C (110° F). The coal liquid was an Exxon Donor Solvent product (i.e., hydrogenated coal liquid) provided from the Exxon Coal Liquefaction Plant. The storage stability was monitored by standard chemical analyses and instrumental analyses which included electron spin resonance (ESR), chemiluminescence (CL), differential scanning calorimetry (DSC) and mass spectrometry (MS). The raw coal liquid exhibited modest changes in properties during 180 days storage at 43.3° C as measured by chemical analyses. Instrumental analyses detected a small amount of reactive species in the coal liquid that underwent rapid changes at ambient temperature and during the first 30 days of storage at 43.3° C. Hydrotreating improved the storage stability of the coal liquid. The coal liquid/petroleum crude oil blend was compatible and possessed satisfactory stability.

6. BOWDEN, J. N., LEE, G. H. II.; SOUTHWEST RESEARCH INST., SAN ANTONIO, TX. SYNCRUDE STABILITY STUDY. FINAL REPORT, JUNE 9, 1980-MARCH 31, 1983. DOE/BC/10188-33, 78 P., 1983.

This program was initiated to investigate the storage stability of syncrudes derived from coal and oil shale. Investigation of other techniques for development of a test protocol that would successfully differentiate between various degrees of storage stability of syncrudes became a second objective of this program. Results of this work indicate that for the particular samples studied, the shale syncrudes are more stable than coal-derived syncrudes, and hydrotreatment of the shale syncrudes for upgrading tends to improve their stability. Thermal analysis by SC and/or TGA appears to show promise in evaluating syncrude stability, although finalized standard procedures still need to be developed.

7. GOETZINGER, J. W., C. J. THOMPSON AND D. W. BRINKMAN. A REVIEW OF STORAGE STABILITY CHARACTERISTICS OF HYDROCARBON FUELS 1952-1982.. DOE/BETC/IC/83/3. OCTOBER 1983.

This compilation is as complete as practical, and represents a broad spectrum of stability data during the specified time frame. In combination, the four sections of the report provide a ready reference source of data for those involved in the study of the storage stability of hydrocarbon liquids.

8. TEWARI, K.C.; INTERNATIONAL COAL REFINING CO., ALLENTOWN, PA. RHEOLOGY AND STABILITY OF SRC RESIDUAL FUEL OILS - STORAGE EVALUATION. SRC-1 QUARTERLY TECHNICAL REPORT, OCTOBER-DECEMBER 1982. SUPPLEMENT. DOE/OR/03054-11-SUPPL., 52 P., JUNE 1984.

A laboratory evaluation characterizing the storage stability of various SRC residual fuel oils showed that molecular weight of the SRC residual-oil components is the main factor in determining the viscosity of the final residual-oil blends. A second series of studies revealed that storage of blends in air increased viscosity compared to blends stored under nitrogen and would require a pumping temperature about 10° F higher than that specified for an unaged blend. It was further determined that some loss of volatiles occurs with high-temperature storage in air or nitrogen. Other studies revealed that SRC residual-oil blends can be used as a No. 6 Fuel Oil substitute using conventional fuel handling equipment. Viscosity characteristics of SRC residual oils depend on solvent boiling range, the type and amount of solid dissolved in the blend, and the heteroatom content. Long-term storage under air in a closed system at 150° F adversely affects the stability of No. 6 Fuel Oil and HSRC residual oils, but has very little effect on TSL SRC residual oils. Long-term storage stability of HSRC residual oils is comparable to that of No. 6 Fuel Oil.

9. BRAUN, R. AND HILFMAN, L.; UOP RES. CENT. TECHNIQUES FOR THE EVALUATION OF COAL LIQUID STABILITY. PREPR. - AM. CHEM. SOC., DIV. PET. CHEM., 29(4), 983-95, 1984.

Coal liquids from the Exxon Donor-Solvent process is moderately stable but does show some instability during storage at both 24° and 43° C. Hydrotreatment increased the stability of the sample. Heteroatom compounds, probably nitrogen compounds, react quickly with oxygen to yield dimers, trimers, and tetramers of the oxidation products. Less reactive compounds (e.g., mercaptans, disulfides, and olefins) also react with oxygen throughout the storage period. These compounds probably are involved via free-radical-chain reactions. Peroxides and acids which result from these continuous reactions account for the continuous rise in acid number.

10. SKINNER, R.W., CUSICK, R.C., STAWASZ, W.W., TIEDGE, W.F.; INTERNATIONAL COAL REFINING CO., ALLENTOWN, PA. LIQUID PRODUCT TECHNICAL REPORT, JULY-DECEMBER 1983. LIQUID PRODUCT TECHNICAL REPORT, 134 P., FEB 1984.

The physical and chemical properties of proposed liquids from the SRC-I Demonstration Plant were measured. Storage stability and compatibility of demonstration plant liquids with No. 2 and No. 6 fuel oils were also determined. Results were compared with ASTM fuel specifications and interpreted in terms of preferred end-use applications. SRC-I middle distillate has reasonably good storage stability. SRC-I heavy distillate had fair/poor storage stability and combined SRC-I heavy and middle distillates were a good cutter stock for reducing the viscosity of petroleum vacuum residuum to meet No. 6 fuel oil specifications.

11. SKINNER, R.W., STAWASZ, W.W., TIEDGE, W.F.; INTERNATIONAL COAL REFINING CO., ALLENTOWN, PA; AIR PRODUCTS AND CHEMICALS, ALLENTOWN, PA. SRC-I TECHNICAL REPORT, JULY-DECEMBER 1983. DOE/OR/03054-94, 77-156 P., JUN 1984 .

Effective marketing of liquid products from the SRC-I depend on the compatibility of these liquids with equivalent petroleum liquids in the customers' storage tanks. Samples representing the various liquid streams from the Wilsonville Advanced Coal Liquefaction Facility and of ALCOA coker condensate were fractionated into light-, middle-, and heavy-oil cuts, which were then characterized. The storage stability of the original and blended samples was then determined by subjecting the aged samples to a series of analytical tests. Finally, a composite sample of naphtha was fractionated into 25° F boiling-range cuts and analyzed to determine the distribution of dicyclics and heteroatomic species.

12. FRANKENFELD, J.W., TAYLOR, W.F., BRINKMAN, D.W.; STORAGE STABILITY OF SYNFUELS FROM OIL SHALE IND. ENG. CHEM., PROD. RES. DEV. (UNITED STATES), 1984.

This three-part paper is a summary of material previously published in a government report. The first part describes the general features of sediment formation in model fuel systems. Part two discusses the effects of nitrogen compound type and the influence of other non-hydrocarbons on sediment formation. Part three describes studies with actual shale-derived middle distillates.

13. HAZLETT, R.N., POWER, A.J., KELSO, A.G, SOLLY, R.K.; MATER. RES. LAB. VICTORIA 3032 AUSTRALIA. THE CHEMISTRY OF DEPOSIT FORMATION IN DISTILLATE FUELS. REP. - MATER. RES. LAB. (AUST.), MRL-R-986 (1986) 64P CHEM. ABSTR. ABSTR.NO. 227394

Addition of 10% of a solvent such as 2-butanone, dipropylamine, isopropanol, or cyclohexanol completely prevented gum formation in coal-derived distillate fuels at 50° C, even after 20 days, and reduced the viscosity increase due to aging. IR and NMR spectroscopy indicate these solvents function by preventing hydrogen bonding of phenols in the coal liquids to form pentane-insoluble gums. Addition of 1% of a metal chelating additive such as EDTA failed to inhibit gum formation.

14. DAVIES, G., EL-SAYED, M.A., EL-TOUKHY A.; NORTHEASTERN UNIV.; ALEXANDRIA UNIV., EGYPT. PREVENTION OF GUM FORMATION AND VISCOSITY INCREASES IN COAL-DERIVED DISTILLATE FUELS. FUEL SCI. TECHNOL. INT. (08843759) V4 N.3 327-43 (1986).

Prevention of gum formation and viscosity increases in coal-derived distillate fuels was studied at 50° C to simulate fuel oxidation in storage by head space air with a 650° F+ residue from SRC-II liquefaction of Illinois No. 6 coal. Addition of 1% of a metal chelating additive such as EDTA failed to inhibit gum formation; however addition of 10% of a solvent such as 2-butanone, dipropylamine, isopropanol, or cyclohexanol completely prevented gum formation, even after 20 days, and reduced the viscosity increase due to aging. IR and NMR spectroscopy indicate these solvents function by preventing hydrogen bonding of phenols in the coal liquids to form pentane-insoluble gums.

15. MUSHRUSH, G.W., COONEY, J.V., BEAL, E.J., HAZLETT, R.N.; NAVAL RESEARCH LAB., CHARACTERIZATION AND STABILITY PROPERTIES OF POLAR EXTRACTS DERIVED FROM A RECENT SHALE LIQUID. FUEL SCI. TECHNOL. INT. V 4:1,. 103-109 P., 1986.

A marginally stable shale fuel has been used as a source of nitrogen-rich polar extracts. Polar compounds were isolated by mild acid extraction followed by silica gel adsorption and were identified by GC/MS. Alkyl-substituted pyridines were the predominant class of compounds present in most extracts. The effects of adding these fractions to a stable shale diesel fuel (D-11) were examined in terms of sediment formation and peroxide number under accelerated storage stability test conditions. The activities of the extracts in inducing fuel instability were correlated with their composition.

16. MEIER, P.F., HANKINSON, R.W., PETREE, D.K., PHILLIPS, N.K.; PARRISH, W.R.; ALLRED, G. C., PHILLIPS PET. CO. A STABILITY STUDY FOR A WESTERN CRUDE SHALE OIL. IND. ENG. CHEM., PROD. RES. DEV. V25 N.2 355-60 (JUNE 1986).

    A stability study for a western crude shale oil showed no significant changes in properties over the eighteen week test, indicating that the oil was stable for a period typical of the time between retorting and refining a crude shale oil. The samples were stored in the absence of light, under a nitrogen blanket, and at room temperature. The measured densities at 100° F showed a statistically significant aging trend, but the 85° C values did not. Simulated distillation GC data showed no change in the oil with time. Most of the nitrogen compounds in this oil were basic and did not contribute directly to sedimentation.

17. FRANKENFELD, J .W., BRUNCATI, R. L.; EXXON RESEARCH & ENG CO. EXTRACTING SHALE OIL WITH BASE TO INCREASE STABILITY. AUSTRAL 581,006, C 89.02.09, F 85.06.19(APPL 43,856/85) (C10G-019/02) AUSTRALIAN OFFIC JPAT V 3, NO 5, P 300, 89.02.09(ABSTRACT ONLY) (AO). AU-581006, 1989.

    A method for enhancing the storage stability of shale oil liquid was characterized by extracting the oil with an effective stabilizing amount of a base solution. The solution was shale oil retort process water having a pH of at least 7.5. This inhibited or reduced the level of sediment and gum that was otherwise formed.

GASOLINE

For many years, two grades of automotive gasolines were marketed in the United States - "premium" and "regular" - and octane number was the main defining property. Until about 1970, nearly all grades of automotive gasolines contained lead alkyl compounds (18) to increase octane rating. In 1971, U.S. passenger car manufacturers began a transition to engines that would operate satisfactorily on gasolines with lower octane ratings. Then in 1974 the U. S. Environmental Protection agency mandated that most service stations have available a grade of unleaded gasoline defined as having a lead content not to exceed 0.05 g of lead per U.S. gallon, and with an octane rating of at least 91. This was ultimately changed to a minimum octane rating of 87 in 1983. Today, lead used in leaded regular U.S. motor gasolines is very low, and is expected to be banned entirely in the future. However, there are now at least four grades of conventional gasoline available. Three of these are labeled as unleaded of various octane ratings while the fourth is called leaded.

Conventional gasolines are blends of stocks derived from straight run petroleum distillates, catalytically-cracked heavy petroleum distillates, and/or thermally-cracked heavy petroleum distillates. Hydrogenation is often used to stabilize these blends by reducing the heteroatom content as well as the olefinic components. Additives including an antioxidant are used to prevent oxidation/polymerization reactions. Other additives include combustion chamber deposit modifiers, metal deactivators, corrosion or rust inhibitors, carburetor antiicing additives, fuel line antifreeze agents, gasoline detergents, gasoline dispersants, and identifying dyes.

In the process of amending the Clean Air Act, Congress has brought a major focus on decreasing automotive emissions through the use of reformulated gasoline or alternate fuels such as M85 (a blend of 85% methanol and 15% gasoline) or compressed natural gas. Although the composition of reformulated gasoline is not yet established, changes are anticipated in properties such as summer Reid vapor pressure which will be further decreased to 8 psi. Aromatics will be limited to about 25 to 30 volume percent, and benzene may be limited to 0.5 to 1.0 volume percent. Olefins content may be restricted to 5% or less and higher boiling point components may be eliminated by lowering the 90% distillation temperature. Oxygenates will be required in order to maintain satisfactory octane quality, and a specific minimum oxygen content may be legally mandated. Potential oxygenates are methanol, ethanol, MTBE (methyl t-butyl ether), ETBE (ethyl t-butyl ether), and TAME (t-amyl methyl ether) with MTBE being the most popular option. Increased use of detergents is also anticipated.

In the United States, the tremendous demand for automotive gasoline assures a rapid turn over of supply and thereby minimizes problems with long term storage. This situation is not true for much of the military in the U.S. or in many foreign countries of the world. It may not be in the United States in the future if supplies of crude are impaired requiring the creation of reserve storage. Gartenmann (20) has reported that gasolines are stored for ten years or more in Switzerland without serious stability problems. Luria (21), reported that gasoline was stored in conventional fuel tanks and in drums in Israel from 60 to 100 months. Only a few cases of catastrophic failure were observed.

By 1993, the California Air Resources Board will lower the allowable sulfur content of gasoline from 0.5% by weight to 0.05%. It will simultaneously reduce the allowable aromatic content by almost 70%. The EPA will adopt the lower sulfur level by 1993 for the rest of the country. Further on the horizon, one can expect greater restrictions on the aromatic content of gasoline, primarily benzene. Since benzene is a naturally occurring high-octane component, its removal means that gasoline will require further processing (at the expense of yield) and/or new octane sources such as oxygenates.

The conversion of cars from regular gasoline to alternate or reformulated gasoline was studied (25) early on. The results were compared in such categories as fuel economy, conversion cost-effectiveness, cold-start, drivability, and acceleration. M85 fuel was used consisting of 85% methanol and 15% hydrocarbons. Methanol's energy content is approximately 50% that of gasoline, but methanol's high octane, latent heat of vaporization, high flame speed, and wide flammability limits increases engine efficiency and performance and lowers emissions. The unburned fuel in a methanol vehicle's exhaust is lower in photochemical reactivity than that of a gasoline vehicle. However, the washing of cylinder walls with methanol makes existing lubricating oils unsuitable and therefore, new lube oils will have to be developed to use alternative fuels such as M85. Further, when methanol is used, co-solvents must be used to help prevent separation of the blend into two phases in the presence of water.

Por (22) reported in 1988 the effect of oxygenates upon stability characteristics of gasoline blends. Oxygenates had little effect upon straight-run gasoline but increased the formation of gums, peroxides and deposits in olefinic gasolines. Antioxidants improve the stability of the oxygenate blends, however.

Alternative fuels will require extensive changes in the entire fuel production and distribution system while reformulated gasoline can be produced in existing refineries with appropriate modifications and supplied through existing distribution systems. It is anticipated that a gasoline reserve established in California would be reformulated gasoline rather than an alternative fuel such as M85.

Morris and others (23) have described improved analytical procedures for predicting motor gasoline stability.

GASOLINE CITATIONS

18. SCHWARTZ, F. G., WHISMAN, M. L., C. S. ALLBRIGHT AND C. C. WARD. STORAGE STABILITY OF GASOLINE. BUREAU OF MINES BULLETIN 660, 1972.

    The Bureau of Mines developed a rapid and precise method for predicting storage stability of motor gasolines of the 1960's. The method resulted from the development of analytical procedures as well as a study of fuel composition and fuel component gum-forming mechanisms.

19. MORGAN, C. R., WARNER, J. P., YURCHAK, S.; MOBIL RESEARCH & DEVELOPMENT CORP. MOBIL RES. DEV. CORP. GASOLINE FROM ALCOHOL. 179TH ACS NATL. MEET. (HOUSTON 3/23-28/80) ACS DIV. PET. CHEM. PREPR. V25 N.1 59-68 (FEB. 1980)

    Gasoline was obtained from a 4 bbl/day methanol fluid bed pilot unit using a Mobil catalyst. It had a RVP of 9 and antiknock performance compared very favorably to 15 commercial U.S. unleaded premium and regular-grade gasolines. Exhaust emissions and fuel economy results were very similar to those for a certification fuel according to the federal exhaust emissions test procedure. A good performance was also obtained with Mobil's multifunctional additive package as determined by 16 week storage stability at 110° F.

20. GARTENMANN, EMIL. TEST METHODS AND EXPERIENCE OF SWITZERLAND ON LONG-TERM STORAGE STABILITIES OF GASOLINES AND MIDDLE DISTILLATES. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

    Gasolines and middle distillates are stored for ten years or more in Switzerland. Periodic tests are performed including gasoline stability tests for existent gum and oxidation stability as well as a bottle storage test. Middle distillates are tested for existent stability by Conradson carbon residue, ASTM color and residue on evaporation. Long-term stability is measured by an accelerated test of storing gasoil four weeks at 40° C.

21. LURIA, DAVID. FIELD TESTS ON STORAGE STABILITY OF GASOLINE, JET FUEL, AND DIESEL FUEL. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

    The storage behavior of gasoline, jet fuel and diesel fuel in conventional fuel tanks and in 210 liter drums in Israel were tested. Storage periods ranged from 60 to 100 months. Cyclic characteristics of oxidation stability of gasoline, diesel fuel and jet fuel were found during long storage periods. No linear or exponential degradation was found and only a few cases of catastrophic failure was observed.

22. POR, N.; STABILITY PROPERTIES OF GASOLINE-ALCOHOL BLENDS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Blends of straight run gasoline, catalytically reformed (aromatic) gasoline and catalytically cracked (olefinic) gasoline with oxygenates were prepared and their stability characteristics were assessed. The oxygenates included methanol, t-butyl alcohol, and methyl t-butyl ether. The oxygenates had little effect upon the straight-run gasoline but increased the formation of gums, peroxides and deposits in the olefinic gasoline. Phenolic and amine antioxidants improved the stability of these oxygenate blends.

23. MORRIS, D. L., J. N. BOWDEN, L. L. STAVINOHA AND M. E. LEPERA. EVALUATION OF MOTOR GASOLINE STABILITY. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Data from the evaluation of methods for the prediction of motor gasoline stability was presented which indicated that ASTM D 525 is not viable as a predictor of gum formation during storage. A modified form of ASTM D 873 was found to be a superior predictor and correlated with both unwashed and existent gum formation of gasolines stored in excess of 2 years under ambient storage conditions.

24. DEKEL, R.; STORAGE STABILITY OF AVIATION GASOLINE. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Aviation gasoline was stored in steel drums under ambient conditions and in polyethylene bottles at 40-50° C. Test data were collected up to 54 weeks of storage. Properties significantly altered during storage under both conditions. Potential and existent gum, distillation and RVP showed greater changes in properties in the polyethylene bottles at the higher temperature. However engine tests before and after storage showed no changes in performance.

25. DELLIS, E. A.; METHANOL MARATHON 1989 (STUDIES METHANOL FUEL FOR GASOLINE ENGINES). AUTOMOT. ENG. (PITTSB.) V97 N.7 28-37 (JULY 1989).

College students took part in a program to learn the problems created by the conversion of regular cars from gasoline to methanol fuel. The results were compared in such categories as fuel economy, conversion cost-effectiveness, cold-start and drivability and acceleration. M85 fuel was used consisting of 85% methanol and 15% hydrocarbons. Methanol increases engine efficiency and performance and lowers emissions. Fuel substitution ratios for gasoline vehicles converted to run on M85 are 1.4-1.8 L of M85 to travel as far as 1 L of gasoline. M85's octane number is typically > 97. The unburned fuel in a methanol vehicle's exhaust is lower in photochemical reactivity than that of a gasoline vehicle.

DISTILLATE FUELS

Generally, the literature addresses No. 2 fuel oil, No. 4 fuel oil, jet fuel, and diesel fuel as distillate fuels rather than as individual entities. This bibliography has been organized to include all fuel oils and diesel fuel under the heading of distillate fuels with separate sections for jet fuels and residual fuel oils (No. 6 and Bunker C).

Grade No. 2 fuel oil is a heavier distillate than grade No. 1. It is intended for use in atomizing type burners that spray the oil into a combustion chamber where the tiny droplets burn while in suspension. This grade of oil is used in most domestic burners and in many medium capacity commercial-industrial burners. Its ease of handling and ready availability sometimes justify its higher cost over the residual fuels.

Grade No. 4 is usually a heavy distillate/residual fuel blend but may be a heavy distillate fuel meeting the specification viscosity range. It is intended for use in burners equipped with devices that atomize oils of higher viscosity than domestic burners can handle. Its permissible viscosity range allows it to be pumped and atomized at relatively low storage temperatures. Thus, in all but extremely cold weather, it requires no preheating for handling.

In ASTM D 975, Grades No. 1-D(diesel) and 2-D(diesel) are distillate fuels that are the types most commonly used in high-speed engines of the mobile type, medium-speed stationary engines, and railroad engines. Grade 4-D covers the class of more viscous distillates and blends of those distillates with residual fuel oils. EPA is currently considering the feasibility of reformulated diesel.

Lower quality distillate fuels are the result of increasing use of low quality crude oils in refinery feedstocks. This is evidenced by increased problems with product stability and compatibility. Problem components increase with increasing boiling point and are highest in the residual fractions. Concern for the long term storage stability of middle distillate fuels was responsible, in the first half of 1982, for an extensive literature survey by Bentley and others (28) and the evaluation of various experimental approaches to assessing storage stability.

A major area of research in middle distillate storage stability has been in developing improved methods for predicting long term storage stability as well as compatibility with other fuels. A second area of research has dealt with the mechanisms of sedimentation resulting in problems such as injector fouling and filter plugging. And still a third area of research has dealt with additives that reduce sedimentation of distillate fuel oils.

Jones et al. (29) attempted to improve empirical predictive storage stability tests for Navy diesel fuel marine (F-76) while Anderson and co-workers (35,40,58) were developing practical test methods useful as screening techniques for predicting stability and compatibility problems of heavy fuel oils. Power (43) used semi-quantitative infrared difference spectroscopy to measure the molar carbonyl group formation in some diesel distillates. Hardy and others (52) concluded that ASTM D2274 was useful as a go/no-go test in the procurement of aged commercial fuels. Pedley and co-workers (62) used IR spectroscopy, pyrolysis, gas chromatography, thin-layer chromatography and mass spectrometry to analyze sediment obtained from an unstable diesel fuel.

Schellhase (63) predicted long term storage stabilities of 14 middle distillate fuels by thermal analysis, i.e, pressure differential scanning calorimetry, under a 600 psi oxygen pressure. Hardy and others (82,85) used a similar technique to force oxygen into the fuel at pressures up to 100 psig. Fuel was then stressed under conditions of accelerated storage and gravimetric determination of the total insolubles formed was correlated with fuel instability. Li and others (79) added copper, aluminum, and iron to a fuel and then measured dissolved metal by ICP-AES or AA. The extent of metal drawn into the fuel was correlated with the extent of deposit formed in degradation of the fuel.

The general concensus of the reaction mechanisms leading to sedimentation and color degradation of middle distillate fuels results from the oxidation of neutral compounds to polar intermediates followed by condensation reactions with nitrogen-containing aromatic compounds (61). Jones and others (30,34) enriched distillate fuels with specific heteroatomic compounds. 2,5-Dimethylpyrrole was especially deleterious to fuel stability followed by quinolines, pyridines, and indoles. Pedley and co-workers (62,65,76,84) found nonbasic nitrogen compounds were important constituents of fuel sediment. They reasoned that the sediment precursor compounds could have been formed by condensation of phenalenones with indoles. Hiley and Pedley (67) also found that the addition of naphthalene sulfonic acid to stable fuels resulted in reaction with non-basic organonitrogen-compound extracts from the fuels to produce highly colored sediment. Tewari (32) found some oxidative polymerization of pentane-soluble oil components that formed higher molecular weight pentane insolubles (asphaltenes and benzene insolubles). Cooney and others (33,42,59) noted that the formation of insoluble sediments and gums is preceded by the accumulation of hydroperoxides and that oxidative condensation reactions of polar compounds are deleterious to stability. In particular, nitrogen containing aromatics (pyrroles, pyridines, and indoles) appear to be very harmful. Sutterfield et al. (75) attempted to interpret reaction data and produce accurate reaction models based on thermodynamic equilibria among species submitted to hydrodesulfurization and hydrodenitrogenation chemistry. They concluded that most problem compounds in hydrodesulfurization contain a thiophenic ring. Thiophenes, pyrroles, and pyridines are the most resistant to present hydrogenation practices.

Hazlett and others (36,46,69) have studied commercial stabilizer additives in freshly refined fuels tested under a wide variety of test conditions. Several commercial additives were effective and the bulk of the remainder were innocuous at the concentration range studied. Sung and Karol (37,38) have patented a diesel fuel stabilizer which reportedly decreases sedimentation rates. Kitchen (41) has also patented a proprietary fuel additive described for improving the combustion efficiency and stability of stored fuel. Roux and Weers (44) studied the ability of stability additives to hinder formation of insoluble residue in diesel fuels. Data suggested that the addition of an additive results in a dramatic decrease in sediment formation under many conditions. Borown and others (66) developed a wax anti-settling flow improver and found that it reduced crystal sizes and kept wax dispersed in diesel fuel near the cloud point. Arfelli and co-workers (72) described a fuel stability foam made from polyurethane that was found to be effective in greatly reducing degradation of unstable diesel fuel on aging. On the other hand Pipenger (73) tested a total of 29 commercially-available additive treatments and found most multifunctional winterizing diesel fuel additives do not adequately protect fuels for long term storage stability. Many even caused rapid degradation of stored fuels.

Bentley and others (28), Schrepfer et al. (31) Taylor and Frankenfeld (54)and Henry (68) have published reviews of diesel fuel stability, reaction mechanisms, stabilizing additives, and evaluation of experimental approaches.

DISTILLATE FUEL CITATIONS

26. HENRY, C. P.; PET. LAB., E. I. DU PONT DE NEMOURS AND CO., INC. THE DU PONT F21 149° C (300° F) ACCELERATED STABILITY TEST. ASTM SPEC. TECH. PUBL., 751(DISTILL. FUEL STAB. CLEANLINESS), 22-33, 1981.

    The relation of the title test to actual long-term storage stability of distillate fuels was discussed. The paper in its entirety was not available for review, however.

27. COONEY, J. V., BEAL, E. J., HAZLETT, R. N.; NAVAL RESEARCH LAB., WASHINGTON, DC. TIME-TEMPERATURE-CONCENTRATION MATRIX FOR INDUCED SEDIMENT FORMATION IN SHALE DIESEL FUEL. 186TH. NATIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY CONFERENCE, WASHINGTON, DC, 28 AUG 1983. PREPR. PAP., AM. CHEM. SOC., DIV. FUEL CHEM. (UNITED STATES) V28:4, 1983.

    Since deterioration in fuel quality during storage has been a major problem with utilization of middle distillate fuels, the relationships between time, temperature, and concentration of dimethylpyrrole (DMP) to the formation of insoluble sediments were investigated. A common reaction pathway appeared to exist for DMP-promoted sedimentation in diesel fuel. A high-precision gravimetric method of fuel storage stability determination was thereafter developed.

28. BENTLEY, J. R., SCHELLHASE, H.U.; BC HYDRO R AND D CENTRE SURREY, BC. FUEL STABILITY AND STORAGE LIFE OF MIDDLE DISTILLATE FUELS. SAE SPEC. PUBL. (UNITED STATES) V SP-548, 63-73 P., AUG 1983.

    Concern about the long term storage stability of middle distillate fuels was responsible, in the first half of 1982, for an extensive literature survey and the evaluation of various experimental approaches. Fuel quality after aging for 12 weeks at 110° F was selected as an accelerated test for the assessment of fuel storage life. Thermal aging for 16 hours at 212° F was adopted for fast fuel screening, and the more severe conditions of 212° F for 60 to 120 hours for the testing of highly stable fuels and additives. A total of seven test fuels and eight fuel additives were tested. Three additives were found to be most effective in controlling thermal aging of ("Keogh") fuel. Initial results of ultrasound aided thermal aging at 110° F seem to indicate that the so called "induction period" is accompanied by poor aging statistics.

29. JONES, L., HARDY, D. R., HAZLETT, R. N.; NAVAL RESEARCH LAB. STORAGE STABILITY STUDIES OF U.S. NAVY DIESEL FUEL MARINE. 186TH. NATIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY CONFERENCE, WASHINGTON, DC. 28 AUG 1983. AM. CHEM. SOC., DIV. PET. CHEM., PREPR. (UNITED STATES), V 28:5, 1157-1164 P., SEPT 1983.

    An attempt to improve empirical predictive storage stability tests for Navy diesel fuel marine was made. The experimental procedure included filtering of insoluble sediments from the fuel sample after some period of stressing. The time and temperature dependence of the sediment formation was investigated.

30. JONES, L., HAZLETT, R. N., LI, N. C., GE, J.; NAVAL RESEARCH LAB., WASHINGTON, DC. STORAGE STABILITY STUDIES OF FUELS DERIVED FROM SHALE AND PETROLEUM. 185TH. AMERICAN CHEMICAL SOCIETY NATIONAL MEETING, SEATTLE, WA, USA, 20 MAR 1983. PREPR. PAP. - AM. CHEM. SOC., DIV. FUEL CHEM. (UNITED STATES) V 28:1, 196-201 P, 1983.

Fuel storage degradation was monitored in the early stages by laser light scattering of developing particles at ambient temperature. Degradation products of distillate fuels were obtained by heat stressing (at 80-120° C) fuels enriched with specific heteroatomic compounds. DMP (2,5-dimethylpyrrole) was especially deleterious to fuel stability, followed in effect by alkyl-substituted quinolines, pyridines and indoles. The oxygen and nitrogen contents of the sediments from shale-derived jet and diesel fuels which contain DMP are almost twice the corresponding value of petroleum-DMP sediment. Oxygen is incorporated in the sediments as carboxylate and carbonyl groups. NMR spectra of several soluble sediments showed a wide range of aromatic signals, indicating that the sediment contained polycyclic material. Deposits formed in the presence of DMP and thiophenol contained significant amounts of nitrogen and sulfur.

31. SCHREPFER, M. W., ARNOLD, R. J., STANSKY, C. A.; UOP PROCESS DIVISION, UOP INC., DES PLAINES, IL. DISTILLATE STABILITY ENSURED BY TESTING, TREATMENT. OIL GAS J. (UNITED STATES) V 82:3, 79-84 P., JAN 1984.

A review with 12 references on the storage stability of middle distillate fuels, stability testing, test significance, and chemical treatment for stabilization is presented in this publication.

32. TEWARI, K. C.; INTERNATIONAL COAL REFINING CO., ALLENTOWN, PA. RHEOLOGY AND STABILITY OF SRC RESIDUAL FUEL OILS. FINAL REPORT. SRC-I QUARTERLY TECHNICAL REPORT. SUPPLEMENT, JANUARY-MARCH 1983. 1-53 P., JUNE 1984.

Single-phase blends of 50 wt % HSRC and TSL SRC in 1:1 mixtures were subjected to storage stability tests at 150° F in nitrogen and air atmospheres. Nitrogen blanketing appears to be important in maintaining the specified viscosity characteristics of the blends during storage. A loss of volatiles undoubtedly occurs during high-temperature storage that contributes to an increase in the viscosity of the blend. In commercial practice, volatile losses are expected to be significantly lower. Analysis of separated fractions suggest that during storage, some oxidative polymerization of pentane-soluble oil components forms higher molecular weight pentane insolubles (asphaltenes and benzene insolubles). Asphaltenes are also involved in the increase in viscosity.

33. COONEY, J. V., BEAL, E. J., HAZLETT, R. N.; NAVAL RESEARCH LABORATORY. MECHANISMS OF SYNFUEL DEGRADATION 1. EFFECTS OF ORGANIC NITROGEN COMPOUNDS ON THE STABILITY OF A SHALE DERIVED DIESEL FUEL. LIQ. FUELS TECHNOL. (UNITED STATES) V 2:4, 395-426 P., 1984.

Diesel fuel instability is usually defined by the formation of insoluble sediments and gums and by the accumulation of hydroperoxides. Gravimetric accelerated storage stability tests conducted with model compounds as dopants in otherwise stable distillate fuels have demonstrated that oxidative condensation reactions of polar heterocyclics are deleterious to stability. In particular, nitrogen containing aromatics (pyrroles, pyridines, indoles, etc.) appear to be very harmful.

34. JONES, L., GE, J., HAZLETT, R. N., LI, N.C.; NAVAL RESEARCH LABORATORY, WASHINGTON, D.C. STORAGE STABILITY STUDIES OF FUELS DERIVED FROM SHALE AND PETROLEUM. FUEL (UNITED KINGDOM) V 63:8., 1152-1156 P., AUG 1984.

Studies on the characterization and mechanisms of formation of deposits in containers used for storage of jet and diesel fuels were aimed at storage times of weeks or months. Development of the amount of sediments depended upon temperature, and the rate of sediment formation was determined by traditional gravimetric procedures. Early stages of fuel storage degradation was monitored by laser light scattering methods. The effects of certain heteroaromatic compounds on the formation of sediments were studied by light scattering techniques, liquid state NMR, solid state NMR, ESCA, and Fourier Transform Infrared Spectroscopy. Oxygen was found to be necessary for the formation of sediments, and 2,5-dimethylpyrrole was the most powerful promoter of deposit formation.

35. ANDERSON, R. P., GOETZINGER, J. W., BRINKMAN, D.W.; NATIONAL INSTITUTE FOR PETROLEUM AND ENERGY RESEARCH. STORAGE STABILITY AND COMPATIBILITY OF HEAVY FUEL OILS. 10TH ANNUAL EPRI CONTRACTOR'S CONFERENCE ON CLEAN LIQUID AND SOLID FUELS: PROCEEDINGS, PALO ALTO, CA, 23 APR 1985. EPRI-AP-4253-SR, 4.1-4.31 P., OCT 1985.

Lower product quality from increased use of low quality crudes in refinery feedstocks is evidenced by increased problems with product stability and compatibility. Problem components increase with increasing boiling point and are highest in the residual fractions. This project had the specific goal of determining practical test methods useful as screening techniques for predicting stability and compatibility problems. Three stable fuels and three which had exhibited instability or incompatibility problems were analyzed in an effort to determine the compound types responsible for the observed problems.

36. HAZLETT, R. N., HARDY, D. R., WHITE, E. W., BAER, L. J.; ASSESSMENT OF STORAGE STABILITY ADDITIVES FOR NAVAL DISTILLATE FUEL. SOCIETY OF AUTOMOTIVE ENGINEERS, INC.,WARRENDALE, PA, TP-851231, 17 P., 1985.

Five of the six additives currently allowed by the military specification were included in this evaluation as were five proprietary products used in diesel fuels and heating oils. This work emphasized tests on five selected fuels which exhibited poor or marginal stability behavior. The results of accelerated storage stability tests with temperature being the main variable were presented. Three laboratories performed stability tests at temperatures from 43 to 95° C. In addition, light scattering intensity measurements were made in conjunction with the gravimetric measurements. Finally the effect of additives on selected fuel properties which might be altered by addition of the tested additives was determined.

37. SUNG, R. L., KAROL, TH. J.; MIDDLE DISTILLATE FUEL OIL OF IMPROVED STORAGE STABILITY CONTAINING CONDENSATE OF MANNICH BASE AND ALKENYL

SUCCINIC ACID ANHYDRIDE. PATENT NO.: US 4,501,595 ASSIGNEES: TEXACO INC. FILED 25 MAY 1984. 6 P., 26 FEB 1985.

Diesel oil of improved storage stability was obtained by adding a condensate of tetraethylenepentamine; paraformaldehyde, 2,6-di-t-butyl phenol; and polyisobutenyl succinic acid anhydride.

38. SUNG, R. L., KAROL, T. J.; MIDDLE DISTILLATE CONTAINING STORAGE STABILITY ADDITIVE. PATENT NO.: US 4,533,361 ASSIGNEES: TEXACO INC. FILED DATE 9 OCT 1984. V P., 6 AUG 1985.

The storage stability of middle distillate diesel fuel was improved by the addition of acylated condensates of an alkenylsuccinic anhydride and a Mannich base. Thus, heating of 2,6-di-tert-butylphenol, HCHO, polyisobutenylsuccinic anhydride, oxalic acid, and pentaethylenehexamine in the presence of diluent oil and a silicone antifoaming agent at 110-160° C for approximately 9 hours gave an additive which, at 25 lb/1000 bbl diesel oil concentration, decreased its sedimentation rating (Potential Deposit Test) to 1.

39. WRIGHT, B. W., HARDY, D. R., HAZLETT, R. N., KALKWARF, D. R., SMITH, R. D.; BATTELLE PACIFIC NORTHWEST LABORATORIES, RICHLAND, WA. STORAGE STABILITY OF DIESEL FUEL MARINE: RELATION TO ELECTRON SPIN RESONANCE (ESR). MEASUREMENTS. FUEL (UNITED KINGDOM), V 64:5, 591-593 P., MAY 1985.

Free radical concentration in several diesel fuel marine samples were determined by electron spin resonance spectroscopy. Sediment formation in these fuels from accelerated storage-stress tests was measured and compared with their free radical concentrations. Radical concentrations ranged over about two orders of magnitude. The highest concentrations corresponded to the fuels with the lowest storage stability. When subjected to photolysis, the free radical concentrations of the fuel samples were significantly reduced.

40. ANDERSON, R. P., GOETZINGER, J. W., BRINKMAN, D.W.; NATIONAL INST. FOR PETROLEUM AND ENERGY RESEARCH. STORAGE STABILITY AND COMPATIBILITY OF HEAVY FUEL OILS. 10TH. ANNUAL EPRI CONTRACTORS' CONFERENCE ON COAL LIQUEFACTION, PALO ALTO, CA, USA, 23 APR 1985. NIPER-65, EP 1986 33 P., 1986.

Lower product quality is the result of increasing use of low quality crudes in refinery feedstocks. This is evidenced by increased problems with product stability and compatibility. Problem components increase with increasing boiling point and are highest in the residual fractions. This project has the specific goal of determining test methods that will be useful as screening techniques for predicting stability and compatibility problems. Three baseline fuels and three which have exhibited instability or incompatibility problems were analyzed in an effort to determine the compound types responsible for the observed problems.

41. KITCHEN, G.H. III; COMBUSTION IMPROVER FUEL ADDITIVE. PATENT NO.: US 4,585,462. FILED DATE 10 JUL 1984, GRANTED 29 APR 1986.

A proprietary fuel additive is described for improving the combustion efficiency and storage stability of stored fuel. It is claimed to be capable of reducing the amount of macroscopic sludge particles formed from polymerization reactions promoted by bacteria and oxidation in fuel. It also claims to improve the combustion efficiency of the fuel and reduce the soot emissions and scale formation of such fuel in a combustion chamber when used in amounts of from about one part of additive composition to between 3000-10,000 parts by weight of fuel. The additive contains a polymerizate of ethylene diamine, a naphtha solvent, a polyalphaolefin based synthetic oil, a miscible biocide, and manganese linoleate.

42. COONEY, J. V., BEAL, E. J., BEAVER, B. D.; MECHANISMS OF SYNFUEL DEGRADATION. 3. INTERACTIVE EFFECTS IN NITROGEN COMPOUND INDUCED STORAGE INSTABILITY IN SHALE DERIVED DIESEL FUEL, NAVAL RESEARCH LAB., FUEL SCI. TECHNOL. INT. (UNITED STATES) V 4:1, 1-18 P., 1986.

Diesel fuel instability is usually defined by the formation of insoluble sediments and gums and by the accumulation of hydroperoxides. Gravimetric accelerated storage stability tests conducted with added model compounds in otherwise stable distillate fuels have demonstrated that oxidative condensation reactions of polar heterocyclics are deleterious to stability. In particular, nitrogen containing aromatics (pyrroles, pyridines, indoles, etc.) are very harmful.

43. POWER, A. J., DAVIDSON, R. G.; MATERIALS RESEARCH LABS., ASCOT VALE, AUSTRALIA. INFRARED SPECTROSCOPY OF CARBONYL SPECIES IN OXIDISED DIESEL DISTILLATES. FUEL (UNITED KINGDOM) V 65:12, 1753-1755 P., DEC 1986.

Semiquantitative infrared difference spectroscopy has shown the extent of molar carbonyl group formation in some diesel distillates to differ by about an order of magnitude for three different fuel aging conditions (100° C/168 hours/O_2 atmosphere: 95° C/16 hours/O_2 sparge; ambient storage). This may partly explain the known unreliability of accelerated oxidation techniques for predicting fuel storage stability. It has also been shown that CO species present in steam-jet gum residues do not represent those in oxidised fuels prior to evaporation.

44. ROUX, KENNETH R. AND JERRY J. WEERS. STORAGE CHARACTERISTICS OF ADDITIVE TREATED DIESEL FUEL. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

The influence of storage conditions on the ability of stability additives to hinder formation of insoluble residue in diesel fuel was studied. Residue levels were determined as a function of storage time, temperature, and additive concentration on a number of fuels. Accelerated stability test data obtained on the treated fuels were compared to results generated under actual ambient storage conditions. Data suggested that the addition of an additive to a diesel fuel results in a dramatic decrease in sediment formation under many conditions.

45. SMITH, R. J. AND L. D. PALMER. AUTOMOTIVE DIESEL FUEL STABILITY-AN AUSTRALIAN VIEWPOINT. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Reliability of long-term storage stability tests of diesel fuel have been studied with the 110° F/13 week test being the most satisfactory. Apart from the 175° F/7 day stability test, other methods are generally unreliable and easily affected by outside influences such as light exposure. Excellent results were obtained in improving storage stability of diesel fuel by caustic washing and additive treatment. No improvement in color degradation resulted from additive treatment, however.

46. HARDY, D. R., R. N. HAZLETT AND E. W. WHITE. ASSESSMENT OF STORAGE STABILITY ADDITIVES FOR NAVAL DISTILLATE FUEL. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

This paper summarizes the effectiveness of five of six allowed military specification stabilizer additives and of five proprietary commercial stabilizer products in five military fuels. A major find was that phenylene diamine type additives seriously degrades the stability of all five fuels used in this program. A second result was that commercial additives used in diesel fuels and heating oils greatly improve the stability of the fuels tested. Hindered phenols exhibited marginal behavior in the stability tests.

47. PALMER, L. D. AND B. V. COPSON. HYDROTREATMENT OF LIGHT CYCLE OIL FOR STABILIZATION OF AUTOMOTIVE DIESEL FUEL. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA, JULY 29 - AUGUST 1, 1986.

Hydrotreatment of only the light cycle oil (LCO) component of automotive diesel fuel was studied as a means of achieving high deposit and color stability. Use of stabilizing additives was compared to hydrotreating. Hydrotreating offers the advantage of good color stability but is the more expensive option. For low sulfur/nitrogen diesel fuel, a selected additive system is capable of efficiently reducing sediment formation.

48. BHAN, OPINDER K., JOHN B. GREEN, DENNIS W. BRINKMAN,AND BILL CARLEY. CAUSES OF COLOR CHANGE AND SEDIMENT FORMATION IN NAVY DISTILLATE FUELS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

This research described detailed compositional studies of stable and unstable diesel fuels with a discussion of the differences observed and the probable mechanisms leading to problems. It was concluded that oxidation of neutral components present in fuel to polar intermediates may be a major pathway for sediment formation and darkening of diesel fuels.

49. HALSALL, R.; EFFECTS OF AN UNSTABLE DIESEL FUEL ON INJECTOR COKING AND VEHICLE PERFORMANCE. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Short-term effects of an oxidatively unstable diesel fuel were investigated in city-suburban service. Effects on injector coking, FTP emission, fuel economy, cold-idle passenger compartment sound pressure, and driveability were monitored. The unstable test fuel caused frequent severe vehicle fuel filter plugging resulting in excessive smoke emission and power loss. Injector coking was also observed but was insufficient to cause adverse effects.

50. WESTBROOK, S. R., L. L. STAVINOHA, J. G. BARBEE AND L. L. BUNDY. APPLICATION OF A FIELD FUEL QUALITY MONITOR TO SURVEILLANCE OF PREPOSITIONED FUEL STOCKS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

A monitor is described to test fuel stability and cleanliness on site. It provides a means to sample the fuel, measure color, estimate particulate contamination, and estimate fuel stability. It was concluded that the monitor had proven to be a valuable tool for monitoring the stability and cleanliness of fuel in storage by enabling an operator to conduct tests on site, thereby eliminating the need to routinely return samples to a laboratory. While the monitor provides actual measure of color and particulates it will not provide an absolute prediction of fuel stability--only providing changes in stability characteristics of the fuel.

51. STRAUSS, KURT H.; A QUALITY CONTROL SYSTEM FOR DIESEL FUEL IN LONG TERM STORAGE. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

A quality control program was designed which was intended to avoid fuel storage stability problems for diesel engines to power emergency-generating equipment for shut-down procedures at nuclear power plants. Portions of the program have been adopted in NRC regulations.

52. HARDY, D. R. AND R. N. HAZLETT. STABILITY MEASUREMENTS OF COMMERCIAL MARINE FUELS FROM A WORLWIDE SURVEY. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986. SAE INT. CONGR. (DETROIT 2/24-28/86) PAP. (ISSN 0148-7191) N.860895 9P (ORDER COPIES OF PAP. #860895 AT $4.50 EACH FROM SAE CUSTOMER SERV., DEP. 676, 400 COMMONWEALTH DRIVE, WARRENDALE, PA. 15096; PHONE 412-776-4970) V., 1986.

Storage stabilities of 36 commercial marine fuels from a worldwide survey were evaluated. Fuels were classified as: marine gas oils, heavy marine gas oils, and marine diesel fuels. Accelerated stability tests included 43° and 80° C bottle tests, and ASTM D 2274 tests at 95° C. Results from two labs indicated very good agreement in assignment of relative storage stabilities to the fuels in each class. The results indicate that D 2274 is useful as a go/no-go test in the procurement of aged commercial fuels.

53. GIANNINI, ROBERT. A RECENT INSTABILITY OCCURRENCE WITH NAVAL DISTILLATE (NATO F-76). 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

The object of the Navy study was to develop test protocols to qualify candidate fuels for use in Navy shipboard combustion equipment. A large quantity of fuel was requisitioned and procured, then stored in a fuel barge. Samples were taken upon receipt which indicated that fuel met the NATO F-76 specifications. Six months later, the fuel was off-specification with respect to color and contained large amounts of particulates. The major conclusion was that the specification in its current form was not adequate to protect against the receipt of a fuel which could develop a stability problem.

54. TAYLOR, WILLIAM F. AND JOHN W. FRANKENFELD. CHEMISTRY AND MECHANISM OF DISTILLATE FUEL STABIITY. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

This is a review of the 1986 knowledge relative to the chemistry and mechanism of distillate fuel stability. Fuels included jet fuel, diesel fuel and heating oil. Subjects covered in the review included: storage stability, thermal stability, storage and thermal stability effects on sediment, peroxide, color and surface deposit formation, relevant pure compound autoxidation kinetic studies with actual fuel, and the current state of knowledge on the effect of fuel composition on the rate of autoxidation and on stability properties such as sediment and surface deposit formation rates. Other subjects included interactions between chemical kinetic and physical rate processes in the overall sediment and surface deposit formation process.

55. MUSHRUSH, GEORGE W., ROBERT N. HAZLETT, DENNIS R. HARDY AND JOHN M. WATKINS, JR.; LIQUID PHASE OXIDATION OF SULFUR COMPOUNDS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Because of the contradiction in the literature regarding the role of organosulfur compounds on the oxidation stability of middle distillate fuels, the oxygen and t-butyl hydroperoxide liquid phase oxidation of hexyl sulfide, dodecyl thiol, thiophene, thiophenol in benzene and model fuel, and tetradecane were examined. Variations in fuel composition, reaction surface, hydroperoxide concentration, dissolved oxygen and reaction temperature all contribute to the variation in observed results. The investigators also studied the reaction between thiophenol and active olefins such as styrene.

56. MILLER, STEPHEN J.; CHEVRON RESEARCH CO. STABILIZING LUBE BASE STOCKS DERIVED FROM BRIGHT STOCK. US PATENT APPL 85-790704 24 OCT 1985, US 4627908 A 9 DEC 1986, 5 PP.

Lubricating base oils, with improved antioxidation and storage stability, are manufactured from a nitroaromatic-containing hydrocracked bright stock by contacting with a sulfided hydrodenitrogenation catalyst in a first stage and then contacting the nitrogen-free product with a hydrogenation catalyst in a second stage. The storage stability (at 250° F) of the resulting product was ≥15 days, compared with ≤1 day for a conventional single-stage process.

57. MILLER, STEPHEN J.; CHEVRON RESEARCH CO. PROCESS FOR IMPROVING THE STORAGE STABILITY AND BULK OXIDATION STABILITY OF LUBE BASE STOCKS DERIVED FROM BRIGHT STOCK. US PATENT APPL 85-807920 11 DEC 1985. US PATENT GRANTED 4657661 A 14 APR 1987, 6 PP., 1987.

Lubricating oil base stocks derived from hydrocracked bright stocks containing nitroaromatic compounds were stabilized by successive steps of catalytic hydrodenitrogenation, mild catalytic hydrofinishing for improvement of oxidation stability, and nonhydrogenative olefinic stabilization with a heterogeneous acid catalyst.

58. ANDERSON, R., GOETZINGER, J., REYNOLDS, J.; NATL. INST. PET. ENERGY RES., STABILITY AND COMPATIBILITY OF RESIDUAL FUEL OILS. ELECTR. POWER RES. INST., [REP.] EPRI AP (PALO ALTO, CALIF.), EPRI AP-5043-SR, PROC. - ANNU. EPRI CONTRACT. CONF. CLEAN LIQ. SOLID FUELS, 11TH, 1986, 4/87-4/122, 1987.

Rapid practical tests were presented which predict potential problems that can occur during use of a residual fuel oil or fuel oil blend (especially those intended for combustion in power generation). A baseline test for determination of stability of residual fuels, involving long-term aging at 80° C, monitors changes in sediment, asphaltene content, and viscosity. A baseline test for incompatibility of blends (e.g., with lighter oils as diluents) involved preparation of blends followed by determination of sediment by hot filtration.

59. BEAL, E. J., COONEY, J. V., HAZLETT, R. N.; NAVAL RESEARCH LAB., WASHINGTON, DC 20375-5000. CHEMICAL FACTORS AFFECTING INSOLUBLES FORMATION IN SHALE-DERIVED DIESEL FUEL. 193RD. NATIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY CONFERENCE, DENVER, CO, 5 APR 1987 PREPR. PAP., AM. CHEM. SOC., DIV. FUEL CHEM. (UNITED STATES) V 32:1. 530-537 P., APR 1987.

To define the stability of shale-derived diesel fuel, the authors conducted gravimetric accelerated storage stability tests at 43 and 80° C using three model nitrogen compounds, 2-methylpyridine, 2,6-dimethylquinoline and dodecahydrocarbazole, as additives in an otherwise stable shale diesel fuel. Also, information about potential interactive effects has been defined for these three model nitrogen compounds in the stable fuel in the presence of a second model dopant (a hydroperoxide, organic acid or base).

60. SUNG, R. L.; STORAGE-STABILIZING ADDITIVES FOR MIDDLE DISTILLATE FUELS. PATENT NO.: US 4,689,051 ASSIGNEES: TEXACO INC., WHITE PLAINS, NY. FILED DATE 28 MAY 1986, V P., 25 AUG 1987.

A storage stabilizing additive for middle distillate fuel oil is described. The additive contains the reaction product of a hydrocarbon-substituted mono primary ether amine and a diabisic acid anhydride to form maleamic acid. This is reacted with an n-alkyl alkylene diamine to produce the storage stabilizing additive.

61. BHAN, O. K., BRINKMAN, D. W., GREEN, J. B.; NATIONAL INSTITUTE OF PETROLEUM & ENERGY RESEARCH, CARLEY, B., DEPT OF DEFENSE, STORAGE STABILITY OF MARINE DIESEL FUELS. FUEL (UNITED KINGDOM) V 66:9, 1200-1214 P., SEP 1987.

Several marine diesel fuels were aged at 65° C for various periods. Aged and unaged fuel samples were chromatographically separated into acid, base and neutral fractions, and the fractions were analyzed in detail to obtain a clearer understanding of the mechanism of color change and sediment formation. The results suggest that oxidation of neutral compounds to polar intermediates may be a major pathway for sediment formation and darkening of marine diesel fuels. Considerable loss of polar compounds to sediment was found. The more aromatic higher molecular weight members were observed to be the most active in sediment formation.

62. PEDLEY, J. F., HILEY, R. W., HANCOCK, R. A.; STORAGE STABILITY OF PETROLEUM-DERIVED DIESEL FUEL. 1. ANALYSIS OF SEDIMENT PRODUCED DURING THE AMBIENT STORAGE OF DIESEL FUEL. FUEL (UNITED KINGDOM) V 66:12, 1646-1651 P., DEC 1987.

The stability of three diesel fuels was monitored during 16 months of ambient storage. Two commercially available stability improving additives had little effect on the storage stability of the fuels tested and had a deleterious effect on fuel filterability characteristics. The sediment produced by the degradation of one of the fuels was characterized by a range of analytical techniques, including IR spectroscopy, pyrolysis, gas chromatography, thin-layer chromatography and mass spectrometry (electron impact and fast atom bombardment ionization). Nonbasic nitrogen compound, in particular alkylindoles, were important constituents of the fuel sediment.

63. SCHELLHASE, H. U., COLWELL, M. J.; BC HYDRO RES. DEV. PREDICTION OF LONG-TERM STORAGE STABILITIES OF (14 MIDDLE DISTILLATE) FUELS BY THERMAL ANALYSIS (PRESSURE-DSC). SAE INT. FUELS LUBR. MEET. (TORONTO 11/2-5/87) PAP. (ISSN 0148-7191) N.872145 18P, 1987.

Prediction of long-term storage stabilities of 14 middle distillate fuels by thermal analysis, i.e, pressure differential scanning calorimetry, under a 600 psi O_2 pressure involved correlation of the reaction enthalpy of gum formation with the total insolubles formed during storage of the fuels for 12 weeks at 43.3° C with a correlation coefficient of about 0.97. The test fuels included winter diesel fuel, synthetic fuel from tar sands and coal, and straight run and cracked fuels from different parts of Canada as well as some of their blends. The relative deviation was 5-12% and should be reduced to less than 5% by improvement of instrumentation and technique. The test is completed in 24 hours, requires only $\leq$100 mg for a complete test, and is suitable for automation with a microprocessor.

64. GURNEY, M. D., STREETS, W.L.; MARINE DIESEL FUEL CRITERIA. NATIONAL INSTITUTE FOR PETROLEUM AND ENERGY RESEARCH, 1987 ANNUAL REPORT. BALL, J.S. (ED.). NIPER-320. 509-511 542 P., OCT 1988.

Blending highly aromatic material derived from processing heavy crude feedstocks and residuum into diesel fuel reduces cetane number and storage stability. The quantity and quality of the cracked stock as a diesel fuel blending component have yet to be determined. The research effort is designed to determine the effects of diesel fuel composition on ignition, combustion, and emissions behavior in high-speed marine diesel engines.

65. PEDLEY, J.F., HILEY, R.W., HANCOCK, R.A.; STORAGE STABILITY OF PETROLEUM-DERIVED DIESEL FUEL. 3. IDENTIFICATION OF COMPOUNDS INVOLVED IN SEDIMENT FORMATION FUEL (UNITED KINGDOM) V 67:8, 1124-1130 P., AUG 1988.

An unstable, raw, catalytically-cracked light cycle oil from a North Sea crude, was analyzed to identify compounds involved in the formation of sediment during its storage. Two groups of non-basic organonitrogen compounds which react in the presence of acid to form the polar, highly-colored fraction of sediment were extracted from the fuel by liquid chromatography on silica gel. They were characterized by thin-layer chromatography, IR spectroscopy, and MS. One group consisted of alkylated indolylphenalenes, and the other of alkylated bis(indolyl)phenalenes. Phenalene itself was detected in an undegraded sample of the fuel. Phenalenones, from oxidation of phenalenes, were detected in the fuel and their concentrations increased with time during ambient storage of the fuel. The sediment precursor compounds could have been formed by condensation of phenalenones with indoles.

66. BOROWN, G. I., TACK, R. D., CHANDLER, J. E.; PARAMINS TECHNOL. DIV. AN ADDITIVE SOLUTION TO THE PROBLEM OF WAX SETTLING IN DIESEL FUELS. SAE INT. FUELS LUBR. MEET. (PORTLAND, OR 10/10-13/88) PAP. N.881652 15P, 1988.

New wax anti-settling flow improvers (WAFI) reduced crystal sizes and kept wax dispersed in the diesel fuel near the cloud point. Improved performance of fuels treated with WAFI was shown in storage tests, a diesel fuel rig, and in diesel trucks on a a cold climate chassis dynamometer. Benefits from the application of WAFI were: reliable cold fuel performance for consumers, improved refinery economics, and the ability to increase diesel fuel production to meet growing demand.

67. HILEY, R. W., PEDLEY, J. F.; STORAGE STABILITY OF PETROLEUM-DERIVED DIESEL FUEL. 2. THE EFFECT OF SULFONIC ACIDS ON THE STABILITY OF DIESEL FUELS AND A DIESEL FUEL EXTRACT. FUEL (UNITED KINGDOM) V 67:4. 469-473 P., APR 1988.

An unstable gas oil was stabilized by desulfurization with aqueous 40 wt % potassium hydroxide, followed by washing with very dilute aqueous HCl and then with deionized water, and then drying. Addition of 10-100 ppm naphthalene sulfonic acid (NSA) to the stabilized fuel, and to a normally stable fuel (a straight-run distillate blended with a hydrotreated catalytically-cracked fuel), promoted formation of sediment during storage in the dark at 43° C for 40 days in loosely-covered borosilicate glass jars. The sediments were virtually indistinguishable from sediments produced under normal fuel storage conditions. The amounts of sediment formed were directly proportional to the amounts of added NSA. NSA reacted with non-basic organonitrogen-compound extracts from the fuels to produce the highly-colored component of the sediment.

68. HENRY, C. P.; ADDITIVES FOR MIDDLE DISTILLATE AND KEROSINE FUELS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986. ASTM SPEC. TECH. PUBL., 1005(DISTILL. FUEL: CONTAM., STORAGE HANDLING) 105-13 (1988) CHEM. ABSTR. ABSTR. NO. 234244 V110 N.26., 1988.

A review with three references of the effects of diesel and jet fuel additives, such as antioxidants, metal deactivators, dispersants, detergents, wax modifiers, etc. on sediment and gum formation in fuel storage.

69. HARDY, D. R., E. J. BEAL, R. N. HAZLETT AND J. C. BURNETT. EVALUATION OF COMMERCIAL STABILITY ADDITIVES FOR NAVAL DISTILLATE FUEL. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

A summary of the effectiveness of nine commercial stabilizer additives in nine freshly refined fuels tested under a wide variety of test conditions was presented. Tests were in bottles between 43 and 80° C, ASTM D2274 and oxygen overpressure tests between 43 and 90° C. Additive effectiveness was estimated by a light scattering test. The fuels selected from U.S. refineries contained a range of catalytically cracked stock from less than 10% up to 40%. It was possible to identify several of the commercial additives as routinely effective and the bulk of the remainder as being innocuous at the concentration range studied in this work (24 to 50 mg/liter).

70. MABLEY, P. B. AND G. M. WALLACE. DISTILLATE FUEL STABILISATION IN A MAJOR EUROPEAN REFINERY. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

A European refinery maximized distillate production through the use of a specifically designed multi-functional stabilizer package. Production of distillate was increased by producing fuel closer to the required specification in terms of sulfur and cetane number. Stability specifications included oxidative stability tests commonly employed in quality control applications and long term storage trials used to ensure good field performance. Test data showed that balanced multifunctional additive packages added to fresh high severity conversion streams inhibit color degradation and sediment formation. This benefit allowed the refiner to optimize distillate production which was previously not possible due to constraints on the hydro-processing route.

71. BERNASCONI, C., A. CHAFFARDON, P. CHARLEUX, J. DENIS, J. GAILLARD AND J. P. DURAND. MIDDLE DISTILLATES STABILITY: COMPOSITION AND ADDITIVE UTILIZATION EFFECTS ON THEIR AGING AT DIFFERENT TEMPERATURES. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Because of increased demand in France for middle distillates, considerable effort has been directed to increased production and evaluation of middle distillate stability and additive effectiveness. Several mixtures of Straight Run Gas Oils and cat-cracked Light Cycle Oils (LCO) have been subjected to different aging methods (2 hours at 120° C, 12 weeks at 43° C, and one year at ambient temperature) followed by color and gravimetric determinations. The first method (120° C) is useful as a screening test, while the second method (43° C) appears closely correlated with the actual storage. Alkylindoles appear to be involved in LCO degradation. LCO fractionation has allowed us to show the important degradation tendency of heavy $315^{\circ+}$ C fraction. Stabilizers such as aliphatic tertiary amines with a metal deactivator minimize the gum and sediment formation, but their action is more obvious if measured by accelerated aging methods; however, color darkening is harder to control.

72. ARFELLI, W. A., J. POWER AND R. K. SOLLY. SOLID ABSORBENTS AS DISTILLATE FUEL STABILITY AGENTS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Fuel stability foam (FSF) made from polyurethane was found to be very effective in greatly reducing degradation of unstable diesel fuel on aging. Only 0.2 grams per liter of fuel produces reduction in total particulate greater than 90% as well as improvement in fuel filterability and finally reduction of color degradation.

Stabilization mechanisms of FSF are suggested to be adsorption of fuel deposit precursors, soluble particulate species, insoluble particulate and degradation catalysts.

73. PIPENGER, G. G.; STORAGE STABILITY CHANGES WITH COMMERCIALLY AVAILABLE DIESEL FUEL WINTERIZING ADDITIVES IN THE UNITED STATES. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

A total of twenty-nine (29) commercially-available additive treatments were tested on three untreated consumer-available fuels. Samples were tested for stability improvement; biocidal effectiveness; cetane number; cloud point; and, pour point. The fuels selected were No-2 diesel fuels supplied to the US transportation markets, all meeting the ASTM specification D975 for diesel fuels. The additive treatments were purchased in the continental United States. Conclusions included that most multifunctional winterizing diesel fuel additives marketed in the United States do not adequately protect fuels for long-term storage stability. Many even caused rapid degradation of stored fuels.

74. BEAL, E. J., D. R. HARDY, R. N. HAZLETT, J. C. BURNETT, R. GIANNINI AND R. STRUCKO. STABILITY MEASUREMENTS OF MILITARY AND COMMERCIAL MARINE FUELS FROM A WORLWIDE SURVEY. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

The storage stabilities of 22 military (NATO F-76) fuels and 26 commercial marine fuels from a worldwide survey taken in 1986 were evaluated. The commercial fuels were very similar to currently used F-76 fuels. Accelerated storage stability tests included 43° C bottle tests, ASTM D 2274 and a new low pressure reactor test at 90° C and 100 psig overpressure of oxygen. Results indicated that the 26 commercial fuels were storage stable and that they appear to be more stable than the fuels from the 1982 survey. The military F-76 fuels were also stable but not as stable as the commercial fuels. It was also concluded that ASTM D2274 correctly assesses the stability of aged fuels or fuels that contain no LCO.

75. SUTTERFIELD, F. D., W. V. STEELE, D. G. ARCHER, R. D. CHIRICO AND M. M. STRUBE. COMPARISON OF THERMODYNAMICS OF NITROGEN AND SULFUR COMPOUNDS IMPLICATED IN FUEL STABILITY PROBLEMS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Because of the increased use of low quality crude oils, present day fuels have higher heteroatom and aromatic contents and a tendency toward instability. Hydrodesulfurization chemistry and hydrodenitrogenation are areas where knowledge of the thermodynamic equilibria among the species is necessary for proper interpretation of reaction data and accurate modeling of reactions. This study concluded that most problem compounds in hydrodesulfurization contain a thiophenic ring. Thiophenes, pyrroles, and pyridines are the most resistant to present hydrogenation practice. These are also considered to be some of the most active gum promoters. In both hydrodesulfurization and hydrodenitrogenation reactions the large exothermic enthalpies of reaction require special attention in plant design and operation.

76. PEDLEY, J. F. AND R. W. HILEY. INVESTIGATION OF 'SEDIMENT PRECURSORS' PRESENT IN CRACKED GAS OIL. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Sediment precursors found and reported in 1986 were isolated into two related groups of compounds from a degrading catalytically-cracked gas oil using chromatography techniques. The isolated groups were characterized and identified as consisting of indoles linked to polycyclic aromatic hydrocarbons. It was concluded that the precursor compounds were formed by the condensation of these oxidation products with indoles.

77. WESTBROOK, S. R., L. L. STAVINOHA AND J. P. HSU. STUDIES OF FUEL DETERIORATION AND ADDITIVE INHIBITION MECHANISMS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Recent studies have shown that acid base or acid-catalyzed reactions are important in the formation of sediments in fuels containing catalytically cracked stock. Fuels with little or no cracked stock form insolubles by different reactions. The type of additive used to reduce insolubles depends, therefore, on the reactions that occur. In this study several commercial fuel stabilizer additives and one pure compound were studied in a straight run fuel, a light cycle oil and a blend of the two. A model was developed based on the analysis which was useful for the study of additive inhibition and insolubles formation mechanisms.

78. KLINKHAMMER, M. D., E. W. WHITE AND K. W. FLOHR. A STUDY OF PRECURSORS IN THE FORMATION OF INSOLUBLE PRODUCTS DURING THE AGING OF MIDDLE DISTILLATE FUELS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

A gas chromatographic (GC) study was conducted of both unstressed fuel and fuel with insolubles following various bottle storage regimes, viz. 43° C for eight weeks, 65° C for one, three, and eight weeks and 95° C for one week. Prior to stressing, all three fuels contained detectable amounts of material similar to the major components later found in the filterable and adherent insolubles. These precursors increased in concentration in the filtered fuels following stressing as the stressing conditions became more severe. It was found that the adherent insolubles and the filterable insolubles were almost identical by gas chromatographic techniques.

79. LI, N. C., H. CHANG, S. M. WANG, P. J. HUANG AND J. R. TZOU. DEVELOPMENT OF PREDICTIVE TESTS FOR FUEL STABILITY. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

As a predictive tests for fuel stability, a metal powder, Cu, Al or Fe, is added to the fuel. Various amounts of unsaturated and S,O,N-containing compounds are added to the fuel to accelerate aging. After standing for various short intervals the metal powder is removed and the metal content in the fuel is determined by ICP-AES or AA. The predictive tests show that the deleterious effects of metals are in the order Cu > Al or Fe. The extents of light scattering and of metal drawn into the fuel from added metal powder are correlated with the extent of deposit formed in degradation of the fuel. A mechanism is suggested for sediment formation with sulfur compounds.

80. ZAHAVI, E., A. B. SHAVIT, J. BEN-ASHER AND N. POR. STUDY OF STABILITY OF DIESEL FUELS UNDER OPERATIONAL CONDITIONS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Formation of degradation products in bus engine fuel systems has been observed by filter clogging and deposit formation. The main cause for these field operational problems may be attributed to the fact that diesel fuel deteriorates at the relatively high temperatures prevailing in part of the fuel system. Two different straight run diesel fuels, a blend of light cycle oil and straight run diesel fuel with and without a stabilizer additive have been studied in buses of the public transportation system during actual road service. Unconsumed gas oils taken from the systems, were evaluated by four different stability tests. It was found that diesel fuel types, tested during this study, deteriorated in stability which resulted in formation of insoluble sediments, increase in acidity and low filtration rates. Addition of fuel stabilizer induced better filterability on the two straight run stocks, accompanied by a reduced rate of filtration of the unstable blend.

81. KALITCHIN, Z. H., S. L. IVANOV, S. TANIELIAN, A. IVANOV, P. GEORGIEV., K. KANARIEV AND M. BONEVA. STABILITY OF MOTOR DIESEL FUELS AND PROGNOSTICATION OF THEIR STORAGE TERMS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Long term storage of diesel fuels is determined by their physical and chemical stability which are a function of acid number, insoluble gum, total insolubles, absorption of oxygen, and optical density. It is generally considered that diesel fuels containing components of direct distillation can be stored for 3 to 5 years. The most important parameters for all types of diesel fuels are considered to be the insoluble gum and total insolubles.

82. HARDY, R. E., J. BEAL, R. N. HAZLETT AND J. C. BURNETT. ASSESSING DISTILLATE FUEL STORAGE STABIITY BY OXYGEN OVERPRESSURE. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

A new method is described for predicting distillate fuel's tendency for forming deleterious fuel insolubles during ambient storage. Oxygen is forced into solution in the fuel at pressures up to 100 psig. The fuel is stressed under conditions of accelerated storage. The method then makes use of gravimetric determination of the total insolubles formed. This rapid and precise method is predictive for up to 3 years of ambient conditions. It has been used to rank additive-free fuels over a wide range of storage stabilities and has also been useful in assessing the relative effectiveness of middle-distillate fuel antioxidant additives.

83. MARTIN, B., X. MONTAGNE AND C. BERNASCONI. OPERABILITY OF AUTOMOTIVE DIESEL ENGINES WITH UNSTABLE FUELS-ACCELERATED STABILITY TESTS RELEVANCE. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Filter plugging or injector fouling may be encountered when using unstable fuels. A study to determine the relevance of accelerated tests for prediction of operability problems was therefore conducted. Fuel was aged in steel tanks at different temperatures and quality during storage was monitored by filterable sediments, filter clogging and injector fouling tendencies. Results confirmed that degradation of fuel is different according to temperature, and aging affects thermal stability and injector fouling tendency of fuels.

84. PEDLEY, J. F., HILEY, R. W., HANCOCK, R. A.; STORAGE STABILITY OF PETROLEUM-DERIVED DIESEL FUEL. 4. SYNTHESIS OF SEDIMENT PRECURSOR COMPOUNDS AND SIMULATION OF SEDIMENT FORMATION USING MODEL SYSTEMS. FUEL (UNITED KINGDOM) V 68:1. 27-31 P., JAN 1989.

Sediments produced during the storage of unstable spiked petroleum-derived diesel fuel consist mainly of indolylphenalenes in salt and possibly oxidized forms. The reactions of indoles with phenalenones result in the formation of fuel-soluble sediment precursor compounds, indolylphenalenes, which subsequently react with acid, to produce sediments. Sediment precursor compounds i.e., 2-methylindolylphenalene and bis(2-methylindolyl)phenalene, were synthesized and used in this sediment formation study.

85. HARDY, D. R., HAZLETT, R. N., BEAL, E. J., BURNETT, J. C.; ASSESSING DISTILLATE FUEL STORAGE STABILITY BY OXYGEN OVERPRESSURE. ENERGY FUEL (UNITED STATES) V 3:1. DATE: JAN-FEB 1989 20-24 P. 198TH ACS NATL. MEET. (MIAMI BEACH 9/10-15/89) ACS DIV. PET. CHEM. PREPR. V34 N.3 65 67 (AUG. 1989).

This paper describes a method for determining a distillate fuel's tendency for forming deleterious fuel insoluble products during ambient storage. Oxygen is forced into solution in the fuel at pressures up to 100 psi at temperatures up to 80° C for up to 96 hours in order to accelerate the reactions which take place at ambient pressure and temperature. The method then makes use of gravimetric determination of the total insolubles formed. The method is predictive for up to three years of ambient conditions, rapid, and precise. It has been used to rank additive free fuels over a wide range of storage stabilities and has also been useful in assessing the relative effectiveness of middle distillate fuel stabilizer (antioxidant) additives.

86. STIRLING, K. Q. AND D. W. BRINKMAN. STABILITY, COMPATIBILITY, AND RELATED PROBLEMS OF ADDITIVES IN NAVAL DISTILLATE FUELS DERIVED FROM LOWER QUALITY FEEDSTOCKS. NATIONAL INST. FOR PETROLEUM AND ENERGY RESEARCH, NIPER-352, 37 P., JAN 1989.

This report documents a study to determine which antioxidants are most effective in delaying fuel degradation in a variety of straight-run middle distillate/light cycle oil (LCO) fuel blends similar to Naval Distillate Fuel. The fuel additives blends contained 30% LCO. The additives were blended with fuels at a concentration of 24 or 50 ppm on the basis of the entire package, not the active ingredient. Freshly refined fuels were used because additives do not behave the same in all fuels.

87. MUSHRUSH, G. W., WATKINS, J. M., BEAL, E. J., MORRIS, R. E., HARDY, D. R.; NRL; GEO-CENTERS INC. INTERACTIVE CHEMICAL EFFECTS AND INSTABILITY OF SHALE DERIVED MIDDLE DISTILLATE ((MARINE DIESEL))FUELS. COLORADO SCHOOL OF MINES - DOE 22ND OIL SHALE SYMPOSIUM (GOLDEN, CO 1989) PROCEEDINGS 172-83 (JULY 1989)

Instability of shale derived middle distillate fuels was determined by accelerated storage at 43° or 80° C in the dark. Instability was defined as the formation of insoluble sediments and the production of peroxides and color bodies. 2-Methylpyridine and 2,6-dimethylquinoline in diesel did not produce sediments by themselves or with added hydroperoxides. Dodecahydrocarbazole triggered instability comparable to the most active pyrroles on a nitrogen concentration basis. Insolubles increased in unvented runs as the nitrogen concentration increased. Thiophene inhibited or controlled peroxide formation in Jet A, Shale-derived JP-5, and petroleum derived Jet A blending stocks. Hydrotreatment reduced the sulfur content of jet fuel and resulted in higher peroxide formation and concentration. There appeared to be a minimum thiophenol concentration for inhibition of peroxide formation. Alkyl disulfides gave less initial control of peroxidation, but some control was noted after 6 wk. In model studies, alkyl disulfides were less susceptible to oxidation reactions than aromatic thiols.

88. BRETZ, E. A.; ENSURE RELIABLE STANDBY SERVICE WITH PROPER FUEL TREATMENT. POWER V134 N.4 47-48,50 (APRIL 1990)

This discussion covers the susceptibility of stored residual and distillate fuel oils to oxidation and deterioration resulting in the accumulation of dirt, sediment, gum deposits, and sludge. It also addresses susceptibility to microbial growth at the fuel/water interface that can cause severe pitting corrosion. Other factors include the harmful effects of byproducts of bacterial growth in fuel systems of engines and turbine/generators and the susceptibility of such fuels to contamination during transport with foreign matter. Also studied was the effectiveness of frequent removal of water bottoms, and use of an effective fuel-soluble biocide to limit microbial growth. A spot test and/or a hot filtration test were used to determine the presence of existing sediment, and an accelerated dry sludge test was selected to monitor formation of sludge during storage. The Bureau of Mines Correlation Index served as a measure of the ability of a fuel to dissolve asphaltenes.

JET FUELS

The first aircraft gas-turbine engines used illuminating kerosine as the fuel because of its ready availability, low-fire hazard, good combustion properties, and not least, the war-time need to conserve gasoline supplies. As engine and fuel system designs became more complicated, so have the fuel specification become more varied and restrictive.

Jet fuel quality worldwide is dictated on the commercial side largely by the British Ministry of Defence (DERD) specifications; those of the airlines; engine manufacturers; and industry groups such as ASTM and the International Air Transport Associations (IATA). At airports around the world, jet fuel for airlines is delivered frequently from jointly operated systems in which fuel from a number of suppliers is comingled. This practice has led to the development of a Joint Fueling Systems Check List, that embraces the most critical requirements of the major specifications.

Aviation turbine fuels are manufactured predominantly from straight-run kerosines, or kerosine/naphtha blends in the case of wide-cut fuel, from the atmospheric distillation of crude oil. Straight run kerosine from some sweet crudes will meet all the requirements of the jet fuel specification without further refinery processing, but for the majority of crudes, the kerosine fraction will contain trace constituents that have to be removed before the kerosine is merchantable as jet fuel. This is normally effected by hydrotreating or by a chemical sweetening process (for example Merox).

Traditionally jet fuels have been manufactured only from straight run components since the incorporation of raw, thermally or catalytically cracked stocks would invariably produce an off-specification fuel. In recent years, however, hydrocracking processes have been introduced that produce high-quality kerosine fractions ideal for jet fuel blending. Recently Hadder et al. (109) discussed commitments by NATO to convert land-based jet aircraft from naphtha-type JP-4 jet fuel to kerosene-type JP-8. JP-8 has safety advantages because of its relatively low volatility.

The production and long term storage stability of jet fuels was reviewed in 1983 by Stansky and Schrepfer (90). A large part of the literature available since 1980 has dealt with the reaction mechanisms responsible for jet fuel deposits during long term storage. In 1984 and 1985, Li (92,93,96,98) described jet fuel degradation that was monitored in the presence of added compounds including 2,5-dimethylpyrrole, N-methyl pyrrole, thiophenol, thiophene, decanethiol, dibutyl sulfide, dibutyl disulfide, tetrahydrothiophene, hexadienes, 1-hexene, indene, and dimethyl quinoline and mixtures. Light scattering results were correlated with the extent of deposit formation and with oxygen uptake which is an accepted measure of stability. Watkins and others (97,105) measured the accumulation of hydroperoxides during the thermal oxidation of a shale oil-derived JP-5 fuel and a petroleum JP-4. Addition of a small amount of thiophenol totally suppressed hydroperoxides in one jet fuel and delayed formation in others. Apparently, severe hydrotreatment of petroleum fuels destroys naturally occurring sulfur compounds which act as antioxidants. Sutterfield and co-workers (102) studied the chemistry of antioxidant additive depletion in jet fuels. They concluded that sediments result from oxidation of alkyl-substituted indans, tetralins, indenes, dihydronaphthalenes, naphthalene, and benzenes. These data support a free radical chain oxidation mechanism. The presence of dimers indicates condensation of oxidation products and the coupling of substrates by peroxides.

Stabilizers for long term storage of jet fuels have been described and studied by Kitchen (94), Turner (95), Morris and Hazlett (100), and Brinkman and others (101,103)

JET FUEL CITATIONS

89. DAHLIN, KENNETH E., DANIEL, STEPHEN R., WORSTELL, JONATHAN H.; DEP. CHEM. GEOCHEM., COLORADO SCH. MINES. DEPOSIT FORMATION IN LIQUID FUELS. 1. EFFECT OF COAL-DERIVED LEWIS BASES ON STORAGE STABILITY OF JET A TURBINE FUEL. FUEL, 60(6), 477-80, 1981.

Techniques for determination of the storage stability of jet fuel are described. Lewis bases, extracted by ligand exchange from a coal-derived liquid, adversely affect storage stability (as determined by an accelerated storage test) when added to Jet A turbine fuel. Alcor jet-fuel thermal-oxidation tests suggest slight decreases in thermal stability of fuel spiked with extract. Addition of individual heterocyclic nitrogen compounds to Jet A turbine fuel produces comparable decreases in storage stability.

90. STANSKY, C. A., SCHREPFER, M. W.; UOP PROCESS DIV., UOP INC. MIDDLE DISTILLATE TREATMENT - A CHANGING NEED. CHEMECA 83 [EIGHTY-THREE]: CHEM. ENG. TODAY, COPING UNCERTAINTY, AUST. CHEM. ENG. CONF., 11TH, 779-89. INST. ENG., AUST.: BARTON, AUSTRALIA, 1983.

The production and long-term storage stability of diesel, jet, and burner fuels are reviewed with 3 references.

91. JOHN WILEY AND SONS; CHICHESTER, ENGLAND. METHODS FOR ANALYSIS AND TESTING. VOL. 1. IP STANDARDS FOR PETROLEUM AND ITS PRODUCTS. PART 1. OXIDATION STABILITY OF AVIATION FUELS (POTENTIAL RESIDUE METHOD), 138.1-138.5 P., 1983.

This method describes a procedure for determining the tendency of aviation reciprocating, turbine, and jet engine fuels to form gum and deposits under accelerating aging conditions. The results may be used to indicate storage stability of these fuels. The method involves oxidizing the fuel under prescribed conditions in a bomb filled with oxygen. The amounts of soluble gum, insoluble gum, and precipitate formed are weighed.

92. LI, N. C.; CATHOLIC UNIV. OF AMERICA, WASHINGTON, DC. DEPT. OF CHEMISTRY. STORAGE STABILITY OF JET FUELS. FINAL REPORT FEBRUARY 1983-AUGUST 1984. AD-A-146360/3/XAD, 45 P., AUG 1984.

Laser light scattering, sediment formation, and oxygen uptake measurements were used to estimate storage stabilities of jet fuels derived from petroleum. Fuel degradation was monitored in the presence of added compounds including: 2,5-dimethylpyrrole (DMP), N-methyl pyrrole (NMP), thiophenol, thiophene, decanethiol, dibutyl sulfide, dibutyl disulfide, tetrahydrothiophene, hexadienes, 1-hexene, indene, and dimethyl quinoline (DMQ) and mixtures of these at various temperatures. The light scattering results were correlated with extent of deposit formation and with oxygen uptake results, which is an accepted measure of stability.

93. LI, J. AND N. C. LI. DEPARTMENT OF CHEMISTRY, CATHOLIC UNIVERSITY OF AMERICA,WASHINGTON, DC. STORAGE STABILITY OF JET FUELS. FUEL (UNITED KINGDOM) V 64:8, 1041-1046 P., AUG 1985.

Storage stabilities of jet fuels derived from petroleum were determined using laser light scattering, sediment formation and oxygen uptake measurements. Fuel degradation was monitored in the presence of the following added specific compounds: 2,5-dimethylpyrrole (DMP), N-methyl pyrrole (NMP), thiophenol, thiophene, decanethiol, dibutyl sulfide, dibutyl disulfide, tetrahydrothiophene, hexadiene, 1-hexene, indene, iron(II), and copper(II)-phthalocyanine (FePc, CuPc) and mixtures of some of these at various temperatures. Light scattering results were correlated with extent of deposit formation and with oxygen uptake which is an accepted measure of stability. Light scattering intensity, weight of deposit, and oxygen uptake increase with increase in storage time, concentration of added specific compound and stress temperature. The first direct evidence has been obtained of the pyrrole radicals in DMP and NMP when a fuel was degraded in the presence of pyrrole. These two pyrrole radicals gave different ESR parameters: g and line width values. The degradation products obtained in the presence of FePc and CuPc show properties which indicate that CuPc interacts with petroleum JP-5 with added DMP more strongly than does FePc.

94. KITCHEN, GEORGE HOLCOM. FUEL ADDITIVE. EP 152209 A2 21 Aug 1985, EP 85-300509 25 Jan 1985. INT. APPL., 17 PP. 3 JAN 1986.

Stabilizers for long-term storage of fuel oils (esp., diesel fuel), present at 1:3,000-10,000 wt. ratio of the additive to a fuel oil, consist of a high molecular weight amine, an aromatic hydrocarbon solvent, a poly(alpha-olefin) synthetic oil and a bactericide. Thus, a fuel additive was added to a fuel oil, resulting in reduction of sludge formation, bacteria, and rust in the fuel storage tank.

95. TURNER, L. M., G. E. SPECK AND C. J. NOWACK. EFFECTIVENESS OF ANTIOXIDANTS IN JP-5. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Hydroperoxides in jet fuel are the cause of degradation of aircraft fuel system elastomers. Military specification therefore requires the addition of an antioxidant to insure the protection against peroxide formation in JP-5. Several approved antioxidants were evaluated in several JP-5 fuels at 100° and 60° C. Antioxidants showing the greatest effectiveness in controlling peroxidation were hindered phenols having a t-butyl group at both ortho positions. At accelerated storage conditions only one-third as much hindered phenol was as effective as three times as much partially hindered phenol.

96. LI, N. C., J. R. TZOU, H. CHANG AND S. M. WANG. STORAGE STABILITY OF KEROSENE AND A JET FUEL. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Storage stabilities of kerosene and JP-5 jet fuel derived from petroleum were determined using sediment formation, laser light scattering, Raman scattering, inductively coupled plasma-atomic emission, nuclear magnetic resonance, electron spin resonance, and ESCA measurements. Fuel degradation was monitored in the presence of phenols, thiophenol, pyridines, and metal powder mixtures at both room temperature and 80° C. A highly hindered phenol was used as an antioxidant. It was concluded that copper promotes rapid deterioration of liquid fuels in the presence of 2-methyl pyridine.

97. WATKINS, J. W., MUSHRUSH, G. W., HAZLETT, R. N.; GEO-CENTERS INC.; NAV. RES. LAB. REACTIONS INVOLVING HYDROPEROXIDE FORMATION IN JET FUELS. 193RD ACS NATL. MEET. (DENVER 4/5-10/87) ACS DIV. FUEL CHEM. PREPR. V32 N.1 513-21 (1987).

The accumulation of hydroperoxides during the thermal oxidation of a shale oil-derived JP-5 fuel, containing an antioxidant, a petroleum JP-4 fuel without antioxidant was monitored for ≤168 hr at 100° C and for kinetically equivalent periods at 80°, 65°, and 43° C. The correlation between the high- and low-temperature hydroperoxide accumulation data was generally poor. The highest hydroperoxide concentrations, especially at 43°-65° C, were measured in the petroleum JP-5 without antioxidant, and the lowest, in the same fuel with antioxidant. In storage stability tests (5 weeks at 65° C). Addition of 0.05-0.1 wt % sulfur as thiophenol totally suppressed hydroperoxides in a hydrocracked petroleum JP-5 and delayed hydroperoxide formation for 2-3 weeks in hydrofined JP-5 and oil shale-derived JP-5 and Jet-A fuels. The sulfur concentration in the fuels decreased during the tests owing to thiophenol oxidation by hydroperoxides. Apparently, severe hydrotreatment of petroleum fuels destroys naturally occurring sulfur compounds, which act as antioxidants.

98. LI, N. C., TZOU, J. R., CHANG H. AND WANG S .M.; DEP CHEM NATL TSING HUA UNIV HSINCHU TAIWAN. A STUDY OF DEGRADATION OF A JET FUEL. J. CHIN. CHEM. SOC. (TAIPEI), 34(2) 91-8 (1987) CHEM. ABSTR. ABSTR.NO. 8531 V108 N.2., 1987.

Storage stability of a jet fuel was determined using sediment formation, laser light scattering, Raman scattering, inductively coupled plasma-atomic emission, nuclear magnetic resonance, electron spin resonance, and ESCA measurements. As a fuel ages, particles grow in size and scatter light, so that light scattering measurement has greater sensitivity for initial deposit formation and could speed up the determination of fuel stability.

99. MALHOTRA, R., ST. JOHN, G. A., HILEY, R. W., PENFOLD, R. E., PEDLEY, J.F.; EXAMINATION OF FUEL DEPOSITS FROM VARIOUS SOURCES BY PYROLYSIS/FIELD IONIZATION MASS SPECTROMETRY. SRI INTERNATIONAL, MENLO PARK, CA. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS. REPORT NO. 880905-VOL.2, 525-537 P. LONDON, 13-16, SEP 1988.

In this paper, the authors identified two major pyrolysis/field ionization mass spectral patterns that recur in deposits from various diesel fuels. Indoles and dihydroquinolines are strongly implicated in deposit formation. The authors conclude that the substances are chemically bonded and both the adherent gum and filtered sediments have the same chemical nature. The study shows that the deposit is not changed drastically by increasing the temperature of aging from ambient to 120° C. Doping with DBSA, unlike that with DMP, results in deposits that resemble those from undoped fuels. Thus, the chemistry leading to the oxidation of sulfur compounds to sulfonic acids appears to be very relevant to the question of storage stability.

100. MORRIS, R. E., HAZLETT, R. N., (NAVAL RESEARCH LABORATORY, WA); MCILVAINE, C. L. III, (GEO-CENTERS, FT. WASHINGTON, MD). EFFECTIVENESS OF SELECTED STABILIZER ADDITIVES IN IMPROVING THE THERMAL OXIDATION STABILITY OF JET FUEL. AMERICAN CHEMICAL SOCIETY DIVISION OF PETROLEUM. TORONTO (CANADA). 5-10 JUN 1988. PREPRINTS (USA) V 33:2, 364 P., JUN 1988.

A hindered phenol, a phenylenediamine, an aliphatic tertiary amine and a metal deactivator were examined during thermal stress in a modified JFTOT apparatus. Experiments were conducted at temperatures up to 310° C. The metal deactivator afforded substantial reductions in insoluble products over the entire temperature range. While all the additives reduced heater tube deposits at 260° C, the effects ranged from innocuous to deleterious at higher temperatures. The phenylenediamine was the most effective in reducing maximum peroxide concentrations, but increased the amounts of insoluble products.

101. BRINKMAN, D. W. AND O. K. BHAN. STORAGE STABILITY OF JP-5. NATIONAL INSTITUTE FOR PETROLEUM AND ENERGY RESEARCH, 1987 ANNUAL REPORT. BALL, J.S. (ED.). NIPER-320. 461-474 542 P., OCT 1988.

Techniques were developed to monitor the depletion of antioxidants used to inhibit fuel degradation. Methods were improved for measuring antioxidants in JP-5 fuels and determining compositional changes that occurred in JP-5-type fuels as antioxidants were depleted. Measurements of peroxides and filterable/adherent sediment were completed for fuels (both neat and with additives) after aging up to 60 weeks at temperatures of 60, 80 and 90° C. Analyses were made on both adherent sediments and a jelly-like material found in one fuel. Hydrocarbon classes, ketones, and diketones were characterized, and alkyl-1-indanones, $C_n H_{2n-10} O$, was the most abundant type.

102. SUTTERFIELD, F. D., D. W. BRINKMAN, O. K. BAHN, J. B. GREEN, J. W. GOETZINGER, G. P. STURM, G. SPECK AND L. TURNER. THE CHEMISTRY OF ANTIOXIDANT ADDITIVE DEPLETION IN JET FUELS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Two refinery hydrocracker streams similar to JP-5 fuel were aged at temperatures of 60° and 80° C neat and blended with two hindered phenol antioxidants. Additive, peroxides, color, filterable sediment, and adherent sediment were determined periodically. Fresh and aged samples without additives and sediments produced by aging were also analyzed. Data from the aging experiments showed an initial induction period followed by a period of rapid depletion of antioxidant and an increase in peroxide. Subsequently peroxides decreased, color darkened and sediments increased. Additives were effective in delaying these reactions. Conclusions were that sediments result from oxidation of alkyl-substituted indans, tetralins, indenes, dihydronaphthalenes, naphthalenes, and benzenes. These data support free radical chain oxidation mechanisms in the formation of sediment. The presence of dimers indicates condensation of oxidation products and the coupling of substrates by peroxides.

103. BRINKMAN. D. W., WHISMAN, M. L., K. Q. STIRLING, C. FRENCH, W. CARLEY AND H. DOGRUL. RESEARCH ON PROBLEMS WITH THE USE OF CURRENT FUEL SYSTEM ICING INHIBITORS IN JET FUELS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

The use of fuel system icing inhibitors (FSII) in military jet fuels was outlined. Strategies for the removal of glycol ether from tank water bottoms before disposal were discussed. It was concluded that the most desirable option would be to avoid the generation of such contaminated water by delaying the addition of FSII to the fuel until it is about to be used.

104. CHENG, CHEU P., WANG, SEN R., HUANG, YANG H., CHANG, SHU C. AND TANG, CHAI P.; DEP. CHEM., NATL. TSING HUA UNIV. SPECTROPHOTOMETRIC STUDIES OF STORAGE STABILITY OF JET FUEL. FUEL, 68(2), 264-7, 1989.

Accelerated oxidation tests, using a modification of the ASTM D 2274 testing method, were carried out on a commercially available Jet A-1 produced by the Chinese Petroleum Co. of Taipei. It contained 2.9 mg/L of added 2,6-di-tert.-butyl-4-methylphenol. The amount of soluble gum in the fuel was followed spectrophotometrically with a gum detection limit of 6 mg/L of fuel using fresh fuel as reference. The activation energy of gum formation was 90.8 ± 0.4 kj/mole and the activation enthalpy of antioxidant consumption was 133.1 ± 0.4

kj/mole. These low activation energies with added accelerators were consistent with the interpretation that in the oxidation test, the short inhibition period for Jet A-1 with factory added antioxidant was due to the presence of some easily oxidized component in the fuel.

105. WATKINS, J. M., G. W. MUSHRUSH, R. N. HAZLETT AND D. R. HARDY. HYDROPEROXIDE FORMATION AND REACTIVITY IN JET FUELS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988. ENERGY FUELS, 3(2) 231-6 (1989) CHEM. ABSTR. ABSTR. NO. 117935 V110 N.14 CA 110:117935, 1989.

Reduction in peroxide formation during the storage of four jet fuels at 65° C was observed when thiophenol was present. Shale-II-derived JP-5, Jet-A, hydrotreated and hyrocracked jet fuel blendstocks were studied and all showed marked reductions in peroxide content when thiophenol was present. The effect was greatest at a thiophenol sulfur concentration of 0.1%, but was significant at 0.01%.

106. WANG, S. M., LI, N. C.; CHANG, H. AND HUANG, P. J.; DEP CHEM NATL TSING HUA UNIV HSINCHU TAIWAN 30043. STUDIES OF THE DEPOSIT FORMATION ON STORAGE OF A HIGH ENERGY FUEL. J. CHIN. CHEM. SOC. (TAIPEI) 36(4) 357-65 (1989) CHEM. ABSTR. ABSTR. NO. 177589 V111 N.20 CA 111:177589, 1989.

Abstract not available from accessed data base.

107. HWANG, D. G., TSAN, Z. AND TANG, C P.; 4TH DEPNG-SHAN INST SCI TECHNOL LUNGTAN TAIWAN 32526. AGING AND ANTIOXIDANT SURVEILLANCE STUDIES ON TURBINE FUEL JP-5 AND JP-10. INT. ANNU. CONF. ICT, 20TH(ENVIRON. TEST. 90'S) 66/1-66/14 (1989) CHEM. ABSTR. ABSTR. NO. 59369 V112 N.8 CA 112:59369, 1989.

Abstract not available from accessed data base.

108. WATKINS, J. M., MUSHRUSH, G. W., BEAL, E. J., HARDY, D. R.; GEO-CENTERS INC.; NAV. RES. LAB. REACTIONS INVOLVING ORGANOSULFUR COMPOUNDS ((OSC)) AND PEROXIDE FORMATION IN JET FUELS. 198TH ACS NATL. MEET. (MIAMI BEACH 9/10-15/89) ACS DIV. PET. CHEM. PREPR. V34 N.4 832-36 (AUG. 1989).

Reactions involving organosulfur compounds and peroxide formation in jet fuels were studied in view of reported attacks on elastomers in aircraft fuel systems by hydroperoxides formed during fuel storage, especially in severely hydrotreated fuels. Hydrotreatment removes certain sulfur compounds present in the fuel which may act as natural inhibitors of hydroperoxide formation. In accelerated oxidation tests (8 weeks at 65° C), simulating fuel storage conditions, a fresh, petroleum-derived JP-5 jet fuel was doped with six model organosulfur compounds to 0.03% sulfur to study the effect of various classes on peroxide accumulation. Addition of nonanethiol totally suppressed hydroperoxide formation during the entire test. With di(n-butyl) sulfoxide, hydroperoxide concentrations during the test were reduced to approximately 10% of those for undoped fuel. The other sulfur compounds tested, including diphenyl disulfide, butylthiophene, benzothiophene, and di(n-butyl) sulfone, were ineffective, with the thiophenes actually promoting hydroperoxide formation in JP-5.

109\. HADDER, G. R. DAS, S., LEE, R., DOMINGO, N. AND DAVIS, R.M.; CORPORATE SOURCE: OAK RIDGE NATIONAL LAB., TN. NAVY MOBILITY FUELS FORECASTING SYSTEM PHASE 5 REPORT: JET FUEL CONVERSION BY PACIFIC FUEL SUPPLIERS AND IMPACTS ON NAVY FUEL AVAILABILITY. CONTRACT NO.: AC05-84OR21400. ORNL-6569. 34 P, SEP 1989.

Commitments by NATO to convert land-based jet aircraft from naphtha-type JP-4 jet fuel to kerosene-type JP-8. JP-8 has safety advantages because of its relatively low volatility. The U.S. military has conducted market surveys to determine the effects of jet fuel conversion in the Pacific basin. The primary objective of the study was to estimate the impacts of conversion on the cost and quality of Navy jet and marine fuels. The study predicts that the average cost increase for producing JP-8 instead of JP-4 is 5 cents per gallon. The associated cost increases for Navy fuels are 0.4 cents per gallon for JP-5 jet fuel, 0.2 cents per gallon for F-76 marine diesel fuel, and 0.4 cents per gallon for F-77 burner fuel oil. Conversion has little effect on the quality of Navy fuels. With or without conversion, the study predicts that Navy fuels produced in the U.S. West Coast could have increased tendencies to form gums and other particulates, with potentially adverse impacts on storage stability.

110\. BIGEARD, P. H. BILLION, A., BOULET, R., GUIBET, J. C. AND HEINRICH, G.; INSTITUT FRANCAIS DU PETROLE, INST. FR. PET. FUTURE PROCESSING REQUIREMENTS? HEAVIER JET FUELS...HIGH DIESEL FUEL QUALITY. NATL. PET. REFINERS ASSOC. ANNU. MEET. (SAN FRANC. 3/19-21/89) PAP. 27P., 1989.

A discussion on research on heavier jet fuels and diesel fuels at Institut Francais du Petrole covers results showing that, other than hydrotreatment of kerosine itself, hydrocracking of atmospheric gas oil and light cycle oils and their blends is a much less expensive route to heavier kerosine jet fuels than is hydrocracking of vacuum gas oil. Discussions included the determination of types and amounts of petroleum hydrocarbons in diesel fuel fractions, and the effects of these hydrocarbons on emissions, fuel cetane number, engine behavior, and fuel storage stability; engine testing of diesel fuels having different hydrocarbon type analyses and sulfur and nitrogen contents to determine their effects on injector fouling and particulate emissions; calculation of diesel fuel cetane number from structural data obtained by proton or carbon-13 NMR, in good agreement with cetane numbers determined by ASTM D 613-84 engine tests; and a study of aging of mixtures of light cycle oils and straight-run gas oils showing that nitrogen but not sulfur concentrates in the sediments.

RESIDUAL FUEL OILS

Residual fuel oils have a minimum flash point of 60° C (140° F), and viscosities that generally vary between 30 and 300 SFS at 50° C (122° F). The oil viscosity required to obtain satisfactory atomization varies according to the type of burner used, and is approximately 40 SFS or 80 cSt for steam atomizing burners and 180 and 200 SUS or 39 to 43 cSt min for mechanical atomizing burners. Therefore, it is necessary to heat the oil in order to achieve the required viscosity reduction. This is done in a heat exchanger, consisting of tube assembly through which the oil flows, placed inside a shell containing the heating medium.

The increasing use of low quality heavy crudes in refinery feedstocks has been paralleled by increasing problems in both processing and product quality.(111). Problems are particularly severe with residual materials that contain the highest levels of problem components such as asphaltenes or heteroatom compounds. Problems with stability are increased as the refiner resorts to increasingly severe processing to increase distillate yields as the demand for residual fuels decreases.

Lewis (120), Anderson (113), Rovesti (118), and others (112,114,117,121) have reported that sludge formation will not take place in a residual fuel oil if the oil phase has sufficient aromaticity to prevent the asphaltenes from flocculating. Asphaltenes are large, complex and highly aromatic molecules that can be distinguished from coke or other contaminants by their solubility in highly aromatic solvents. The stability is governed by a balancing mechanism, which depends on the chemical nature of the asphaltenic molecules present and of the oil surrounding them. This balance is described in terms of the required aromaticity for the asphaltene molecules to remain in solution, and the available aromaticity (peptizing power) of the oil phase. This insight into the mechanisms responsible for sedimentation of residual fuel oils has led to the development of simple and practical tests that can be used to predict fuel stability as well as compatibility. The tests involve monitoring changes in sediment determined by hot filtration, asphaltene content, and viscosity. It was found that incompatibility of residual fuel oils is usually predicted by measurements of the solvent quality and the solvent quality demand. The first can be determined by the Bureau of Mines Correlation Index, and the latter by toluene equivalence tests.

Por, Brauch, and Brodsky (114) conducted a study in the early 1980's of the mechanism of residual fuel instabilities and incompatibilities, as well as the factors affecting them, so that undesirable processes could be identified. As a result of this study it was recommended that the severity of cracking/visbreaking conditions be carefully controlled using estimates such as xylene equivalent values that should be below 50, and asphaltenes peptization state levels that should exceed the value of 2.

In 1988, Por and co-workers (117) reported results of a continuation of the work described earlier (114). The later study emphasized the effect of visbreaker operating conditions, and visbreaking technology on residual fuel oil stability and effective process control. They concluded that visbreakers employing soakers yield fuel oils of better stability properties than visbreakers operating without soakers, and therefore, at higher temperatures. For stability and compatibility estimates, they found a preference for asphaltene peptization state determinations and hot filtration test values.

RESIDUAL FUEL OIL CITATIONS

111. ANDERSON, R. P., J. W. GOETZINGER, AND D.W. BRINKMAN. NATIONAL INSTITUTE FOR PETROLEUM AND ENERGY RESEARCH,BARTLESVILLE, OK. STORAGE STABILITY AND COMPATIBILITY OF HEAVY FUEL OILS. 10TH ANNUAL EPRI CONTRACTOR'S CONFERENCE ON CLEAN LIQUID AND SOLID FUELS: PROCEEDINGS. REPORT NO.: EPRI-AP-4253-SR. PALO ALTO, CA. 23 APR 1985, NIPER-65, 33 P., SEP 1986.

The increasing use of low quality crudes in refinery feedstocks has caused increasing problems in processing and product quality as evidenced by increased problems with product stability and compatibility. This project has the specific goal of determining the types of components causing problems to provide practical test methods that will be useful as screening techniques for predicting stability and compatibility problems. Three nonproblem fuels and three which have exhibited instability or incompatibility problems were analyzed in an effort to determine the compound types responsible for the observed problems.

112. KAMIYAMA, HIROKI, HIROSHI ISHIKAWA AND CHIKARA SERA. STORAGE STABILITY OF HYDROTREATED RESIDUAL OILS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

A study was made of the stability of hydrotreated residual oils produced by a pilot plant from high sulfur heavy residue. The stability, its causes and means of improvement were investigated. It was found that stability of the hydrotreated residual oils depends upon the kind of feedstocks and operating conditions. Unstable oils show an increase of organic sludge during storage. The overall stability closely relates to the polar fraction content and solvent power of maltene in the hydrotreated residual oils. The stability can be improved by adding a small amount of the polar fraction.

113. ANDERSON, RAYMOND P., DENNIS W. BRINKMAN, JOHN W. GOETZINGER AND JAMES W. REYNOLDS. STORAGE STABILITY OF RESIDUAL FUEL OILS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA.

Stability problems with residual fuels are particularly severe because they contain the highest levels of problem components such as asphaltenes or heteroatom compounds. Experience has shown that conventional fuel analyses are inadequate to allow prevention or even prediction of handling difficulties resulting from instability or incompatibility. A number of fuel oils were analyzed for chemical and physical characterization in order to understand the reasons for reported problems. These tests have been used as a basis for evaluation of rapid tests which can be used for prediction of potential problems.

114. POR, N., R. BRAUCH AND N. BRODSKY. STABILITY PROPERTIES AND COMPATIBILITIES OF RESIDUAL FUELS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

The purpose of this study was to determine the mechanisms of residual fuel instability and incompatibility as well as factors affecting them so that means for minimizing these undesirable processes could be recommended. Conclusions included a recommendation that the severity of cracking/visbreaking be carefully controlled. Storage temperatures should not be excessive and exposure to air should be minimized. When blending, stocks or diluents should have an aromatic reserve as high as possible. They also recognized the need for minimizing water, sand, corrosion products, dust, etc.

115. WINKLER, MATTHEW F.; OPERATIONAL PROBLEMS WITH MARINE FUEL OILS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Since ocean-going vessels do not have environmental air quality restrictions, the most heavily cracked, highest sulfur, lowest quality residual fuel oils have been routed into the Marine Bunkers. These fuel oils have the poorest ignition properties, the highest sulfur, metallics, and contaminant levels and the highest boiling point hydrocarbons and have therefor created many difficult Marine operational situations which result in fouling, deposits, corrosion, incompatibility, and instability.

116. NOMURA, HIROTSUGU, NAGASAWA, TAKAO AND YOSHIDA, EIICHI. CENT. TECH. RES. LAB., NIPPON OIL CO. LTD. STABILITY OF RESIDUAL FUEL OILS. SEKIYU GAKKAISHI, 30(2), 67-76, 1987.

The storage stability of heavy fuel oils can be continuously monitored by an optical apparatus in which a stream of the oils is passed through a loop or elongated conduit. A flocculating agent is progressively added to the stream at a series of spaced-apart stations in the loop which defines separate segments. These progressive additions enhance the effect of the flocculating agent in the oils to a point where flocculation occurs. Each segment of the loop is characterized by near-IR spectroscopy. A suitable signal, whether audible or visual, can then be provided to indicate the occurrence of flocculation at each segment.

117. POR, N., R. BRAUCH, N. BRODSKY AND R. DIAMANT. RESIDUAL FUEL OIL STABILITY AND COMPATIBILITY STUDIES. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

This is the continuation of a study reported at the 2nd International Conference on Long Term Storage Stabilities of Liquid Fuels in July 1986. The present work places an emphasis on the mechanisms of the processes associated with degradation product formation during storage and use. Recommendations are available for both the operation of visbreaker processes and the technologies involved. All samples have been subjected to conventional as well as specially devised tests and laboratory processes. Data obtained show the advantages of using the asphaltene peptization state phenomenon as an indication of the stability and compatibility properties of the residual fuels and for the desired optimized severity of visbreaker operations.

118. ROVESTI, W. C. AND R. P. ANDERSON. PREDICTION OF STORAGE STABILITY AND COMPATIBILITY OF RESIDUAL FUEL OILS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

The occurrence of problems in the storage and handling of residual fuel oils in the United States Electric Utility Industry has increased with the increased use of lower quality crudes. The authors reported earlier on simple rapid test methods which showed promise for the prediction of stability and compatibility characteristics of residual fuels. Further evaluation shows the results of rapid test methods correlate with baseline laboratory tests for stability and compatibility. The most promising predictive tests have undergone implementation in selected electric utility laboratories as part of an overall program to relate the test results to actual plant performance of heavy fuel oil blending, storage and handling.

119. RUZICKA, D. J. AND OSTVOLD, G.; SENTER INDUSTRIFORSK. DO ADDITIVES REDUCE SLUDGE? MAR. ENG. REV. (ISSN 0047-5955) 27-28,30 (SEPT. 1988).

Tests were conducted at 60° -100° C on straight run low- and high-sulfur residue, visbroken low- and high-sulfur residue, and FCC residue oils to study the dependence of engine fuel oil sludge formation on storage conditions and sludge formation mechanisms. Visbroken residues, particularly high-sulfur residues, were the least stable in storage. Contact with oxygen, seawater, or corrosion products of the storage tank materials accelerated sludge formation. Sludge, oxygen, and asphaltenes contents increased significantly, but the amount of oxygen absorbed by the stored residual oil did not correlate with the amount of sludge formed. The increase in the amount of high molecular weight components and the significant oxygen absorption during storage suggested that sludge formation could be oxygen-initiated polymerization of residual constituents. The study also showed that suitable additives can retard sludge formation in residues.

120. LEWIS, C. P. G. AND F. DE JONGE. EFFECTS OF STORAGE ON THE STABILITY OF RESIDUAL FUEL OIL. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

This paper presents the results of investigations into the effects of storage on stability. It has been found that the stability of a stable residual fuel composed of normal refinery streams does not deteriorate perceptibly during storage for two years at temperatures up to 75° C. However, a significant change in the viscosity and in the asphaltenes content is observed as a result of the conversion of resins into newly formed (peptized) asphaltenes due to oxidation/polymerization reactions. The rate of change depends markedly on the scale and temperature of storage. The significant role of oxygen in the flocculation process has been demonstrated, i.e. in its absence flocculation is strongly delayed and the possibility of flocculation inhibition by chemical compounds is discussed.

121. POGONOWSKA-FABRIEF, W. AND P. HOLBROOK. THE INFLUENCE OF LUBRICATING OILS ON THE COLLOIDAL STABILITY RESERVE OF RESIDUAL FUEL OILS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

The stability reserve of 20 fuel oil/lubricating oil blends were assessed as hot filtration solids content - straight and following thermal and chemical acceleration. The predominantly aliphatic lubricating oils considerably reduced the stability reserve of some fuel oils even at low concentration. NMR aromaticity measurements on the fuels and lube oils were reported and may serve as a tool to assist in the prediction of residual fuel oil stability reserve.

122. HARA, T., K. YANAGIDA AND A. OKANO. QUALITY OF FUELS FORMED BY SEVERE HYDROTREATMENT OF VACUUM RESIDUES. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Heteroatom functionalities from vacuum residues of various petroleum crude oils were quantitatively analyzed. Distribution of acidic NH group and OH groups were measured by infrared spectrum in very dilute solution using 2 cm KBr liquid cells. The structure and nature of such functionalities have been characterized for petroleum vacuum residues, compared with those involved in other hydrocarbon resources such as oil sand bitumen, shale oil, coal liquefaction products and coal pyrolysis tar. Structural change of such polar functionalities caused by various conditions of hydroprocessing has been analyzed in the hydrotreatment of vacuum residues derived from various resources.

CRUDE OIL

Crude oil is the lifeblood of America's economy. Each day over 16 million barrels of petroleum is used in the United States to power or heat the nation's factories, businesses, and homes, to produce gasoline and other fuels for transportation, and to manufacture a variety of chemical products ranging from paints to plastics. Crude oil accounts for about 40 percent of the energy consumed.

The need for a national oil storage reserve was recognized as early as 1944 when Secretary of the Interior Harold Ickes advocated stockpiling of emergency crude oil. Truman proposed a strategic oil supply in 1952, and Eisenhower suggested an oil reserve after the 1956 Suez crisis. But few events so dramatically emphasized the need for a strategic oil reserve as the 1973-74 oil embargo. The cutoff of oil flowing into the United States from many Arab nations sent economic shockwaves through this nation and much of the industrialized world. In the aftermath of the oil crisis, America established the Strategic Petroleum Reserve. This reserve is an emergency supply of crude oil stored in huge underground salt caverns along the coastline of the Gulf of Mexico. It represents the largest stockpile of crude oil in the world.

Crude oil does not require processing prior to storage. However, OSPR has established applicable crude oil specifications used in acquiring SPR oil.

Samples of crude oil are periodically withdrawn from each U.S. SPR reservoir at specified depth intervals for comprehensive analytical study. Additionally, samples of both the brine and sludge underlying the crude oil are obtained for analysis.

Inspection tests are first run on the crude oils. These tests include gravity (specific and °API), pour point, sulfur, nitrogen, viscosity (2 temperatures), and Karl Fisher water determination. Sludge inspection tests include water by Karl Fisher reagent. Other inspection tests of the sludge are run on either whole or centrifuged sample, and include water, gravity, pour point, nitrogen, sulfur, salt, wax, neutralization number, sediment by extraction and ash.

The crude oil analysis includes the above inspections tests, plus determinations of carbon residue, metals (nickel, vanadium, and iron), organic chlorides, color, UOP "K", ERVP, hydrogen sulfide, and mercaptans.

Distillations are then performed at atmospheric pressure, 100 mm Hg, 10 mm Hg, and 1 mm Hg by ASTM D 2892 and ASTM D 1160. The volume of each fraction obtained from the distillations are recorded, and appropriate fractions are further analyzed for gravity, sulfur, mercaptans, hydrogen sulfide, organic chlorides, aniline point, neutralization number, cetane index, naphthalenes, smoke point, nitrogen, viscosity, freezing point, cloud point, pour point, metals (nickel, vanadium, and iron) and carbon residue. Low boiling distillation fractions (C_5 to 420° F) obtained by ASTM D 2892 are analyzed by a chromatographic PIANO method that provides total paraffins, total iso-paraffins, total aromatics, total naphthenes, total olefins and other species. The method also provides the carbon number distribution by hydrocarbon type, and quantitation of individual components.

Brines and sludges are submitted for microbiological activity tests. Giles and others (131) have reported the biogeochemistry of sludge that forms in salt dome caverns used for strategic storage of crude oil. They found the emulsified sludge to have both a complex and variable composition with high wax and acid contents. The emulsions were very stable, and only minor bacterial activity was detected with no measurable degradation of the crude oil occurring.

All the data are tabulated in reports from the National Institute for Petroleum and Energy Research (NIPER) (133). Some reports are available through NIPER, P.O. Box 2128, Bartlesville, OK 74005, (918) 337-4256.

Water is probably the most significant contributor to crude oil degradation in long-term storage because it provides a favorable environment for microorganisms and fungi that can metabolize hydrocarbons. This microbial activity is highest at the oil/water interface of the reservoir.

Bosecker and others (128) studied crude oils from the Gifhorn Trough in Germany and from the Maracaibo Basin in Venezuela for their content of microorganisms capable of biodegrading crude oils. It was shown that the microorganisms active in degradation could easily survive a period of inactivity due to missing nutrients, and could be reactivated within hours to degrade newly added crude oil. Under oxygen-limiting conditions selectivity of degradation was found, destroying short-chain n-alkanes (C_{20}, C_{21}) at a faster rate than long-chain n-alkanes (C_{30}, C_{31}).

The storage of crude oil underground for extended periods has been practiced in Europe and in South Africa for over 20 years. Although no systematic study of the South African stability of stored crude was found in the literature, a comprehensive investigation in Germany has been reported (123,134).

In South Africa, an abandoned coal mine was converted for strategic crude oil storage in about 1967, and has been in continuous use since then. Although little data is available on the quality of the crude oil, that is principally Iranian Light, it is reported (126) to be readily refineable. Emulsions, that are difficult to break, are apparently accumulating at the oil/water interface within the mine. These emulsions are believed to be caused mechanically by the action of the submerged pumps used to remove the ground water seeping into the mine. These emulsions may also be the result of microbial activity, since growth of anaerobic bacteria at the oil/water interface was noted; yet no hydrogen sulfide was reported to be present. Crude oil stored in surface tanks with floating roofs is also reported to be readily refineable, although some anaerobic bacteria are present. Growth of the anaerobic bacteria is controlled by periodically removing the water bottoms.

In the United States, a buildup of hydrogen sulfide attributed to anaerobic bacterial activity has occasionally been noted in surface tanks used for crude oil storage at refineries and terminals. The common remedy is to inject a suitable biocide into the water bottoms that are subsequently withdrawn and disposed of. Except for some corrosion of the tank shell, no other deleterious effects have been reported.

In the most comprehensive studies published to date, Niederhoff (123) and Giles et al.(131,134) reported detailed analyses of crude oil from three of Germany's strategic storage sites and crude oil stored in the United States' Strategic Petroleum Reserve. At Etzel, West Germany, one of the 33 cavities had contained over 260,000 cubic meters of four different Middle East crude oil streams and a tank farm crude oil composite for approximately two years. Twenty-two samples were collected from various depths within this cavern, and subsequently analyzed comprehensively.

The bulk of the crude oil contained negligible sediment and water, probably as a result of these having settled out. Density and viscosity were virtually constant, suggesting that total mixing of the different crude oils had taken place, and that stratification was not occurring. Distillation yields were somewhat variable, but also do not indicate any differentiation. The geothermal gradient within the Etzel salt mass is on the order of 3 to 4° C per 100 m, and the temperature of the salt at the bottom of the cavern is approximately 15° C greater than at the top. Convection within the stored oil induced by this temperature differential probably promotes thorough mixing. The other variation was random with no noticeable trends. In general, the data for these twenty samples indicate that the different crude oil streams stored are moderately well mixed with little or no evidence of stratification.

The crude oil surveillance assessment program to monitor crude oil in the U.S. SPR has provided data defining the quality of the mixed oil streams stored in individual caverns. Despite convective mixing, sediment, water, waxes, and certain heterogeneous compounds indigenous to the crude settle out and form a sludge layer at the brine-oil interface of some storage caverns. This sludge does not appear to be result of incompatibility, however. Viable aerobic and anaerobic bacteria have been found in some storage caverns, but physical and chemical evidence overwhelmingly demonstrates that these bacteria are not degrading the stored crude. The oil exhibits no increase in salt content and no deleterious changes in quality were observed during nine years of storage.

CRUDE OIL CITATIONS

123. NIEDERHOFF, PETER. KBB INC., WASHINGTON, D.C. EVALUATION OF THE EFFECTS OF LONG-TERM STORAGE IN SALT CAVERNS ON THE PHYSICAL AND CHEMICAL PROPERTIES OF CERTAIN CRUDE OILS AND DISTILLATE FUEL OILS, FINAL REPORT. U.S. DOE CONTRACT NO. EL-78-C-01-7151, AUGUST 1979.

To evaluate the long-term storage behavior of crude and fuel oil stored in salt caverns, KBB Inc, USA, and KBB, Germany, were commissioned to investigate three caverns in West Germany which had contained either crude or fuel oils for several years. The results showed that mixing had taken place to a certain degree and property variations were negligible. Some primary layers were still recognizable. They found that mixing occurs more easily when a heavy crude is stored above a light one. In the fuel oil cavern, no emulsion strata was found.

124. BRINKMAN, DENNIS W., JOHN N. BOWDEN AND HARRY N. GILES. CRUDE OIL AND FINISHED FUEL STORAGE STABILITY: AN ANNOTATED REVIEW. DOE/BETC/RI-79/13, FEBRUARY 1980.

A review and assessment of storage effects on crude and product quality was undertaken through a literature search by computer accessing eight data bases. Two-hundred seventy references are included as well as a history of underground storage of crudes and fuel oils.

125. SNOW, R. H. AND D. C. WARD. NATIONAL INST. FOR PETROLEUM AND ENERGY RESEARCH. STABILITY AND PROCESSING RESEARCH FOR CRUDES, INTERMEDIATE AND PROCESS STREAMS AND FINISHED FUEL. NIPER-20, 251-274 P., 28 FEB 1985.

The intent of this project was to demonstrate that refinery products quantities and qualities can be predicted based on the composition of the feedstock and the upgrading conditions, even for very heavy, low quality crudes. It is postulated that satisfactory relationships can be derived given detailed compositional and physical property analyses. A Wilmington, CA, crude having an API gravity of 14 was distilled, and the heavy distillate was hydrotreated at a number of conditions. Preliminary analyses have been completed on the resulting upgraded samples. In addition, facilities for supercritical extraction and hydrotreatment of residues have been modified for automated operation. A storage stability test that is applicable to small samples has been completed and is in the process of being modified for use with heavy fractions.

126. GILES, H. N., J. N. BOWDEN AND L. L.STAVINOHA. OVERVIEW ON ASSESSMENT OF CRUDE OIL AND REFINED PRODUCT QUALITY DURING LONG-TERM STORAGE. DOE/FE-0048, 37 P. JUN 1985.

This report presents the findings of a number of studies on the qualitative effects on petroleum resulting from prolonged storage primarily in deep underground caverns, but also in above ground tanks. It is demonstrated conclusively that both crude oil and refined products can be stored for prolonged periods without undergoing deleterious changes in quality. The most practical and economic mode of storage is in caverns in salt deposits. Moisture is likely the single most significant contributor to petroleum degradation because it will harbor microorganisms and fungi which metabolize hydrocarbons. Long-term storage stability can be enhanced by selecting products which are inherently stable and are additive treated. The storage stability of the product should be thoroughly evaluated, and a monitoring program instituted to periodically assess the quality of the petroleum in storage.

127. HARA, TAKAO. LONG-TERM STORAGE STABILITIES OF CRUDE OIL RESERVED BY JAPAN NATIONAL OIL CORPORATION. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Japan National Oil Corporation has been practicing long-term strategic storage of crude oil since 1978 in above-ground, floating-roof tanks located in northern Japan. Crude oils are reserved for 2-3 years and are chosen for storage stability. Samples are withdrawn from different levels in the tanks at each periodic analytical check for distillation behavior, GC profiles and heteroatom functionalities of vacuum residues.

128. BOSECKER, K., M. TESCHNER AND H. WEHNER. IN VITRO BIODEGRADATION OF CRUDE OILS. 2ND INTERNATIONAL CONFERENCE ON LONG-TERM STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA, JULY 29 - AUGUST 1, 1986.

Japan has practiced long-term strategic storage of crude oil since 1978. Storage is in above-ground, floating-roof tanks. Five kinds of crude are stored for a period of 2-3 years and are tested frequently for storage stability. Oxygen and nitrogen compounds are condensed to asphaltenes during long-term storage of crude oil. Such species may constitute water-oil emulsions prior to the formation of sludge.

129. GILES, HARRY N., PAUL W. WOODWARD, JOHANNA SHAY AND REX A. NEIHOF. BIOGEOCHEMICAL STUDIES OF CRUDE OIL STORED IN THE UNITED STATES' STRATEGIC PETROLEUM RESERVE. 194TH NATIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY, GEOCHEMISTRY DIVISION PROGRAM, NEW ORLEANS, LA, 1987.

Samples periodically collected from the caverns in which the OSPR stores crude oil reserves undergo a detailed analysis that includes whole crude properties, characterization of distillate and residual fractions, trace element analysis, stable isotope ratio, and microbiological studies. No deleterious changes in quality have been observed in crude oil stored for as long as nine years.

130. BRINKMAN, D.W., GREEN, J.B., STURM, G.P., BHAN, O.K.; DETERMINATION OF THE COMPOSITION AND CHEMISTRY OF HEAVY CRUDES, INTERMEDIATE PROCESS STREAMS, PRODUCTS, AND BY-PRODUCTS. NATIONAL INSTITUTE FOR PETROLEUM AND ENERGY RESEARCH, 1987 ANNUAL REPORT. BALL, J.S. (ED.). NIPER-320, 542 P, 1987.

The processing of lower-quality fossil fuel feedstock results in a number of problems which include instability and incompatibility of fuels, corrosiveness, high energy and hydrogen consumption, and catalyst poisoning. One general way of handling heavy crudes is to hydrogenate the feed before processing. Various compositional studies were started. The storage stability of hydrotreated Wilmington and Mayan fractions was examined. The distribution of metals and sulfur by molecular weight in various Wilmington and Mayan fractions was obtained. The nickel and vanadium porphyrins in Mayan and Wilmington samples were determined. A general analysis of the condensed liquids from high-severity batch hydrogenation of Wilmington and Mayan residues was made.

131. GILES, HARRY N., PAUL W. WOODWARD, JOHANNA SHAY AND REX A. NEIHOF. BIOGEOCHEMICAL STUDIES OF CRUDE OIL STORED IN THE UNITED STATES' STRATEGIC PETROLEUM RESERVE. 194TH NATIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY, GEOCHEMISTRY DIVISION PROGRAM, NEW ORLEANS, LA, 1987.

Analyses are performed on samples periodically collected from the caverns in which the OSPR stores crude oil reserves. These tests include whole crude properties, characterization of distillate and residual fractions, trace element analysis, stable isotope ratio, and microbiological studies. Deleterious changes in quality have not been observed in crude oil stored for as long as nine years.

132. GILES, HARRY N., PAUL W. WOODWARD AND REX A. NEIHOF. U.S.DOE, WASHINGTON, DC, NATL INS PET ENERGY RES., BARTLESVILLE, OK, AND U.S. NAVAL RES. LAB., WASHINGTON, DC. BIOGEOCHEMISTRY OF SLUDGE THAT FORMS IN SALT DOME CAVERNS USED FOR STRATEGIC STORAGE OF CRUDE OIL. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

In many salt dome caverns used for storing crude oil, a sludge or emulsion layer accumulates over time at the oil/brine interface. This layer comprises less than 0.5 percent of the total crude oil stored. The sludge is enriched in trace metals and acidic components; has a high sediment, water, salt, and ash content; exhibits a bimodal distribution of the paraffins and is depleted in basic components, nitrogen, and sulfur. Although aerobic and anaerobic bacteria have been found in some storage caverns, the bacteria are apparently dormant.

133. WOODWARD, P. W.; QUARTERLY TECHNICAL REPORT, STRATEGIC PETROLEUM RESERVE SUPPORTING RESEARCH, NIPER BO6807-17 THROUGH -24, JUNE 1988 - MARCH 1990.

The basic objective of the research reported in these technical reports has been to provide technical support to the U.s. Department of Energy's Office of Strategic Petroleum Reserve. Support has included, but is not limited to, analysis of crude oil destined for storage in the SPR as well as analysis of samples taken from various depths within the storage caverns. These analyses are performed to assure the integrity of the stored crude oil. Additionally, research has been conducted and reported to determine the physical/chemical/microbiological cause and effect of sludge that forms at the oil/brine interface of some storage caverns.

134. GILES, H. N. AND P. NIEDERHOFF. THE QUALITATIVE EFFECTS ON PETROLEUM RESULTING FROM PROLONGED STORAGE IN DEEP UNDERGROUND CAVITIES. THE POTENTIAL OF EARTH SHELTERED AND UNDERGROUND SPACE, T. L. HOLTHUSEN (EDITOR), PP. 475-492, PERGAMON PRESS, N.Y.

A sampling and analysis program was undertaken to assess the qualitative effects on petroleum resulting from prolonged storage in underground cavities. Two salt dome solution cavities and a converted potash mine containing crude oil, and a salt dome solution cavity containing distillate fuel oil were studied. A series of samples was collected from each of the cavities and each was subsequently analyzed comprehensively. The analyses did not indicate any deleterious qualities which would require special handling at a refinery for the bulk of the crude oil. The distillate fuel oil samples exhibited some slight differences in quality but, overall, the product conformed to standard specifications. These studies demonstrateed conclusively that crude oil and distillate fuel can be stored in large underground cavities for prolonged period without undergoing deleterious changes in quality.

BIODEGRADATION

The science of microbiology is the study of microorganisms and their activities. It is concerned with their structure, form, physiology, reproduction, metabolism and identification (137). Microbiology generally deals with unicellular microscopic organisms. All their life processes are performed in a single cell. They have a requirement for the elements carbon, nitrogen, and phosphorus in order to build cell structure. Water is required for the passage of nutrients and waste materials across the cell wall of the microorganisms. In addition, certain elements such as sulfur, iron and manganese, are required in trace quantities for the production and functioning of the enzymes needed for uptake and breakdown of nutrients.

Microorganisms causing problems in the oil industry are of three main groups:

Bacteria
Fungi (Yeasts and Molds)
Algae

Bacteria are capable of living on a wide variety of materials such as organic carbon compounds, inorganic compounds, or sunlight as a source of energy. Fungi are larger, more complex organisms and can exist as molds or yeasts. They depend on organic carbon such as sugars for energy. Algae are all photosynthetic organisms using sunlight as a source of energy and carbon dioxide as a source of carbon for cell growth.

The growth of microorganisms in water under a protective layer of oil is a special case of a common phenomenon which occurs widely in nature in marine sediments, underground water and other places where the access to atmospheric oxygen is limited (141). The consequences of such growth can be unpleasant odors from the reduction of sulfate in the water to hydrogen sulfide. In addition to the toxicity and foul smell, serious corrosion problems arise from the dissolution of sulfides and sulfur in the oil. In addition substantial quantities of emulsions and sludges are formed at the oil water interface unless the water is a brine which inhibits the growth of microorganisms.

Bosecker and others (135) found that crude oils from West Germany and Venezuela were found to survive a period of inactivity due to missing nutrients and then could be reactivated within hours. Fass and co-workers (142,144) found during a five-year study that aerobic-anaerobic microbiological sequences may induce fuel acidity and corrosiveness. In Swedish rock caverns used for long term storage of different petroleum products, Norqvist (143) observed microbial problems with jet fuel and heavy fuel oil. Hydrogen sulfide was produced in caverns with jet fuel which gave rise to corrosive fuel. Microbes produced methane in caverns storing heavy fuel oil. Conclusions included the need to take both rock and water quality into account when choosing storage sites.

Reynders and Stegmann (152) observed biofouling, biocorrosion and degradation of diesel fuel in large storage containers. Four fungi and nineteen bacteria species were isolated. Miller-David and Pipenger (155) reported that microbial proliferation is neither regional nor seasonal since most under ground reservoirs are maintained at a relatively constant temperature year-round.

Biocides (136,138-140,146,148,151,154,156) and good housekeeping practices are generally recommended to control microbiological activity.

BIODEGRADATION CITATIONS

135. BOSECKER, K., M. TESCHNER AND H. WEHNER. IN VITRO BIODEGRADATION OF CRUDE OILS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILIT'ES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

    Crude oils from West Germany and Venezuela were analyzed for microorganisms capable of biodegrading crude oils. Isolated cultures were found to survive a period of inactivity due to missing nutrients and could be reactivated within hours to degrade newly added crude oil. Under oxygen limited conditions short-chain n-alkanes were degraded at a faster rate than long-chain n-alkanes.

136. WATER MANAGEMENT CHEMICALS LTD.; MICROBIOCIDE GIVES 'ALL-ROUND' PROTECTION TO STORED FUELS. ANTI-CORROS. METHODS MATER. V33 N.3 18 (MAR. 1986).

    A new microbiocide kills bacteria and fungi in the water and oil phases of diesel and other fuels. It is more soluble in the fuel phase than conventional microbiocides, and has been formulated for tanks storing diesel, kerosine, paraffins, or similar distillate fuels which develop a water and a fuel phase. Contaminants in the fuel phase block filters and fuel lines, but the new microbiocide possesses a spectrum of cidal activity against bacteria and fungi that reduces or eliminates the corrosion, degradation, and fouling associated with stored distillate fuels. It has a long life, low toxicity, and is non-flammable and non-foaming. Independent test data show that the microbiocide at standard concentrates has no adverse effect on fuel, storage tanks, or engine performance.

137. HOLMES, STEVEN.; MICROBIOLOGY OF HYDROCARBON FUELS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Growth of microorganisms in fuel oil is common and can present a number of problems in fuel oil storage and distribution systems. Once potential growth is realized, steps can be taken to reduce the problems with good housekeeping procedures and the use of biocides. A microbiology lab can help identify problems and make recommendations for cures or prevention of the problems.

138. ANDRYKOVITCH, G. AND R. A. NEIHOF. FUEL-SOLUBLE BIOCIDES FOR CONTROL OF FUNGAL CONTAMINANTS IN HYDROCARBON FUELS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Water in fuel systems can allow a select group of microorganisms to grow to produce troublesome amounts of particulates. One method of dealing with this problem is the use of biocides which have the dual property of being soluble in the fuel and of partitioning sufficiently into any water phases to inhibit microbial growth. Five such biocides were evaluated in this study. A mixture of isothiozolin compounds proved effective in controlling fungal growth to concentrations of less than one part per million and still showed no tendency to be inactivated by sludge.

139. DOCKS, E. L. AND C. R. BENNETT. THE USE OF DIOXABORINANES TO CONTROL MICROBIAL GROWTH IN LIQUID FUELS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Microbial growth occurs in liquid fuels contaminated with water. This can also cause tanks to corrode, gaskets and coatings are attacked, valves and gauges plug, and fuel deteriorates. Eliminating water from the fuel handling system is one way of preventing the problems. Since this may not be possible, organoborates can be used to control the growth of microorganisms in water contaminated fuels. These appears most effective in Jet A fuel at low concentrations. They are toxic to both fungal and bacterial organisms at low concentrations and non-toxic to mammals at use concentrations.

140. MEEKS, J. A. AND W. F. MCCOY. THE USE OF METHYLCHLORO/METHYLISOTHIAZOLONE IN CONTAMINATED DISTILLATE FUELS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Biological efficacy of methylchloro/methylisothiazol in distillate fuels was determined in laboratory tests by measuring the concentration of viable microorganisms in the aqueous phase at regular time intervals. Microbial contaminants were reduced by 99% in 24 to 48 hours after treatment with 1.4 ppm active ingredient. Long-term effectiveness was demonstrated in both laboratory and field trials.

141. NEIHOF, REX A.; MICROBES IN FUEL: AN OVERVIEW WITH A NAVAL PERSPECTIVE. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

A brief review of the history of microbial contamination of hydrocarbon fuels is followed by descriptions of the types of organisms responsible for major objectionable effects. A discussion of selected aspects of growth requirements of these organisms and interactions among the different types of organisms as well as methods of control are presented.

142. FASS, R., Y. GEVA AND A. MIZRAHI. THE IMPACT OF MICROBIAL ACTIVITY ON THE QUALITY OF JET AND DIESEL FUEL STORED IN MODELS FOR WET ROCK CAVERNS 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Microbiological aspects of long term storage of jet and diesel fuel in Israel were studied in pilot rock models simulating the environmental conditions at a sedimentary rock formation. Results of five years of study of the microbial activity and its impact on stored fuels indicated that aerobic-anaerobic microbiological sequences may induce fuel acidity and corrosiveness. It was concluded that fuel and water soluble biocides must be added while using such a storage technology, in order to assure the long term storage stability of the stored fuel.

143. NORQVIST, A., R. ROFFEY AND A. EDLUND. MICROBIOLOGICAL STUDIES IN ROCK CAVERNS WITH JET FUEL, HEAVY FUEL OIL AND CRUDE OIL. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

In Swedish rock caverns used for long term storage of different petroleum products, some microbial problems were observed with jet fuel and heavy fuel oil. Hydrogen sulfide was produced in caverns with jet fuel which gave rise to corrosive fuel. Microbes produced methane in caverns storing heavy fuel oil. Conclusions included the need to take both rock and water quality into account when choosing storage sites. Bedwater volume should be minimized. Temperature is another factor as is the type of product.

144. FASS, R., J. BEN-ASHER AND A. B. SHAVIT. EFFECT OF MICROBIAL CONTAMINATION IN STORAGE TANKS ON THE LONG TERM STABILITY OF JET FUEL. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Long term stability of jet fuel in contact with active microbial cultures was studied. Field investigations showed jet fuel stored in large storage tanks with floating roofs became heavily contaminated by microbial cells. However, no deterioration of fuel properties could be detected. The main risk to jet fuel stored for long periods, with biocide treat, is the formation of corrosive sulfur compounds, and surface active materials by the combined action of microorganisms feeding on hydrocarbons and sulfate reducing bacteria which flourish at the tank's bottom. Anticipated risks may be minimized by draining operations which remove the bottom layer from the storage tank.

145. ROFFEY, R. A. NORQVIST AND A. EDLUND. METHODS TO MONITOR BIODETERIORATION OF JET FUEL DURING LONG-TERM STORAGE IN ROCK CAVERNS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

In order to study the problems with biodegradation and increased corrosivity of jet fuel during storage, it was necessary to develop more sensitive methods to monitor these processes. A more sensitive and quantitative method to measure corrosivity is based on piezoelectric crystals. Elemental sulfur in the range of 1-5 mg/L was found to be important for the corrosive effect so a polarographic method was developed with a sensitivity down to 0.1 mg/L.

146. ANDRYKOVITCH, G. AND R. A. NEIHOF. GEO-CENT INC WASHINGTON DC USA. FUEL-SOLUBLE BIOCIDES FOR CONTROL OF CLADOSPORIUM RESINAE IN HYDROCARBON FUELS. J. IND. MICROBIOL., 2(1) 35-40 (1987) CHEM. ABSTR. ABSTR.NO. 42738 V107 N.6, 1987.

Water frequently present in fuel systems may allow a select group of microorganisms to grow and produce accumulation of troublesome particulates. A possible method of dealing with this problem is to add a biocide to the fuel which has the properties of solubility in the fuel and of partitioning into any water phase to inhibit microbial growth.

147. ROFFEY, R. AND A. EDLUND. BIODEGRADATION OF STORED HEAVY FUEL OIL WITH PRODUCTION OF METHANE IN UNLINED ROCK CAVERNS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Storing heavy fuel oil for long periods on a waterbed in unlined rock caverns creates problems with degradation of oil and production of methane gas. Chemical and microbiological studies at two storage facilities with problems showed that anaerobic conditions existed in the bedwater and that a complex microbial community was present. Four methods were evaluated to inhibit the methanogenic activity but only addition of 0.5 g/L of a nitrate solution gave satisfactory inhibition.

148. KLEIN, F. T.; STUDIES ON A U.S. MILITARY APPROVED FUEL PRESERVATIVE AND STABILISER. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

MIL-S-53021 is the military specification for a stabilizer additive for use in diesel fuels and fuel oil intended for intermediate or long term storage. Angus Chemical Company completed a test program which showed that their proprietary additive FUELSAVER was equal to or better than the approved biocide in the military formulation.

150. CARLSON, P. , S. NIEMELA AND E. TENHUNEN. A SURVEY OF THE MICROBIAL CONTAMINATION LEVEL OF SOME FINNISH FUEL STORAGE SYSTEMS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Nine storage systems for jet fuel and light heating oil in Finland which included both rock caverns and above ground and subsurface steel tanks were studied to estimate the degree of microbial contamination. No corrosiveness was found in the fuel samples studied nor were water bottoms found in the jet fuel storage systems. Few microbes were found in the fuel itself. In the light heating oil, water bottoms were present with microbial counts higher.

151. ELSMORE, R. AND W. G. GUTHRIE. THE USE OF BNPD TO CONTROL MICROBIAL GROWTH IN DIESEL FUEL SYSTEMS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

This study reports the evaluation of Bronopol (2-bromo-2-nitropropane-1,3-dial, BNPD) as a biocide for microbial contamination in fuel systems. Fuel compatibility studies confirmed that BNPD does not adversely affect the normal fuel performance parameters. BNPD achieved good control of aerobic and anaerobic bacteria in water bottoms and good control of fungi was also shown.

152. REYNDERS, M. P. AND P. STEGMANN. A BIOLOGICAL MONITORING AND CONTROL STRATEGY FOR LARGE DIESEL FUEL STORAGE FACILITIES. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Biofouling, biocorrosion and degradation of diesel fuel in large storage containers was studied. Four fungi and nineteen bacteria species were isolated from contaminated diesel fuel and blocked filters. Two bacteria species were found to be the most common cause of filter blockages due to their ability to form spores and to inhibit the growth of other microorganisms. The use of a water soluble biocide treatment proved successful and prevented the blockage of fuel filters, the corrosion of containers, pipelines and meters and the degradation of the fuel.

153. HILL, E. C. G. C. HILL AND D. A. ROBBINS. MICROBIOLOGICAL TEST METHODS FOR FUELS IN THE LABORATORY AND ON SITE. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Testing for microorganisms in distillate fuels is itself a challenge to microbial technologists but the subsequent interpretation requires knowledge of the system, the exact location of the sampling point and the history of the sample. Frequently, the only sample available is the fuel phase.

154. MORCHAT, R. M. A. J. HEBDA, G. M. JONES AND R. G. BROWN. BIOCIDES FOR MICROBIOLOGICAL CONTAMINATION CONTROL IN NAVAL DISTILLATE FUEL. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

To identify a biocide which could be used to treat microbiological contamination problems in fuel on ships, five commercial biocides were evaluated. Results indicated that none of the biocides tested were able to inhibit all of the culture types, under the experimental conditions.

155. MILLER-DAVID, P. J. AND G. G. PIPENGER. EVALUATION AND COMPARISON OF MICROBIAL GROWTH IN DISTILLATE FUELS. 3RD INTERNATIONAL CONFERENCE

ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Since most fuel storage tanks in the United States are under ground and maintained at a relatively constant temperature year-round, microbial proliferation is neither regional nor seasonal. This contamination, however, is blamed for fuel system corrosion, filter and line plugging, and fuel degradation. Bacterial growth was isolated from 56% of the stored fuel systems in the U.S. By isolating specific organisms from fuel which show adverse conditions, the fuel user can select treatment method most effective against those organisms.

156. DORRIS, M. M., D. P. CARMODY AND D. G. PITCHER. FIELD TRIALS ILLUSTRATING THE LONG TERM EFFECTIVENESS OF METHYL-ISOTHIAZOLONES IN THE PRESERVATION OF LIQUID FUELS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Methyl-isothiazolone biocides have been used in Europe and the United States since 1983. Two field trials of this biocide were conducted at a utility and one for the French Navy. In these trials, a single does of biocide (2.8 ppm active ingredient based on the total tank volume) protected stored fuel from microbiological contamination for two years.

ANALYTICAL METHODS

Without practical, sensitive, reproducible, and accurate test methods, many of the problems associated with storage stability of petroleum and fuels would not be solved. The following citations are all related to storage stability and are in addition to those methods discussed in previous and following sections.

ANALYTICAL METHODS CITATIONS

157. GOETZINGER, J. W., BRINKMAN, D. W.; NATIONAL INST. FOR PETROLEUM AND ENERGY RESEARCH. DEVELOPMENT OF A NEW SMALL-SCALE STORAGE STABILITY TEST FOR PETROLEUM FUELS. NIPER-68, 18 P, APR 1985.

A new storage stability test has been developed in which 10-ml aliquots of hydrocarbon liquids are aged at 65° C in small glass bottles containing nylon membrane filters at the bottom of the bottle. Sediment that forms in the liquid during aging precipitates onto the filter. At the end of the aging period the filter is removed from the bottle, washed with solvent, dried, and weighed to determine the weight of deposited sediment. Materials which are very viscous or even solid at the aging temperature can be tested by dissolving the sample in a solvent.

158. MAES, JEAN PIERRE; TEXACO BELGIUM N. V. OPTICAL METHOD TO STUDY THE STABILITY OF COLLOIDAL SYSTEMS. US PATENT APPL 84-641228 16 AUG 1984, US 4628204 A, 12 PP., 9 DEC 1986.

The storage stability of heavy fuel oils is continuously determined by an optical apparatus in which a stream of the oils is passed through a loop or elongated conduit; a flocculating agent is progressively added to the stream at a series of stations in the loop which defines separate segments. These additions progressively enhance the effect of the flocculating agent in the oils to a point where flocculation occurs. Each segment of the loop is characterized by near-IR spectroscopy. A suitable signal, whether audible or visual, can then be provided to indicate the occurrence of flocculation at each segment.

159. WRIGHT, B. W., H. T. KALINOSKI, H. R. UDSETH AND R. D. SMITH. CHEMICAL CHARACTERIZATION OF FUEL SEDIMENTS USING ANALYTICAL SUPERCRITICAL FLUID METHODOLOGIES. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Direct supercritical fluid extraction-mass spectrometry (SFE-MS) provides a means of extracting high molecular weight material for on-line analysis of sediments from diesel fuel. By utilizing the mass selective detection capabilities of the mass spectrometer, numerous alkylated families of polar components can be discerned.

160. MORRIS, D. L., J. N. BOWDEN, L. L. STAVINOHA AND M. E. LEPERA. METHODOLOGY FOR EVALUATING THE STABILITY OF MOTOR GASOLINES. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

The object of this research was to develop improved methods for evaluating motor gasoline stability. Results showed that a new test (Oxidation Stability: Total Gum Method; a modification of ASTM D 873) is a viable alternative to existing methods and warrants consideration by ASTM for adoption as a standard. The test is being used in Europe and has been applied to evaluate antioxidant effectiveness in the refinery blend stocks in this country.

161. FODOR, GEORGE E. AND DAVID W. NAEGELI. DEVELOPMENT OF A TEST METHOD TO DETERMINE POTENTIAL PEROXIDE CONTENT IN TURBINE FUELS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.
The relative ratings of four selected fuels' oxidative tendencies were established using 43° C bottle storage. To develop a test method for the prediction of peroxide potential of fuels, experimental conditions were sought that would require less than 48 hours. Oxidations were carried out in a stirred pressurized reactor at 60°, 80°, and 100° C under oxygen pressure ranging from 19 to 150 psig for periods up to 70 hours. Oxidation rates at 100° C agreed with those from bottle storage for the most and least stable fuels showing that it is possible to predict peroxide buildup in jet fuels at ambient conditions from timely stress tests performed at elevated temperatures.

162. WHITE, E. W.; A STUDY OF TEST VARIABLES AFFECTING RESULTS OBTAINED IN THE ASTM D2274 ACCELERATED STABILITY TEST. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

This study was performed to understand the poor reproducibility among laboratories using the ASTM D 2274 test for the storage stability of distillate fuels. Factors contributing to the problem included the substitution of techniques at most laboratories for those specified in the method; the operator factor; and the need to rewrite the method to emphasize the critical factors and to encourage exact adherence to the procedure. Tests involving several time periods are needed to obtain sufficient information on a fuel's potential behavior.

163. LEE, GEORGE H. II AND LEO L. STAVINOHA. SUMMARY OVERVIEW OF SOURCES OF ERROR IN ACCELERATED STABILTY TEST METHODS FOR DIESEL FUELS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

The effect of fuel additives on particle distribution and growth in diesel fuels has been determined. These determinations were accomplished using particle in liquid measurements as well as gravimetric determination of the fuel insoluble materials. It appeared that dispersants in some fuel stabilizers act to control particle size although the chemical mechanisms of particle formation was not altered. It was also found that the quantity of particulates remains larger and wall adherents smaller as container size increases. Wall adherents appear to form after particulate formation first takes place.

164. RUSSO, P. J., FLORKY, G. R., AGOPSOWICZ, D. E.; ESSON BIOMED. SCI., INC. ; EXXON CO. A PERFORMANCE EVALUATION OF A GASOLINE VAPOR SAMPLING METHOD. AM. IND. HYG. ASSOC., J. (ISSN 0002-8894) V48 N.6 528-31 (JUNE 1987).

Collection efficiencies (% recovery) in charcoal tubes were determined at 20° C and <40% humidity for isobutane, n-butane, and isopentane in gasoline equilibrium headspace vapor samples. Collection efficiencies for total hydrocarbons, butanes, and isopentane were >75% in all cases. Storage stability tests showed that gasoline vapor samples collected under these conditions could be stored at room temperature for up to 14 days without hydrocarbon loss. The results indicated that water vapor adversely affects collection efficiency. The results are relevant to the monitoring of worker exposure to gasoline vapors.

165. PEDLEY, J. INSTITUTE OF PETROLEUM UK, R. AEROSPACE ESTABL. REPORT ON THE THIRD INTERNATIONAL CONFERENCE ON STORAGE AND HANDLING OF LIQUID FUELS. FUEL STABILITY AND HANDLING. PET. REV. V42 N.503 25-28 (DEC. 1988).

The 3rd Institute of Petroleum [U.K.] Stability & Handling of Liquid Fuels International Conference (9/13-16/88) covered papers on test methods, such as ASTM D4625 and D2274, to predict diesel fuel storage stability, to study the effectiveness of additive treatment to improve diesel fuel stability, and to study the chemical causes of diesel fuel instability; test methodology to predict jet fuel thermal stability, including the Jet Fuel Thermal Oxidation Tester; metal deactivators as jet fuel stability additives; chemical aspects of jet fuel stability; types of residual fuel stability; diesel fuel storage, filtration and handling; and microbiological growth in fuels.

166. RUSSELL, J. A., B. K. BAILEY AND J. P. BUCKINGHAM. NUCLEAR MAGNETIC RESONANCE TECHNIQUES FOR PREDICTING THERMAL STABILITY OF JET AND DIESEL FUEL. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

The correlation between distillate fuel thermal stability and structural parameters from NMR measurements was investigated. The structural factor exerting the greatest influence was found to be total aromatic protons. Results were presented for a set of coal-derived liquids and clay-treated pure hydrocarbons. All of the hydrocarbons had breakpoints in excess of 750° F with the exception of mixed methylnaphthalenes.

167. WHITE, E. W., BOWEN, R. J., HILEY, R. W., PENFOLD, R. E. AND PEDLEY,J. F. (EDS.). STUDY OF VARIABLES AFFECTING RESULTS OBTAINED IN THE ASTM D2274 ACCELERATED STABILITY TEST. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS. LONDON, 13-16 SEP 1988

Effects of oxygen concentration, catalytic phenomena, oxidation vessel and constant temperature bath configuration, and filtered insolubles drying time on the results of D2274 tests were examined. Oxygen was found to exert a strong effect upon the results and the presence of metallic copper had catalytic effect. Exposure to ultraviolet light caused significant increases as did air sparging before testing. The geometry of the oxidation cell and its age made only minor differences. Drying time of the filtered insolubles was found to be critical and an increase from 1 hour to 2.5 hours was recommended.

168. AMERICAN PETROLEUM INSTITUTE; BIOSPHERICS INC. SAMPLING AND ANALYTICAL METHODS FOR MIDDLE DISTILLATE AIRBORNE CONTAMINANTS. TESTS WITH CHARCOAL "IMPREGNATED PTFE ((POLYTETRAFLUORETHYLENE))". API HEALTH ENVIRON. SCI. DEP. REP. (FEB. 1988) 17P (ORDER AS API ABSTRACT NO. 36-30040 FROM THE INFORMATION SPECIALIST, API HEALTH ENVIRON. SCI. DEP., 1220 L ST., N.W., WASH. D.C. 20005), 1988.

A GC method for separating and quantitating petroleum middle distillate mists and vapors was modified by replacing the granular activated charcoal in an annular diffusive sampler with a PTFE web impregnated with petroleum-based charcoal. Tests with K-1 kerosine, varnish makers, and painters naphtha showed the charcoal web to be a viable alternative to granular charcoal. Two-week storage stability, and 7 hr sampling stability studies gave recoveries >100%. A higher than desirable standard deviation for the K-1 kerosine was observed in the desorption efficiency test also. Further work is needed on the hardware.

169. DATSCHEFSKI, G. OLD AND NEW WAYS OF USING THE JFTOT FOR AVIATION FUEL STABIITY RESEARCH. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

The use of the JFTOT in research is contrasted with its principle function as a specification tool. Modifications to the apparatus and method which enhance its value as a research tool were considered and methods of breakpoint estimation from single test results were shown.

REACTION MECHANISMS

The increased use of low quality crude oil refinery feedstocks has brought an attendant increase in storage and thermal stability properties as well as compatibility among fuels. Reddy and others (187) reported that future fuels will have relatively high contents of heteroatomic species which are reactive constituents and known to promote fuel degradation.

Worstell and others (170,171) have studied the influence of substituted quinolines, pyrroles, indoles, and pyridines on deposit formation in diesel and jet fuels. Significant increases in deposition rate were found. Heneman (172) has similarly added alkyl sulfides and disulfides to jet fuel and suggested that deposit formation is due to sulfur base catalysis.

Powers (173) found that a caustic treatment of distillate fuels helped prevent the formation of insoluble gum and color degradation in long term ambient storage. This is in line with the findings of Hazlett and Kelso (184) who found that carboxylic and organic sulfonic acids added to distillate fuel blends increased deposit formation. Kendall and co-workers (189) extracted polar compounds from jet fuels and evaluated their influence on stability. The polar extracts were rich in sulfur and had three acidic fractions. Strong interaction with fuel acid fractions was confirmed and acids are strong promoters of deposition in their own right. Hazlett (191) presented the thesis that solids and particulates formed during storage of cycle oil involves acid-base phenomena, most likely acid-catalyzed polymerization.

Beaver and others (190) found that free-radical autoxidative oligomerization of dimethyl pyrrole to form oxygen-containing polymers which retain the pyrrole nucleus is part of the reaction mechanisms of sediment formation in diesel and jet fuels.

Sutterfield and others (194) have studied the chemistry of antioxidant additive depletion in jet fuels while Damin (180) suggested a process for inhibiting the deposition of paraffins in oils and petroleum fractions through the use of additives.

REACTION MECHANISM CITATIONS

170. WORSTELL, JONATHAN H., DANIEL, STEPHEN R. AND FRAUENHOFF, GREG. DEP. CHEM. GEOCHEM., COLORADO SCH. MINES. DEPOSIT FORMATION IN LIQUID FUELS. 3. THE EFFECT OF SELECTED NITROGEN COMPOUNDS ON DIESEL FUEL. FUEL, 60(6), 485-7, 1981.

The influence of substituted quinolines, pyrroles, indoles, and pyridines on deposit formation in a diesel fuel was evaluated. Significant increases in deposition rate were found which depended upon the basicity of the nitrogen compounds (within a given compound class). These effects corresponded closely to those produced in a Jet A fuel. Removal of highly polar fuel components rendered the nitrogen compound influence inoperative. These components are therefore participants in deposit-forming reactions.

171. WORSTELL, JONATHAN H., DANIEL, STEPHEN R.; DEP. CHEM. GEOCHEM., COLORADO SCH. MINES. DEPOSIT FORMATION IN LIQUID FUELS. 2. THE EFFECT OF SELECTED COMPOUNDS ON THE STORAGE STABILITY OF JET A TURBINE FUEL. FUEL, 60(6), 481-4, 1981.

The influence of substituted pyridines, pyrroles, indoles, and quinolines on the storage stability of conventional Jet A turbine fuel was evaluated. The amount of deposit formed in accelerated storage tests increased upon addition of these compounds at levels as low as one ppm nitrogen. The effect is correlated with basicity of the nitrogen compound within a given compound class, but the correlation does not hold between classes (pyridines, quinolines, etc.). Steric hindrance at the nitrogen atom greatly inhibits deposit promotion. The characteristics (but not the elemental composition) of deposits varied with the identity of the added nitrogen compound and with deposition temperature.

172. HENEMAN, FREDERICK C.; ARMY MILITARY PERSONNEL CENT. THE EFFECTS OF ORGANOSULFUR COMPOUNDS UPON THE STORAGE STABILITY OF JET A FUEL. REPORT, ORDER NO. AD-A103486, 87 PP. AVAIL. NTIS, GOV. REP. ANNOUNCE. INDEX (U. S.) 1981, 81(26), 5656, 1981.

Alkyl sulfides and disulfides increased the stability of jet A turbine fuel, but all thiols and thiophene derivatives decreased fuel stability (i.e., increased deposit formation) at selected temperatures and sulfur concentrations. According to linear Arrhenius plots of sulfur-spiked samples, deposit formation decreased with increasing slope for all alkyl sulfides, alkyl disulfides, thiols, and thiophene derivatives. A plot of deposit vs. concentration of added alkyl sulfide gives a negative slope. The inhibition by alkyl sulfides results from the compounds' reactivity with soluble deposit precursors in the fuel. A NMR method of approximation of the relative basicity of weak organosulfur bases linearly correlated the logarithm of the weight of deposit to the shift difference between neat and complexed sulfides and thiols, thus suggesting that deposit formation is due to sulfur base catalysis.

173. POWERS, E. J., WOTRING, W. T.; STANDARD OIL CO. STABILIZATION OF NO. 2 FUEL OILS WITH CAUSTIC TREATING AND ADDITIVES. ASTM SPEC. TECH. PUBL., 751(DISTILL. FUEL STAB. CLEANLINESS), 92-102, 1981.

A combination of caustic treating and additives is used to stabilize No. 2 distillate fuels, to prevent the formation of insoluble gum and color degradation in long-term ambient storage. Cracked components are treated with caustic to remove reactive compounds such as thiophenols. Blends of treated cracked components and untreated straight-run components can be further stabilized with commercial additives to limit insoluble gum formation to 2 mg/100 cm^3 after storage for 16 weeks at 43.3° C.

174. FRANKENFELD, J. W., W. F. TAYLOR AND DENNIS W. BRINKMAN. FUNDAMENTAL SYNTHETIC FUEL STABILITY STUDY. DOE/BC/10045-23. MARCH 1982. IND. ENG. CHEM. PROD. RES. DEV., 22(4), 622-7, 1983.

This three-part paper is a summary of material previously published in a government report. The first part describes the general features of sediment formation in model fuel systems. Part two discusses the effects of nitrogen compound type and the influence of other non-hydrocarbons on sediment formation. Part three describes studies with actual shale-derived middle distillates.

175. YAGGI, N. F., LEE, S. H., GE, J. AND LI, N. C.; DEP. CHEM., DUQUESNE UNIV. OXYGEN ABSORPTION AND LIGHT SCATTERING STUDIES OF THE STABILITY OF LIQUID FUELS. PREPR. PAP. - AM. CHEM. SOC., DIV. FUEL CHEM., 29(1), 178-85, 1984.

The storage stability of SRC II, H-Coal middle distillates, their hydrotreated liquid products, and petroleum-derived JP-5 jet fuels, in terms of sediment and gum formation was determined by the amounts of oxygen uptake and light scattering of the fuels in relation to the presence of particular nitrogen compounds. The coal-derived middle distillates had a higher oxygen uptake than the hydrotreated coal liquids, which had slightly higher oxygen uptake than the petroleum jet fuels. 2,5-Dimethylpyrrole promoted oxygen absorption, light scattering, and deposit formation much more than N-methylpyrrole. These three quantities may be correlated with instability of liquid fuels. The synergistic effects between nitrogen- and sulfur-containing compounds were evident.

176. LI, NORMAN C., HAZLETT, ROBERT N., GE, JOHN, YAGGI AND NORBERT F.; DEP. CHEM., DUQUESNE UNIV. LIGHT SCATTERING STUDIES OF THE STABILITY OF LIQUID FUELS. FUEL, 63(9), 1285-9, 1984.

The storage stabilities of upgraded coal-derived liquids, JP-5 jet fuels derived from petroleum and oil shale, and a petroleum-derived diesel fuel were compared by laser light scattering. The most severely hydrotreated coal-derived liquids were comparable in stability to the jet fuels derived from petroleum and oil shale. Fuel degradation was monitored in the presence of added heteroatom compounds. Pronounced enhancements of light-scattering intensity was observed for coal-derived liquids containing heteroatom-metallic compounds. Phenolic oxidative coupling was confirmed as an important reaction responsible for the aging of coal-derived liquids. Pyridine and dimethylquinoline complexed with Cu are catalysts for oxidative coupling. 2,5-Dimethylpyrrole by itself is deleterious to fuel stability in that it promotes sediment formation and light scattering. During accelerated aging of upgraded H-Coal liquids in the presence of 2,5-dimethylpyrrole, a sediment formed with empirical formula $C_7H_8NO_{13}$, which was further characterized by solid-state 13C NMR and XPS.

177. COONEY, J. V., HAZLETT, R. N. AND BEAL, E. J.; NAVAL RESEARCH LAB. MECHANISMS OF SYNCRUDE/SYNFUEL DEGRADATION. SECOND ANNUAL REPORT, OCTOBER 1, 1982-SEPTEMBER 30, 1983. DOE/BC/10525-8, 122 P., MAY 1984.

Polar compounds were isolated from two different shale sources by acid extraction and silica gel adsorption. The identification of the extracted components was accomplished by combined gas chromatography mass spectrometry. Accelerated storage stability tests employing these polar extracts as dopants indicated a range of activities with respect to the promotion of insolubles formation. Nitrogen base extracts exhibited moderate activity. Highly polar extracts showed the greatest activity. The autoxidation of 2,5-dimethylpyrrole (DMP) in shale-derived diesel fuel was examined by the techniques of x-ray photoelectron spectroscopy (XPS or ESCA), fluorescence-phosphorescence, and by monitoring rates of oxygen absorption by stressed fuel. High temperature (100 to 120° C) stress in DMP-doped fuel samples displayed different kinetic behavior from that observed at 43 to 80° C, suggesting that mechanistic changes occurred at the higher temperatures.

178. COONEY, J. V., BEAL, E. J. AND HAZLETT, R. N.; NAVAL RESEARCH LAB. EXAMINATION OF SHALE-DERIVED POLAR COMPOUNDS AND THEIR EFFECTS ON DIESEL FUEL STABILITY. 187TH. NATIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY CONFERENCE, ST. LOUIS, MO, 8 APR 1984 . DIV FUEL CHEM PREPRINTS.

This study was an examination of the effects of adding shale-derived polar fractions to a stable shale base fuel. Polar compounds were isolated from two different shale sources by mild acid extraction followed by adsorption on silica gel. The identification of the extract components was made by combined gas chromatography - mass spectrometry. Results of accelerated storage stability tests were described in this paper.

179. MAYO, F. R.; SRI INTERNATIONAL, MENLO PARK, CA. BASIC STUDY OF FUEL STORAGE STABILITY. FINAL REPORT 15 JULY 1980-30 MARCH 1984. AD-A-142194/0, 13 P., MAY 1984.

The goal of this research was to determine the chemistry of deposit formation on hot parts of diesel and jet turbine engines and thus to predict and prevent deposit formation. These deposits were assumed to come mostly from soluble gum formed on storage. The fuels used for the study were distilled at low pressure and stored under nitrogen and refrigeration. Oxygen absorption rates were measured from air, R_0 and total gum formation, r_g at 130° C without initiator and at 100° with added t-butyl hydroperoxide. The gum measured was mostly or wholly soluble in the fuel. Insoluble gum, if any, was a minor product.

180. DAMIN, B., FAURE, A., MALDONADO, P. AND VOLLE, J. I.; A PROCESS FOR INHIBITING THE DEPOSITION OF PARAFFINS IN CRUDE OILS AND PETROLEUM FRACTIONS. GR BRIT 2,144,448A, P 85.03.06, F 84.07.17, PR FR 83.07.21 (APPL 8,312,074) (SOC NATL ELF AQUITAINE) (10 CLAIMS), 1985.

A process is described for inhibiting the deposition of paraffins in oils and petroleum fractions that remains effective during storage and transportation. The additives make it possible to maintain in dispersion, the whole range of paraffins and also to prevent the deposition of the heavier paraffins on the walls of the storage vessels or transport pipes. The process consists of supplementing the crude oil or petroleum fraction with an additive which is a nitrogen-substituted succinimide ether in a concentration of 5 to 3,000 ppm by weight.

181. POWER, A. J. AND DAVIDSON, R. G.; MATERIALS RESEARCH LABS., ASCOT VALE, AUSTRALIA. INFRARED SPECTROSCOPY OF CARBONYL SPECIES IN OXIDISED DIESEL DISTILLATES. FUEL (UNITED KINGDOM), V 65:12, 1753-1755 P., DEC 1986.

Five petroleum diesel distillates were aged by ambient storage at 20°-30° C for 1 year, by sparging with O_2 at 95° C for 16 hours (ASTM D2274), and by storage under O_2 at 100° C for 168 hours (modified ASTM D873). The three methods yielded carbonyl concentrations, estimated from IR difference spectra, of <0.01, approximately 0.2, and approximately 1.5 mM, respectively, possibly partly explaining the known unreliability of accelerated oxidation tests for predicting fuel storage stability. The carbonyl species present in gum residues, isolated by the conventional steam-jet evaporation method for determining soluble gum contents in oxidized fuels, did not represent those in the oxidized fuels prior to evaporation.

182. POWER, A. J. AND DAVIDSON, R. G.; AUST. DEP. DEF. MATER. RES. LAB. INFRARED SPECTROSCOPY OF CARBONYL SPECIES IN OXIDISED DIESEL DISTILLATES. FUEL (ISSN 0016-2361) V65 N.12 1753-55 (DEC. 1986).

Five petroleum diesel distillates were aged by ambient storage at 20°.-30° C for 1 year, by sparging with O_2 at 95° C for 16 hours (ASTM D2274), and by storage under O_2 at 100° C for 168 hours (modified ASTM D873). The three methods yielded carbonyl concentrations, estimated from IR difference spectra, of <0.01, approximately 0.2, and approximately 1.5 mM, respectively,. The carbonyl species present in gum residues, isolated by the conventional steam-jet evaporation method , did not represent those in the oxidized fuels prior to evaporation.

183. MORRIS, R. E. AND K. W. FLOHR. INFLUENCES OF SULFUR, NITROGEN AND OXYGEN BEARING COMPOUNDS ON DIESEL FUEL STORAGE STABILITY. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

The effects of selected sulfur, nitrogen and oxygen compounds on the storage stability of a shale-derived diesel fuel have been examined. Fuels were aged in bottles at elevated temperatures using gravimetric determinations of insoluble products as a measure of inherent storage stability. Sulfur-bearing compounds included sulfides, disulfides, thiols, and a sulfonic acid--all of which were used as dopants. None significantly degraded fuel stability when used alone but in combinations with an active nitrogen compound they were found to exert differing influences on insoluble product formation.

184. HAZLETT, ROBERT N. AND GORDON KELSO. ACID BASE PHENOMENA IN DISTILLATE FUEL STABILITY. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Carboxylic and organic sulfonic acids added to distillate fuel blends containing catalytically cracked stock increase deposit formation. These acids enhance deposit formation by catalytic action and are not incorporated into the deposit. Organic sulfonic acids may fit into the unified acid catalysis pattern but await resolution of ionization phenomena in non-aqueous solution. A tertiary aliphatic amine stabilizer was effective for reducing deposit amounts from fuel blends containing the acids. Other amines exerted favorable behavior only if they were strong organic bases.

185. HILEY, R. W. AND J. F. PEDLEY. FORMATION OF INSOLUBLES DURING STORAGE OF NAVAL FUELS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Insoluble particulates formed during storage of naval distillate fuel (F-76) has been identified as a major cause of fuel filter blockage in gas turbine powered warships. The study included five trials in which stable and unstable fuels were stored in 1000 gallon steel tanks under ambient conditions. Formation, agglomeration and settling of insoluble particles were monitored over a period of a year. Two stability improving additives were ineffective in inhibiting the degradation of an unstable fuel. Preliminary results indicated that a significant amount of the "precursor fraction" of the sediment is present in solution in the unstable fuel. The conversion of this material into more polar sediment components by treatment with acid leads to the postulation that the final stage in diesel fuel sediment formation is an acid catalyzed process.

186. LEE, GEORGE H. II AND LEO L. STAVINOHA. STUDIES RELATING TO THE MECHANISMS OF DIESEL FUEL DETERIORATION AND ADDITIVE INHIBITION. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

The effect of fuel additives on particle distribution and growth in diesel fuels has been determined. These determinations were accomplished using particle in liquid measurements as well as gravimetric determination of the fuel insoluble materials. It appeared that dispersants in some fuel stabilizers act to control particle size although the chemical mechanisms of particle formation was not altered. It was also found that the quantity of particulates remains larger and wall adherents smaller as container size increases. Wall adherents appear to form after particulate formation first takes place.

187. REDDY, K. T., N. P. CERNANSKY AND R. S. COHEN. EFFECT OF NITROGEN AND SULFUR CONTAINING COMPOUNDS ON THE DETERIORATION OF FUELS AT ELEVATED TEMPERATURES. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Future fuels will have relatively high contents of heteroatomic species which are reactive constituents and are known to promote fuel degradation. The study of a single component model fuel, n-dodecane, singly and in combination with heteroatomic species, was undertaken. The fuels, n-dodecane and n-dodecane plus dopants were stressed on a modified JFTOT between 200° and 400° C. Gas chromatography and mass spectrometry yielded reaction mechanism information. The polar fraction was mainly tetrahydrofuran derivatives, dodecanol and dodecanone isomers and dodecylhydroperoxide decomposition products. Both 2,5-dimethylpyrrole and 3,4-dimercaptotoluene were added to n-dodecane as dopants and introduced cooxidation reactions and inhibited ROOH formation. Dibutylsulfide dopant added to n-dodecane promoted dodecanol and dodecanone formation and inhibited ROOH formation.

188. POWER, A. J.; AUST. DEP. DEF. MATER. RES. LAB. ACCELERATED OXIDATION OF DIESEL DISTILLATE: INFRARED SPECTRA OF SOLUBLE AND INSOLUBLE GUMS. FUEL V65 N.1 133-37 (JAN. 1986).

Five Australian petroleum diesel distillate oil samples from refineries or tanker distribution depots of five oil companies, which had been stored for <3 weeks, were subjected to ambient aging (for 1 year in darkness in stoppered glass bottles at 20°-30° C, and also to the ASTM accelerated oxidation stability test (sparging with O_2 at 95° C for 16 hours). Soluble gum yields after ambient aging were 6-94 mg/L depending on the fuel vs. 32-105 mg/L after accelerated aging; insoluble gum yields after ambient aging were all less than the deterioration limits for U.S. military diesel fuels. The soluble gums formed during accelerated oxidation had higher proportions of oxygenated carbon functional groups than did the soluble gums formed during ambient aging. The opposite was true for the insoluble gums. For the ambiently aged oils, the spectra of the soluble gums were markedly different from those of the insoluble gums.

189. KENDALL, D. R., R. H. CLARK AND P. A. STEVENSON. THE INFLUENCE OF POLAR COMPOUNDS ON THE STABILITY OF JET FUEL. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

The development of a flask oxidation test to directly measure oxidation rate of jet fuels at high temperatures has permitted resolution of the oxidation into initiation and inhibition stages. The rate of initiation is a good indicator of future fuel deposits under thermal stress. Polar compounds were extracted and their influence on stability was evaluated. The polar extracts were rich in sulfur and had three acidic fractions. Work with model sulfur compounds confirmed the possibility of strong interactions with fuel acid fractions and that acids are strong promoters of deposition in their own right.

190. BEAVER, B. D., HAZLETT, R. N., COONEY, J. V. AND WATKINS, J. M.; DUQUESNE UNIV. ; NAV. RES. LAB. UNIV. MIAMI ; GEO-CENT. INC. THE SIGNIFICANCE OF THE OXIDATION OF 2,5-DIMETHYLPYRROLE ((DMP)) IN OXIDATIVE FUEL STABILITY. 193RD ACS NATL. MEET. (DENVER 4/5-10/87) ACS DIV. FUEL CHEM. PREPR. V32 N.1 538-46 (1987).

A literature survey was conducted on the promoting effect of alkylpyrroles, including dimethylpyrrole (DMP), on sediment formation during storage of petroleum and oil shale-derived diesel and jet fuels. It covered the fundamental chemistry of sediment formation in hydrocarbon fuels by reaction with O_2; studies on O_2 absorption kinetics by DMP-doped fuels and on the chemical structure of the sediments formed in such fuels. It appears that free-radical autoxidative oligomerization of DMP to form oxygen-containing polymers which retain the pyrrole nucleus is part of the reaction mechanisms. The alternative mechanism is that of "electron transfer-initiated" oxidation of alkylpyrroles in model solvents or fuels. Also discussed is the relative contributions of the free radical-initiated and electron transfer-initiated oxidation mechanisms to sediment formation in fuels doped with alkylpyrroles of different structure.

191. HAZLETT, R. N.; U. S. NAVAL RES. LAB. ACID BASE PHENOMENA IN OXIDATIVE STABILITY OF DISTILLATE FUEL. PREPR. - AM. CHEM. SOC., DIV. PET. CHEM., 32(3-4), 847-52, 1987.

The formation of solids and particulates during storage of cycle oil involves acid-base phenomena, most likely acid-catalyzed polymerization. This thesis is supported by data obtained by aging a light cycle oil at 65° or 80° C for 14 or 28 days, and observing the effect of acids (PhSH, decanoic, furoic, chloroacetic, dodecylbenzenesulfonic) and a tert-amine stabilizer (FOA 3). An increase in the total H+ concentration (i.e., H+ from acid less H+ reacted with FOA 3) gave a linear increase in the solid impurity concentration in the cycle oil.

192. REDDY, K. T., N. P. CERNANSKY AND R. S. COHEN. THE ROLE OF ALKYLPEROXY AND ALKYL RADICALS IN FUEL DEPOSIT AND GUM FORMATION. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Fuel degradation mechanisms were hypothesized based on the quantification and identification of soluble degradation products. The mechanisms proposed suggest that at temperatures below 300° C, alkylperoxy radical reactions are most important, while between 300°-400° C, alkyl radical reactions become predominant. Data for the production of C_5-C_{10} alkanes, alkenes, aldehydes, tetrahydrofurans, dodecanol and dodecanone from dodecane stressed in a JFTOT apparatus were presented.

193. MUSHRUSH, G. W., R. N. HAZLETT, D. R. HARDY AND J. M. WATKINS. JET FUEL INSTABILITY; ORGANO-SULPHUR HYDROPEROXIDE INTERACTIONS. 3RD

INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

The reaction between t-butyl hydroperoxide and several sulfur compounds were studied in tetradecane and deaerated benzene at 120° C. The major product found from hexyl sulfide was the corresponding sulfoxide. Dodecyl disulfide was the major product from dodecanethiol with the sulfoxide also being found. Thiophenes did not yield simple compounds but tetrahydrothiophene gave the corresponding sulfoxide. Results from storing jet fuels doped with various sulfur compounds at 65° C were reported.

194. SUTTERFIELD, F. D., D. W. BRINKMAN, O.K. BAHN, J. B. GREEN, J. W. GOETZINGER, G. P. STURM, G. SPECK AND L. TURNER. THE CHEMISTRY OF ANTIOXIDANT ADDITIVE DEPLETION IN JET FUELS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Two hydrocracked jet fuel components were aged at 60° and 80° C, neat and with added phenolic antioxidants. Color, insolubles and peroxide formation were monitored throughout the accelerated aging period ranging up to 68 weeks. Peroxidation was first observed in the neat fuels but this peaked and fell at the same time that insolubles began to form. Two different phenolic antioxidants delayed the onset of peroxidation. Aged fuels and insolubles from additive-free fuels were analyzed using MS, GC/MS and IR spectroscopy. It was concluded that the insolubles resulted from the oxidation of alkyl-substituted indans, tetralins, indenes, dihydronaphthalenes, and benzenes.

195. BEAVER, B. D., HAZLETT, R. N., COONEY, J. V. AND WATKINS, J. M.; DUQUESNE UNIV. ; NAV. RES. LAB. ; UNIV. MASS. MED. CENT. ; GEO-CENT. INC. A NEW LOOK AT THE MECHANISMS OF OXIDATIVE SEDIMENT FORMATION IN FUELS. FUEL SCI. TECHNOL. INT. (ISSN 0884-3759) V6 N.2 131-50 (1988).

2,5-Dimethylpyrrole (DMP), has been shown to undergo rapid oxidation to a brown sediment containing no fuel-derived constituents and in which the pyrrole nucleus is intact. Following a critical review of mechanisms of sediment formation in jet and diesel fuels by reaction with O_2 in storage, in particular on the acceleration of sediment formation in shale-derived diesel fuel by 2,5-dimethylpyrrole (DMP), it was concluded that the initiation step involves electron transfer from DMP to O_2 to form a complex in equilibrium with endoperoxide. The high electron density of DMP thus explains why it forms sediment so much faster than other pyrroles. This mechanism occurs in parallel with the usual peroxy radical chain mechanism. The generality of the electron transfer mechanism, which in this case is faster than the radical chain mechanism, explains the ineffectiveness of the usual radical scavenger antioxidants.

196. HAZLETT, R. N. AND POWER, A. J.; DSTO MELBOURNE. PHENOLIC COMPOUNDS IN BASS STRAIT DISTILLATE FUELS: THEIR EFFECT ON DEPOSIT FORMATION. FUEL V68 N.9 1112-17 (SEPT. 1989).

Approximately 100 phenolic compounds were identified, by GC and IR spectroscopy, in a caustic extract from a catalytically cracked light cycle oil (LCO) from Bass Straight crude oil. The extract contained 0.2 wt % sulfur and

<0.5 wt % nitrogen. Addition of the extract to other, more stable distillates (an automotive distillate oil and a hydrotreated LCO) from the same crude caused them to yield larger amounts of total insoluble material during accelerated thermal aging at 65° for 42 days or 80° C for 14 days (both corresponding to about 2 years of storage at 20° C). IR spectra indicated that oxidative coupling of the phenols was the most probable mechanism responsible for the decreased stability of the fuels. The role of such coupling, in conjunction with other fuel degradation mechanisms, were presented.

197. MUSHRUSH, GEORGE W., WATKINS, JOHN M., BEAL, ERNA J., MORRIS, ROBERT E., COONEY, JOHN V. AND HAZLETT, ROBERT N., NAV. RES. LAB. CHARACTERIZATION OF POLAR EXTRACTS FROM TWO PETROLEUM-DERIVED FUELS. FUEL SCI. TECHNOL. INT., 7(7), 931-49, 1989.

Components of the polar extracts of two marginally stable low-nitrogen petroleum JP-5 fuels were isolated by mild acid extraction followed by silica gel adsorption and characterized and identified by combined capillary column gas chromatography-mass spectroscopy. Both fuels were studied by two methods under accelerated storage conditions, (1) bottle tests, and (2) oxygen overpressure. Bottle tests were conducted at 80° C for 14 days and in 99.5% oxygen at 65° C for 6 days and 43° C for 4 weeks. Filterable insolubles and adherent gum were measured for both methods. Peroxide numbers were determined by ASTM D3703-85 for both stressed and original fuel samples. The main class of heteroatom substances identified were pyridines. Pyridines identified in the basic nitrogen compound fraction were primarily mono-alkyl substituted while those in the non-basic nitrogen compound fraction were highly branched.

198. WECHTER, M. A. AND HARDY, D. R.; SOUTHEAST. MA UNIV. THE ISOLATION OF PRECURSORS RESPONSIBLE FOR INSOLUBLES FORMATION IN MID-DISTILLATE DIESEL FUELS. FUEL SCI. TECHNOL. INT. V7 N.4 423-41 (MAY 1989).

Extraction of mid-distillate fuels with methanol reduced the tendency of the fuels tested to form insolubles under conditions of accelerated aging. The effect was most pronounced among fuels which contained catalytically cracked light cycle oils. Extraction of four test fuels (70/30 blends of straight run stocks and light cycle oils) with aqueous base indicated that base extraction had little or no effect on insolubles formation. Blending several straight runs with various light cycle oils, implicated catalytically cracked light cycle oils as primary repositories of the precursor materials of insolubles. The methanol extract may serve as a chemical probe for the sediment precursors and may thus function as an indicator for instability under long-term storage conditions.

199. TAM, P. S., KITTRELL, J. R. AND ELDRIDGE, J. W.; UNIVERSITY OF MASSACHUSETTS/KSE INC DESULFURIZATION OF FUEL OIL BY OXIDATION AND EXTRACTION--2. KINETIC MODELING OF THE OXIDATION REACTION. INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH V29 N.3 324-29 (MARCH 1990).

Experimental data suggested that the oxidative desulfurization of middle distillate fractions via oxidation with nitric acid or NO_2 is similar to, but much faster than, the oxidation of such fuels during storage in air. Both processes produce heteroatom-rich residues or sediments with similar elemental compositions.

CONTAINMENT

Storage of crude oil or products derived from petroleum or alternate organic liquids is typically in steel tanks above ground with floating or fixed dome roofs. Two modes of long term underground storage have been used in various parts of the world since about 1915. These are porous media and open cavities. Porous media storage includes depleted gas or oil fields and aquifers. The open cavities have been abandoned mines carved from granite, rock salt or other suitable rock formations as well as solution-mined cavities in salt. Salt domes do not exist in some countries, hence storage is in surface or undergound steel tanks, in giant floating barges and some in underground concrete tanks.

In addition to crude oil, a variety of refined products are stored in European reserves. These products include aviation turbine fuel, automotive and marine diesel fuels, and home heating oil.

Giles and Niederhoff (134) have reported on studies of bulk distillate fuel oil stored in a solution-mined cavern in salt at Lesum, West Germany for about 18 months. Little difference in quality among samples was observed and, the variations were attributed to differences in quality originally present.

Gartenmann (20) has reported that in Switzerland, gasolines and middle distillates are stored for ten or more years. Periodic controls are performed for the middle distillates including the existent stability as measured by the Conradson Carbon Residue, ASTM color, and residue on evaporation. The storage is mostly in underground tanks at 10° C. However, above ground floating roof tanks for gasoline are also employed. One obvious problem with floating-roof storage tanks is the infiltration by rain water because of the annular space between the roof and the wall of the tank. Evaporation losses of product in warm climates can also occur.

Storage of No. 2 fuel oil has been reported in long-term storage for 9 years before an accelerated aging test indicated certain instability in the future. In still another case, a gas oil that was stored for 20 years in a fixed-roof tank above ground showed the oil was good and accelerated aging tests after 20 years of storage indicated a further long-term storage potential of several years.

No. 6 fuel oil presents additional problems of containment because of its viscous nature and the need for heat input to maintain pumpability. Even underground storage containment requires heat and all above ground lines must be heated in cool to cold climates.

Aviation turbine fuels are inherently more stable than gasolines, primarily because of stringent end-use specifications that limit their aromatic hydrocarbon content to a maximum of 25 volume percent and, alkene content to a maximum of 5 volume percent. These fuels are composed of the more stable alkanes and cycloalkanes.

Azev and others (203), in 1976, reported no changes in the properties, including thermal stability, of jet fuels after five years of storage in rock salt caverns at 26° C, nor did the amount of sodium in the fuel exceed that found in freshly refined fuel. Ivanov and others (202) and Sablina and co-workers (201) earlier reported an increase in gum precursors and, a decrease in thermal stability after three years of storage.

Giles and others (126) referenced studies as early as 1952 conducted by the United States Air Force in which JP-4 jet fuel was stored in a cavern within a salt formation for six months. Following storage, the fuel was used to run a jet engine for 80 hours in cyclic tests. No adverse effects on the engine were found following this test.

The storage of crude oil underground for extended periods has been practiced in Europe and, in South Africa for over 20 years and a comprehensive study of the stability of stored crude in Germany has been reported.

In South Africa, an abandoned coal mine was converted for strategic crude oil storage in about 1967, and has been in continuous use since then. Although little data is available on the quality of the crude oil, that is principally Iranian Light, it is reported (126) to be readily refineable. Emulsions, that are difficult to break, are apparently accumulating at the oil/water interface within the mine. These emulsions are believed to be caused mechanically by the action of the submerged pumps used to remove the ground water seeping into the mine. These emulsions may also be the result of microbial activity, since growth of anaerobic bacteria at the oil/water interface was noted; yet no hydrogen sulfide was reported to be present. Crude oil stored in surface tanks with floating roofs is also reported to be readily refineable, although some anaerobic bacteria are present. Growth of the anaerobic bacteria is controlled by periodically removing the water bottoms.

In the United States, a buildup of hydrogen sulfide attributed to anaerobic bacterial activity has occasionally been noted in surface tanks used for crude oil storage at refineries and terminals. The common remedy is to inject a suitable biocide into the water bottoms that are subsequently withdrawn and disposed of. Except for some corrosion of the tank shell, no other deleterious effects have been reported.

In the most comprehensive studies published to date, Giles and others (134,205,226) reported detailed analyses of crude oil from three of Germany's strategic storage sites and crude oil stored in the United States' Strategic Petroleum Reserve. At Etzel, West Germany,one of the 33 cavities had contained over 260,000 cubic meters of four different Middle East crude oil streams and a tank farm crude oil composite for approximately two years. Twenty-two samples were collected from various depths within this cavern, and subsequently analyzed comprehensively.

The bulk of the crude oil contained negligible sediment and water, probably as a result of these having settled out. Density and viscosity were virtually constant, suggesting that total mixing of the different crude oils had taken place, and that stratification was not occurring. Distillation yields were somewhat variable, but also do not indicate any differentiation. The geothermal gradient within the Etzel salt mass is on the order of 3 to 4° C per 100 m, and the temperature of the salt at the bottom of the cavern is approximately 15° C greater than at the top. Convection within the stored oil induced by this temperature differential probably promotes thorough mixing. The other variation was random with no noticeable trends. In general, the data for these twenty samples indicate that the different crude oil streams stored are moderately well mixed with little or no evidence of stratification.

The crude oil surveillance assessment program to monitor crude oil in the U.S. SPR has provided data defining the quality of the mixed oil streams stored in individual caverns. Despite convective mixing, sediment, water, waxes, and certain heterogeneous compounds indigenous to the crude settle out and form a sludge layer at the brine-oil interface. This sludge does not appear to be result of incompatibility, however. Viable aerobic and anaerobic bacteria have been found in some storage caverns, but physical and chemical evidence overwhelmingly demonstrates that these bacteria are not degrading the stored crude. The oil exhibits no increase in salt content and no deleterious changes in quality were observed during nine years of storage.

CONTAINMENT CITATIONS

200. JENSEN, J. T. AND C. M. BUSTON. UNDERGROUND SALT CAVERN STORAGE OF JET FUEL. MEMORANDUM REPORT NO. MCQEC-51, U. S. AIR FORCE, WRIGHT-PATTERSON AIR FORCE BASE, OHIO,. APRIL 17, 1953.

Abstract was not available from accessed data base.

201. SABLINA, Z. A., A. A. GUREEV, A. A. KUKUSHKIN, N. I. MELENT'EVA, B. A. ENGLIN AND A. M. FOMINA. CHANGES IN THE HIGH-TEMPERATURE PROPERTIES OF JET FUELS DURING PROLONGED STORAGE (IN RUSSIAN). KHIM. TEKHNOL. TOPL. MASEL, V. 15, N. 12, PP 39-42, 1970.

Abstract was not available from accessed data base.

202. IVANOV, A. L., A. N. ROMANOV, V. A. GLADKIKH, G. V. KACHURINA, M. P. ALEKSEEVA, B. A ENGLIN AND E. P. SEREGIN. CHANGE IN THE PROPERTIES OF HYDROGENATED FUELS DURING LONG-TERM STORAGE (IN RUSSIAN). KHIM. TEKHNOL. TOPL. MASEL, N. 5, PP. 27-30, 1975.

Prolonged storage of hydrogenated jet fuels containing no additives produced changes only in the thermal stability determined under dynamic conditions. Fuels lost their original high thermal stability after 2-3 years storage. Good thermal stability of combined hydrogenated fuels could be maintained 5 years without change by the addition of an antioxidant and dispersing additives.

203. AZEV, V. S., E. P. SEREGIN, V. A. GLADKIKH, N. V. STRYUK, G. B. SKURODIN AND L. N. KUZNETSOVA. LONG-TERM STORAGE OF JET FUEL T-1 IN UNDERGROUND RESERVOIRS FORMED IN ROCK SALT FORMATIONS (IN RUSSIAN). TRANSP. KHRANENIE NEFTI NEFTEPROD, N. 4, PP 19-22. 1976.

The effect of prolonged storage in rock-salt caverns on the quality of jet fuel was reported. The fuel was stored for 5 years over brine inside a subterranean hollow in a rock-salt formation at 26° C. It was then pumped into steel tanks on the surface, with samples being taken every 10% of the volume transferred. Differences in composition and properties of the three main parts of the fuel were within experimental error. The stored fuel could be used directly in all the applications of conventionally-stored fuel.

204. KITCHEN, G. H.; PRIVATE COMMUNICATION TO STRATEGIC PETROLEUM RESERVE OFFICE, BELL LABORATORIES, MURRAY HILL, NJ, MARCH 2, 1978.

Abstract not available.

205. NIEDERHOFF, PETER; KBB INC. EVALUATION OF THE EFFECTS OF LONG-TERM STORAGE IN SALT CAVERNS ON THE PHYSICAL AND CHEMICAL PROPERTIES OF CERTAIN CRUDE OILS AND DISTILLATE FUEL OILS. CONTRACT EL-78-C-01-7151. U.S. DOE, OFFICE OF STRATEGIC PETROLEUM RESERVE, FINAL REPORT 1979.

A knowledge of the possible formation of emulsion layers during storage is necessary for the discharge of crude oils from long-term storage caverns. The discharging of such layers with the crude oils should be avoided although the decomposition of emulsions of this type seems to be possible. These emulsions have a low viscosity and are relatively non-stable. They can develop as a very viscous intermediate layer between brine and oil. One can control such emulsification with the addition of emulsion breakers. It is important that mixing an oil rich in asphaltenes with another that is rich in paraffins may result in the precipitation of asphaltenes.

206. BOWDEN, J. N. AND D. W. BRINKMAN. STABILITY SURVEY OF HYDROCARBON FUELS. U. S. DEPARTMENT OF ENERGY REPORT BETC/1778-4, 1979.

The purpose was to develop storage stability data on currently available fuels to serve as reference data. Ten samples of diesel fuel, JP-4, unleaded gasoline, and leaded gasoline were obtained from across the United States. Each sample was analyzed for physical and elemental composition. Samples were then stored in glass at 43.3° C. Samples were removed from storage and analyzed for soluble and insoluble gum and for precipitate after 4, 8, 16, and 32 weeks.

207. STAVINOHA, L. L., J. N. BOWDEN, S. R. WESTBROOK AND H. N. GILES. FINAL REPORT ON ASSESSMENT OF CRUDE OIL AND REFINED PETROLEUM PRODUCT QUALITY DURING LONG-TERM STORAGE. AFLRL REPORT NO. 121, DECEMBER 1979, 60 P.

A program was undertaken to assist in ensuring that products considered for long-term storage would remain of usable quality. The authors concluded that strategic storage of crude oil and refined products could be successfully accomplished if sites were properly chosen and crudes and products to be stored were selected properly, with additives being necessary in the refined products.

208. PREECE, D. S. AND STONE, C. M.; SANDIA NATIONAL LABS. VERIFICATION OF FINITE ELEMENT METHODS USED TO PREDICT CREEP RESPONSE OF LEACHED SALT CAVERNS. ISSUES IN ROCK MECHANICS (23RD CALIF UNIV, BERKELEY, ET AL ROCK MECH SYMP (BERKELEY, CALIF, 82.08.25-27) PROC) PP 655-663 SOCIETY OF MINING ENGINEERS, NEW YORK, 1982.

The Strategic Petroleum Reserve stores large quantities of crude oil in leached salt caverns in the Texas-Louisiana Gulf Coast area. Formerly, cavern stability was predicted based on experience with other caverns in the vicinity. With the development of good nonlinear finite element structural computer programs, it became possible to predict stability before the cavern was created. The analytical data come from finite element analyses of a specific cavern where the laboratory determined material properties and an approximation to the cavern geometry are used as input. Such comparisons were made for caverns in Bayou Choctaw Dome (Louisiana) and Eminence Dome (Mississippi).

209. BECK, J., GASTON, G., ILG, R., JAMES, W. P. AND JEFFREY, L.; WEST HACKBERRY STRATEGIC PETROLEUM RESERVE SITE BRINE DISPOSAL MONITORING, YEAR 1 REPORT. FINAL REPORT. US DEP ENERGY FOSSIL ENERGY REP NO DOE/PO/10288-2, V 1-5, 2,024 PP, FEB 1983 (V 1, "EXECUTIVE SUMMARY" (DE83016195); V 2, "PHYSICAL AND CHEMICAL OCEANOGRAPHY" (DE83016196); V 3, PT 1, "BIOLOGICAL OCEANOGRAPHY" (DE83016197); V

3, PT 2, "BIOLOGICAL OCEANOGRAPHY: ZOOPLANKTON" (DE83016198); V 4, "BIBLIOGRAPHY AND SUPPORTING DATA FOR PHYSICAL OCEANOGRAPHY" (DE83016199); V 5, "SUPPORTING DATA FOR ESTUARINE HYDROLOGY, 1983.

The West Hackberry salt dome, located in Cameron Parish, LA, is designed to store 241 million barrels of crude oil. Brine generated during the leaching of the salt dome required disposal off shore through a pipeline and diffuser system. Discharge was monitored continually. A study of the environment before and after discharge was made to assess physical, chemical, and biological attributes and to determine if significant adverse changes in the ecosystem productivity and stability of the biologic community were occurring.

210. SABERIAN, A.; LEACHING DESIGN CONSIDERATIONS FOR DEVELOPMENT OF LARGE CRUDE OIL STORAGE CAVITIES. IN SITU V 7, NO 4, PP 313-343, 1983.

Large salt cavities are the most economical way of storing large volumes of crude oil. High circulation rates are required for development of large cavities in the shortest time. Leaching procedures for these cavities were the subject of this study. Operational leaching during the storage life span of a cavity must be predetermined and properly incorporated into the cavity design. The development of a conical roof, which is thought to enhance the stability of the cavity should be considered in the leach/fill type operations. Injection tubing plug-up associated with accumulation of insolubles at the cavity bottom can be effectively dealt with by maintaining continuous, high circulation rates.

211. KATZ, E.L., VOGEL, L.W. AND SMITH, R.E.; AEROSPACE CORP., EL SEGUNDO, CA; AEROSPACE CORP., EL SEGUNDO, CA (USA); US DOE ASSISTANT SECRETARY FOR ENVIRONMENTAL PROTECTION, SAFETY AND EMERGENCY PREPAREDNESS, WASHINGTON, DC. OFFICE OF THE DEPUTY ASSISTANT SECRETARY FOR STRATEGIC PETROLEUM RESERVE. UNDERGROUND STORAGE OF LARGE VOLUMES OF CRUDE OIL: THE US STRATEGIC PETROLEUM RESERVE PROGRAM. U.S. DEPT ENERGY REP NO DOE/NBM-3014042, 28 P., 1983. (DE83014042) ($8.50); ABSTR NO 40192, ENERGY RES ABSTR V 8, NO 17, PP 5329-5330, 1983.

The Energy Policy and Conservation Act provided for the storage of up to one billion barrels of crude oil in underground caverns. The Strategic Petroleum Reserve (SPR) funding, however, provides for the construction of storage facilities for 750 million barrels. No plans existed in 1983 for developing storage for the final 250-million-barrel increment. The approximate amount of oil in storage as of June 30, 1983, was 330 million barrels; at that fill rate, the SPR would contain approximately 370 million barrels at the end of 1983, or about 100 days of supply in the event of a complete embargo of imported oil to the United States. This paper presents a comprehensive coverage of the SPR program as it was in 1983. The following topics were discussed: (1) system description; (2) funding; (3) storage medium which covers selection, salt dome geology, cavern design; (4) storage and distribution of SPR crude oil which includes SPR crude oil specifications, SPR crude oil acquisition and inventory, sale and distribution of SPR oil; SPR readiness testing; and (5) technical issues which covers crude oil storage stability, environmental issues, site operations model, hazard study, and drawdown without pumps.

212. SATO, S. AND TAGAWA, K.; DOUBLE HULL TYPE OIL TANK SYSTEM WHOSE INNER TANK IS IMMERSED IN WATER. CAN 1,157,217, C 83.11.22, F 82.02.12, PR JAPAN 81.03.31 (APPL 48,092/81) (NIPON KOKAN KK), 1983.

A double hull type of oil tank system consists of an inner tank which is immersed in water. This eliminates vapor loss of stored oil and has fire, earthquake, and weather resistance. The oil tank system is constructed by fixing the peripheral wall of the inner tank (whose roof is fitted with an oil inlet-outlet pipe) to the bottom of an outer tank which is open at the top. The walls of the inner and outer tanks are connected by coupling members to provide a double-hull structure. A water pipe and water pump are connected to the lower portion of the outer tank and an overflow pipe is mounted on the upper portion of the outer tank. A port is drilled in the lower portion of the inner tank for communication between inner and outer tanks. The system is designed to store oil in the inner tank floating on water added from or returned to the outer tank.

213. PREECE, D. S. AND WAWERSIK, W. R.; SANDIA NATIONAL LABS. LEACHED SALT CAVERN DESIGN USING A FRACTURE CRITERION FOR ROCK SALT. 25TH NORTHWESTERN UNIV ET AL US ROCK MECH SYMP (EVANSTON, ILL, 84.06.25-27) PROC (ROCK MECHANICS IN PRODUCTIVITY AND PROTECTION) PP 556-565, 1984.

In 1975, Congress passed the Energy Conservation Act to establish a U.S. Strategic Petroleum Reserve (SPR) with a capacity of 750 million barrels of crude oil. The economic storage medium was determined to be salt caverns leached in salt domes in Louisiana and Texas. Salt caverns existed at several sites when the Reserve was created. These were obtained by the U.S. Department of Energy and were used to initiate SPR oil storage. To meet the storage capacity approved by Congress, new caverns also had to be leached. To support the resulting design effort, finite element computer programs were used to determine the creep closure and structural stability of salt caverns. Using site specific material properties, including creep models, elastic moduli and fracture data, the finite element analyses replaced earlier empirical approaches to cavern design. These numerical predictions indicated that cavern design was safe.

214. CALMINDER, A. AND SAGEFORS, I.; WP SYSTEM A/B. INNOVATIVE UNDERGROUND STORAGE FOR HEAVY CRUDES AND SENSITIVE PETROLEUM PRODUCTS. UNDERGROUND SPACE V 8, NO 1, PP 31-35, 1984.

Multi-tank underground oil storage can provide storage plants which are more versatile than previous designs for above ground and underground storage facilities. These plants can be constructed for the storage of numerous types of petroleum and petroleum products, even in the event of fundamental changes in storage conditions. The overall economics of vertical storage facilities will, in most cases, be more favorable than that of any storage alternative because of improvements in operation, particularly in operational safety.

215. PREECE, D. S. AND FOLEY, J. T.; SANDIA NATIONAL LABS. FINITE ELEMENT ANALYSIS OF SALT CAVERNS EMPLOYED IN THE STRAGEGIC PETROLEUM RESERVE. 6TH SALT INST ET AL SALT INT SYMP (TORONTO, CAN, 83.05.24-28) PROC V 2, PP 49-63, 1985.

A fine element computer program, developed previously to predict the creep response of bedded rock salt, has also been used to successfully predict the creep closure rates of several caverns using an approximation of the cavern geometry and material properties from the site. The caverns at Bryan Mound, Texas, have been analyzed with this program by approximating each with a two dimensional axisymmetric finite element mesh. Initial leaching and thermal effects were treated in an approximate manner. An element deletion technique was used to simulate the leaching that occurs when oil is withdrawn and replaced with fresh water. Each cavern was analyzed for 30 years and an indication of the long-term stability and volume change was obtained. This information will be used in the formulation of operating procedures for the cavern.

216. WOUCH, M. L. AND MARTINEZ, J. D.; TEXAS OIL & GAS CORP. SALT DOME PLUMES AND DISSOLUTION FEATURES : ARE THEY RELATED? 6TH SALT INST ET AL SALT INT SYMP (TORONTO, CAN, 83.05.24-28) PROC V 2, PP 159-175, 1985.

Salt domes, historically of interest in hydrocarbon production and salt mining, were later recognized for their value as reservoirs to store petroleum; for energy stored as compressed air; and possibly for hazardous wastes. One of the problems encountered when drilling into the salt stock, prior to the leaching of a cavity, is a loss of drilling fluids in the cavernous zones which overlie many salt domes. Of particular interest are cavernous zones at the salt-caprock interface where active dissolution of the salt by circulating ground water is most likely to occur. The salt-caprock interface zone may be characterized by a tight, a cavernous, or a sandy (granular anhydrite) contact. The condition of the salt-caprock interface not only affects solution mining of cavities where lost circulation hinders drilling operations prior to penetrating the salt, but also may have implications for the long-term hydrologic stability or degree of ongoing dissolution of the dome for consideration in planning storage projects. A positive correlation between dissolution features at the interface and the presence of saline plumes in surrounding aquifers could be useful in the prediction of drilling problems at the interface when planning salt dome utilization projects.

217. SULLIVAN, P. J. E., ONABOLU, O. A. AND KHOURY, G. A.; IMPERIAL COLL, LONDON. INTERACTION OF CRUDE OIL AND CONCRETE IN OFFSHORE OIL STORAGE TANKS. 4TH DELFT UNIV TECHNOL ET AL BEHAV OF OFFSHORE STRUCT (BOSS '85) INT CONF (DELFT, NETH, 85.07.01-05) PROC (ELSEVIER DEVELOP MAR TECHNOL SER VOL2) PP 881-888, 1985.

A research program was undertaken to study the effect of hot crude oil on concrete used in North Sea oil storage tanks. Early results suggested that the compressive strength of concrete soaked at ambient temperatures in crude oil of low acid content is less affected than suggested by previous investigations. However, a reduction in strength appears to take place with time if the concrete is soaked in the oil at elevated temperatures up to 80° C. A study of the effect of bacterial activity on the composition of the crude oil has, furthermore, shown that although the inorganic acid content of the crude oil is unlikely to increase, an increase in the organic acid content may take place.

218. MEETING PAPER TEXT.; 31ST ANNU. WEST VIRGINIA UNIV. APPALACHIAN UNDERGROUND CORROSION SHORT COURSE (MORGANTOWN, W. VA, MAY 1986) PROC. PP 3-288 WEST VIRGINIA UNIV, MORGANTOWN, (236 PP)., 1986.

This collection of papers presented at the Appalachian Underground Corrosion Short Course (Morgantown, WV, May 1986) gives information on various aspects of underground corrosion and corrosion control. Pipeline corrosion, underground storage facility corrosion, and corrosion potential were discussed.

Basic electrical and corrosion fundamentals were explained, and methods of corrosion prevention and resistance by means of anodes, coatings, and cathodic protection systems were discussed. Measurement and computation techniques were also discussed. Selected papers were listed at the back of Petroleum Abstracts, V 27, No 22, 5/30/87, as appendix A.

219. THRASHER, JOSEPH E. AND CHARLES S. DUNN. IN-GROUND CRUDE OIL STORAGE CONTAINERS. "FROM WHENCE IT CAME". 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

The authors provide a discussion of the management for the design and construction of large in-ground concrete storage tanks in the Republic of South Africa for the purpose of storing crude oil. Constructed in balanced excavations, these high-density polyethylene encased and gravel-covered concrete tanks provide most of the security of an underground storage cavern while being more like extremely large surface storage tanks operationally. Although quite secure, the tanks were built with provisions for rapid injection of fire-fighting foam under the tank roofs in the unlikely event a tank roof was ruptured and a fire ignited. The tanks were sited on a ridge which offered elevation above the surrounding terrain and insured that the bottom of each tank was several meters above the water table. Elevation is also an advantage when crude oil is being withdrawn. The tanks were more economical to construct for crude oil reserves than conventional steel surface tanks providing equivalent capacity.

220. POLISHOOK, B.; EFFECTS OF POLYMERIC COATING SYSTEMS FOR CONCRETE FUEL TANKS ON THE QUALITY OF JET FUEL. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Four commercial polymeric coating systems for concrete fuel tanks were tested for compatibility with jet fuel and for potential microbial growth. Two of the polymeric membranes had a deteriorative effect on jet fuel and were excluded from further consideration. Another membrane accelerated the growth of microorganisms and although this did not affect the chemical properties of the stored jet fuel it was considered wise to add a biocide to stored fuels in contact with this coating material.

221. GOVERNMENT REPORT.; ADDITIONAL GEOTECHNICAL STUDIES : STRATEGIC PETROLEUM RESERVE (SPR), WEEKS ISLAND, LOUISIANA. SANDIA NAT LAB REP NO SAND-86-7181 (DE87007360), 251 PP., DEC 1986.

Previous studies undertaken at the Weeks Island Strategic Petroleum Reserve site placed high risk potential on shaft leakage that could lead to shaft failure and ultimately to loss of the crude oil containment. As a result, a geotechnical investigation was undertaken to define the stratigraphy and hydrologic conditions around the shafts in an attempt to quantify the actual risk potential and to define various failure scenarios. It was concluded that an uncontrolled leak developing in the shafts could result in rapid flooding of the mine workings, with water flowing from the water courses surrounding the dome. The oil withdrawal system could be inoperable. Subsequent erosion/solutioning of the salt around the oil containment bulkheads could lead to the ultimate loss of oil. Alternative precautionary and remedial actions considered to reduce the risk of flooding and improve the stability of the shafts were recommended.

222. CHESNEAU, HOWARD L.; UPDATE ON FUEL TREATMENT PROGRAM FOR MIDDLE DISTILLATE LONG-TERM FUEL STORAGE AND STORAGE TANK CORROSION. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

This study was covered in a two-part presentation. In the first part microbial slimes appearing in gas turbine distillate fuel storage tanks were discussed. These tanks had a capacity of 180,000 barrels, so emptying and cleaning was virtually impossible. An additive program was initiated which used a fuel biocide and a fuel stability package. While the oil was sterilized quickly, the sludge material took up to a year before microbial activity ceased. Eventually, all of the tanks were emptied and cleaned. Thereafter all incoming fuel was treated with the biocide/stabilizer package. Only after water was removed from the tanks, incoming fuel was treated, and careful period monitoring was initiated, was the problem solved. The second part discussed legislation under Subtitle 1 of the RCRA which brings under Federal control underground storage tanks. Of an estimated two to three million tanks buried underground in the United States, surveys have established that over 100,000 of these tanks are already leaking. At least 10% of tank leaks are from the inside out and microbial corrosion is probably a large factor. Small tanks are usually a bigger problem than large tanks because of the inability to inspect the interior of the smaller tanks.

223. REINOSO, E. H., O. FLEISCHMACHER, S.M. DOVALLE, P. GUIAMET AND H.A. VIDELA. EFFECT OF MICROBIAL CONTAMINANTS ON THE CORROSION OF FUEL STORAGE TANKS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

The electrochemical behavior of SAE 1020 steel and 2024 aluminum alloy was studied to estimate the corrosion hazard in storage tanks due to the presence of microbial contaminants of kerosene type fuels. Microbial growth facilitates the corrosion process mainly through the accumulation of aggressive metabolites in the medium near the metal surface. The complex sequence of interactions that develop at the metal/aqueous environment interface has to be properly evaluated when corrosion protection and prevention is to be considered.

224. ROUW, HART C., VAN DER POEL, HENDRIK, BRAEKEN, JOZEF AND LABOFINA S.; ANTIFOULING AND ANTICORROSIVE COATING FOR UNDERWATER STRUCTURES. BRIT. UK PAT. APPL., 9 PP, GB 86-11623 13 MAY 1986, GB 2190380 A1 18 NOV 1987. .

Coatings, with good stability and flexibility, contain epoxy resins, curing agents, aromatic pitch or thermoplastic hydrocarbon resins, and mixtures of ZnO, triorgano tin salts, metal alkylenedithiocarbamates, and ≤ 7 vol.% Cu_2O or CuSCN. A mixture of Epikote-828, coal tar, Bu_3SnF, ZnO, Zn ethylenebisdithiocarbamate, Cu_2O, and bentone was thinned with xylene-$EtO(CH_2)_2OH$ mixture to give a paint with viscosity 12 and 14 P after 0 and 6 months, respectively, at 40°., that was mixed with 10% m-xylylenediamine, coated (150 mμ) on steel, and exposed to a marine environment in south Holland for 18 months. The panels remained free of barnacles and algae, vs. 100% coverage by algae after 2 months without Zn ethylenebisdithiocarbamate and Cu_2O.

225. PELLETIER, E. AND BROCHU, C.; PROTOTYPE, MESOSCALE SIMULATOR FOR THE STUDY OF OIL WEATHERING UNDER SEVERE CONDITIONS. CAN ENVIRON STUD RES FUNDS REP NO 086, 61 PP., NOV 1987.

A low-cost simulation tank was developed to study long term fate of crude oil under severe weather conditions and also in the presence of an ice cover. The prototype was an outdoor tank with the surface exposed to natural weather conditions. The tank contained seawater. The water column was protected from extreme temperature variations. Experimental features such as a conical bottom, sediment trap, deck, and a small instrument room were included. The report gave a technical description of the prototype and describes the results of three long term weathering experiments conducted in 1986 and 1987 using chemically dispersed crude oil. Stability of oil dispersions at near- or sub-zero temperatures, and the relative role of evaporation and biodegradation in weathering of surface emulsions and water column oil were also studied.

226. GILES, HARRY N., PAUL W. WOODWARD, JOHANNA SHAY AND REX A. NEIHOF. BIOGEOCHEMICAL STUDIES OF CRUDE OIL STORED IN THE UNITED STATES' STRATEGIC PETROLEUM RESERVE. 194TH NATIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY, GEOCHEMISTRY DIVISION PROGRAM, NEW ORLEANS, LA, 1987.

Samples periodically collected from the caverns in which the OSPR stores crude oil reserves undergo a detailed analysis that includes whole crude properties, characterization of distillate and residual fractions, trace element analysis, stable isotope ratio, and microbiological studies. No deleterious changes in quality have been observed in crude oil stored for as long as nine years.

227. VORSTER, O. C.; COATING SYSTEMS FOR THE INTERNAL LINING OF METHANOL AND METHANOL-CONTAINING FUEL STORAGE TANKS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Desirable properties in coating systems for concrete and steel tanks used to store petroleum fuels, methanol and blends were studied. Results of tests on a series of coatings based upon different binders and on a three-coat system combining desirable properties were reported. The authors concluded that coating systems do exist that can be used to coat the insides of steel and concrete storage tanks that are to be used for the storage of petroleum, diesel fuel, jet fuel and crude methanol. Steel and concrete tanks require different coating systems.

228. HANKS D. C.; WATER MANAGE. CHEM. LTD. CORROSION IN FUEL STORAGE TANKS. PET. REV. (ISSN 0020-3076) V42 N.493 38-39 (FEB. 1988).

Corrosion in storage tanks containing fuels such as crude oils, kerosine, gas oils, and motor spirit is caused by water in the fuel, water which collects in the tank bottom during tank sweating, water injection during pipeline repairs, water in barge or sea fed depots, and rain water entering the tank. The water supports the bacterial and fungal growth responsible for fuel fouling, fuel degradation, and storage tank corrosion. Periodic tank draining, good housekeeping procedures, and tank coating to prevent the buildup of water; the mechanism of corrosion by sulfate-reducing bacteria (SBR); identification of bacterial contamination; and elimination of SBR by the addition of biocides are required.

229. DUNCAN, K. J.; INGROUND CONCRETE TANKS FOR STORAGE OF PETROLEUM PRODUCTS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Advantages of concrete storage tanks constructed in the ground for the storage of crude oil and refined products are outlined. The chief benefits to be gained are a reduction in contact with air, evaporation losses, and greater security against accidents, fire and explosions.

230. NEAL, J.; SANDIA NATIONAL LABS. SUBSIDENCE MONITORING AND EVALUATION PLAN FOR STRATEGIC PETROLEUM RESERVE STORAGE SITES. SANDIA NAT LAB REP NO SAND-88-1175 (DE89001059)AUG 1988 (1 MICROFICHE WITH 36 PP; 30 REFS)K, 1988.

Subsidence is occurring at all six Strategic Petroleum Reserve (SPR) sites. It results from a combination of cavern closure, Frasch-process sulfur extraction, fluid withdrawal, and natural causes. Cavern closure resulting from salt creep is the predominant source. A subsidence monitoring program is recommended that includes continuation of annual releveling; quadrennial determination of horizontal drift; triennial measurement of gravity values to determine elevation change and to validate releveling data; air photos quadrennially; coordination of other subsidence monitoring efforts, especially those involving regional subsidence; continuation of cavern creep modeling; engineering evaluation of observed and predicted subsidence effects; and information dissemination in the form of an annual review and report. A priority sequence (by location) is suggested that considers observed subsidence and operational factors such as oil inventories and risk appraisal.

231. JOHNSON, S. D.; COOK PAINT & VARNISH CO. FRP (FIBERGLASS REINFORCED PLASTIC) LININGS FOR TANK BOTTOM REPAIR. MATER PERFORMANCE V 27, NO 8, PP 32-34, AUG 1988.

Fiberglass-reinforced plastic linings were developed in response to the need for protection against leakage from corrosion pits on the flat bottoms of large petroleum storage tanks. These tanks hold crude oil, gasoline, diesel fuel, and other refined petroleum products. Tank bottoms usually exhibit more severe corrosion than tank shells or the undersides of floating roofs or fixed cone roofs. The corrosion potential of the tank bottom, combined with the relative difficulty of detecting leaks in the bottom vs the shell, dictate the use of a thick section-reinforced lining. High film thickness minimizes the chances of pinhole formation in the lining, while fiberglass reinforcement provides assurance against leakage by bridging small holes and providing structural support in the event of soil side perforation. A fiberglass reinforced plastic lining normally spans the entire bottom and extends about two feet up the shell. Thin film coatings are then used to coat the remaining internal surfaces. The installed cost of such a plastic bottom is substantially lower than that of a new steel bottom.

232. CATHODIC PROTECTION CO LTD.; PROTECT AGAINST (FUEL OIL TANK) CORROSION. ANTI-CORROS. METHODS MATER. V35 N.9 11 (SEPT. 1988).

Corrosion control systems similar to Cathodic Protection Co. Ltd.'s system used on a sewage tank can be used to protect buried fuel tanks. In the sewage tank application, the tank was flushed out with fresh water. After drying, the corrosion scale was removed by hand from the tank's inside before shot blasting.

Plasgard 570, a polyamide cured coal tar epoxy coating, was applied by hand to the tank's inside surfaces and was allowed to dry. Internally installed anodes were lowered to within 1 in. of the tank bottom. Current flows from these anodes into the sewage and then into any possible coating deterioration areas on the tank walls to prevent corrosion. The number and position of the anodes for the internal and external surfaces were designed to distribute current evenly to the whole tank surface. At the World Trade Centre in Kaula Lumpur, buried LNG tanks have been protected using Maflowrap 50/150 wrapping tapes and a strip anode sacrificial cathodic protection system.

233. SIGMA COATINGS.; BALLAST TANK PROTECTION. SHIPCARE MARIT. MANAGE. (ISSN 0263-7944) V20 N.4 17 (JUNE-JULY 1988).

Sigma Coatings developed its Sigmacover because of the premature failure of coatings in ballast tanks and similar environments. The product is maintenance-free and provides long-term protection to ballast tanks and related structures of gas carriers and specialized tankers for up to 15 years. It provides high build coverage of edges, seams, and other critical points. It also exhibits exceptional non-aging characteristics and, with its inherent flexibility, provides excellent resistance to mechanical damage and fatigue during its life. Additional features include its solvent-free design which is beneficial in confined spaces associated with ballast tanks, making it useful as a refurbishing system as well as for new buildings. The product resists abrasion and mild pollutants, particularly when ballast water is taken on board in non-tidal, shallow, and industrialized areas. The product is compatible with cathodic protection systems. Sigmacover is suitable for arctic and tropic climates, and for the internal temperature variations in vessels such as LPG carriers and chemical tankers carrying cooled or heated cargoes.

234. MABLEY, P. B. AND G. M. WALLACE. DISTILLATE FUEL STABILISATION IN A MAJOR EUROPEAN REFINERY. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

The use of an additive package (composition not specified) to optimize refinery economics in the production of distillate fuel was described. The additive reduced color degradation and insoluble formation in blends containing LCO and visbroken gas oil. the resultant levels were comparable to, or better than, hydrotreated distillate.

235. U S NATIONAL BUREAU OF STANDARDS; ASHLAND PETROLEUM CO. STEEL OIL STORAGE TANKS SHOULD BE REEVALUATED, NEW NBS ((U.S. NATIONAL BUREAU OF STANDARDS)) STUDY NOTES. HYDROCARBON PROCESS. (ISSN 0018-8190) V67 N.8 17-18 (AUG. 1988).

A new NBS study notes that steel oil storage tanks should be reevaluated. In its investigation of the rupture of the Ashland Petroleum Co. steel storage tank which spilled approximately one million gallons of oil into the Monogahela River in January 1988, the NBS concluded that the shell steel did not meet recognized current standards for fracture toughness; that the quality of the welds did not meet current standards but did not contribute to the brittle fracture that began as a 0.75 in. flaw in the tank shell; and that welding adjacent to the flaw embrittled the metal surrounding the flaw and made the brittle fracture more likely. Foundation instability or excessive settlement which might have increased stresses in the tank shell were not evident. The NBS recommended review of standards to identify those with provisions for sufficient fracture toughness to prevent catastrophic brittle fracture at design stresses and temperatures; compliance, with such provisions, of steel for new or reconstructed tanks; documentation of tanks to prove adequate fracture toughness; conversion (to higher-temperature use), retirement, or reinforcement (with crack arrestors) of tanks with inadequate fracture toughness; and standard tests of the fracture safety of steel in tanks lacking adequate documentation.

236. GRASSO, P., MAHTAB, A., PELIZZA, S., PEREGO, P. AND VITALI, G.; GEODATA; INTECH; SNAM. OPTIMIZATION OF FEASIBILITY DESIGN OF LARGE, NEAR-SURFACE LNG STORAGE CAVERNS IN WEAK ROCK. NORWEGIAN INST TECHNOL ET AL STORAGE OF GASES INROCK CAVERNS INT CONF (TRONDHEIM, NORW, 89.06.26-28)PROC PP 251-258, (ISBN 90-6191-896-0; 3 REFS), 1989.

This work discusses the geomechanical feasibility of underground storage of liquefied natural gas (LNG) near Portoveriere along the Ligurian Coast of Italy. The problem of underground storage is complicated by the need to locate the caverns near the coast and at shallow depth. A feasibility study was made for subsurface storage of about 240,000 cubic meters of low-pressure LNG. This work describes the optimization of the storage caverns with specific reference to the size and location of the caverns, potential failure of rock having a range of geomechanical characteristics, and the rock stabilizing options which include the concepts of effective cohesion of reinforced rock. Sensitivity analyses for the optimization were performed using numeric method of analysis for stresses and formations around the caverns.

237. BEREST, P.; ECOLE POLYTECHNIQUE. ACCIDENTS OF UNDERGROUND OIL AND GAS STORAGES - CASE HISTORIES AND PREVENTION. NORWEGIAN INST TECHNOL ET AL STORAGE OF GASES INROCK CAVERNS INT CONF (TRONDHEIM, NORW, 89.06.26-28)PROC PP 289-301, (ISBN 90-6191-896-0; 17 REFS), 1989.

There are only two basic ways of storing large quantities of hydrocarbons: (1) underground storage, and (2) steel and concrete tank farms at the ground surface. All types of underground storage have several advantages in terms of safety and environmental impact. The hydrocarbons are separated from the oxygen in the air necessary for combustion by several hundred meters of in situ ground. This same natural barrier protects them from fire, willful damage, aircraft impact, and other such accidents that may occur at the ground surface. High storage pressures present no problem insofar as such high pressures are the natural state of the fluids underground. Underground storage is extremely economical on land area. The description of several accidents in underground storage facilities reveals some basic safety problems that must be considered. Mechanical stability, gas and oil tightness, and eruption hazards are considered, and acceptable loss level must be factored in.

238. POPOVIC, R., AVDAGIC, M., HADZIHRUSTIC, I., KLECEK, Z., JOVANOVIC, P. AND GORJACKOVSKI, O. POSSIBILITY OF GAS AND OIL STORAGE IN YOUNGER MIOCENE SALT DEPOSITS. NORWEGIAN INST TECHNOL ET AL STORAGE OF GASES INROCK CAVERNS INT CONF (TRONDHEIM, NORW, 89.06.26-28)PROC PP 137-142, (ISBN 90-6191-896-0; 2 REFS), 1989.

Considerable improvement was made in the last 30 years in leaching underground cavities in salt rock for oil and gas storage. The new method of salt leaching by boreholes from the surface, as well as safety, economic and ecologic reasons have justified the use of underground cavities for gas and oil storage. In this work a comparative analysis of underground storage capacity in salt massif is presented. Salt rock deposit Tetima offers a possibility of storing 424 x 10^3 cubic meters of gas in the Tuzla area.

239. MEBON PAINTS LTD.; COST-EFFECTIVE, HIGH-PERFORMANCE COATINGS FOR TANK SHELLS. ANTI-CORROS. METHODS MATER. V36 N.6 18 (JUNE 1989).

Cost-effective, high-performance coatings for tank shells and other structures in the petroleum, petrochemical, and process industries have been introduced by Mebon Paints Ltd. The Mebopro coating system can be applied successfully over manually cleaned steel contaminated with sand, rust, moisture, and well-adhered aged coatings. The system is chemically inert, tough, and adherent when applied in one 100 mμ brushcoat. Unlike air-drying coatings, Mebopro does not embrittle with age. The system consists of a primer called Meboprime topcoated with Mebopro, which contains micaceous iron oxide (a lamellar pigment) which forms a plate-like barrier with Mebopro and significantly retards ingress of moisture. Mebopro Colourcoat, a high-sheen architectural finish, is then applied for cosmetic appearance. The Mebopro system is particularly beneficial on the outside shells of, e.g., storage tanks and gasholders. The Mebopro system was recently used to renovate an aging tank in terms of corrosion protection and appearance without prior blast-cleaning; the life-expectancy of the coating system in this case is >10 years.

240. DEAN, S. W.; AIR PROD. CHEM. INC. ASSURING PLANT RELIABILITY THROUGH OPTIMUM MATERIALS SELECTION (AND EQUIPMENT MAINTENANCE). CHEM. ENG. PROG. V85 N.6 36-41 (JUNE 1989).

A discussion covers examples of recent major equipment failures in U.S. processing plants, including failure of a large carbon steel storage tank, which led to a spill >1 million gallons of No. 2 fuel oil and a crack, due to hydrogen embrittlement, in an acid gas scrubbing unit, which caused fire and explosion with loss of life. National Bureau of Standard statistics show that material failures due to corrosion caused a loss of .approximately $143 billion (4.2% of Gross National Product) in 1982, including $21 billion in preventable losses. A survey of 35 U.S. industrial chemical and synthetic materials manufacturers, showed that in 1987, these companies spent an average of 5.4% of plant investment on maintenance, accounting for 20-40% of controllable manufacturing costs. The study includes an examination of possible ways to reduce maintenance costs while minimizing material failures by improving equipment design and materials selection, operating procedures, equipment maintenance, and training of operating and maintenance personnel; and some recommendations for avoiding material failure problems.

241. LAPP, K. AND ROUSSAKIS, N.; WESTECH IND. LTD. SAFEGUARDS CUT TANK EXPLOSION RISK DURING GAS FLARING. 4TH CAN. GAS PROCESS. ASSOC. Q. MEET. (CALGARY 11/18/88) (ADAPT.) OIL GAS J. V87 N.33 41-44 (8/14/89).

A discussion of some operational and system safeguards that can significantly reduce the risk of oil-storage tank explosions in gas-flaring operations, based on ten different explosion investigations by Westech Industrial Ltd., covers Alberta's flaring requirements, particularly those concerning sour gas; various ways of air entry into the tank, including new and previously unused tanks; flame-arrester failures, including those involving the flare stack as the most common ignition source in tank explosions; certification and testing of flame arresters; failure characteristics of flame arresters, including such problems as elements constructed with loose-fitting mandrels and damage caused to an element while in use or being serviced; tank purging or air elimination as an important explosion preventive measure that can be carried out with natural gas or propane, or with inert gases such as CO2 or nitrogen; completion of a purge, requiring the use of a flow-metering device to accurately indicate the purge gas' flow rate; and protection against other ignition sources such as static electricity and oxidation of ferric sulfide coating.

242. BARRETT, A. E.; COLONIAL PIPELINE CO. INSTALLATION OF GEODESIC DOME ROOFS ON PETROLEUM PRODUCT TANKS. API PIPELINE CONF (DALLAS, 89.04.17-18) PROCPP 167-177, 1989.

A pipeline company has established an ongoing program for using geodesic dome roofs on tanks in liquid petroleum product service as its standard. The company adopted geodesic dome roofs, in conjunction with internal floating decks, to replace worn, external floating roofs on existing tanks storing gasoline and for use on new tanks in all type of product service.

243. WIT, J. DE; BRITTLE FRACTURE OF OLD STORAGE TANKS CAN BE PREVENTED. OIL & GAS JOURNAL V88 N.8 40-44 (2/19/90).

A discussion of brittle fracture leading to catastrophic spills of hydrocarbon materials from older storage tanks covers some preventive measures including tank insulation, not filling the tank to maximum level during lowest temperatures, fully water-testing the tank, repairing serious corrosion, releveling the tank, and avoiding shock loads on the tank shell. The study included an examination and comparison of four tanks containing crude oil, gas oil, fuel oil, and diesel fuel that failed due to embrittlement; causes of brittle fracture including tank shell's minimum design metal temperature, shell plate material's notch toughness, plate thickness, presence of crack-like defects, acting tensile stress on tank shell, and water test's overloading effect; effect of waxy fuel oil in one of the four tanks on tank failure; lower weld quality at the time of construction of older tanks compared with that of today's tanks; and suggestions for old tanks based on experience gained from the four failed tanks.

244. WILSON, F. D.; WIL-COR INC. THE RIGHT MATERIAL FOR THE RIGHT JOB. MATER PERFORMANCE V 29, NO 2, PP 32-35, FEB 1990.

The petroleum industry, while producing the raw materials that go into manufacturing thermoset Epoxy and Polyester resins, have created corrosion problems that are solved with the Epoxy and Polyester resins. The oil industry has always been aggressive testing and using materials that solve corrosion, structural, and safety problems. Without the willingness of the industry personnel to try different materials and use educated gambles, the coatings and linings industry would be 20 years behind. The RCRA legislations has the full attention of the industry. No products shall contaminate the soil. Secondary containment is now as important as primary containment was prior to RCRA. The industry was satisfied with concrete containment and asphalt expansion joints to contain spills. There has been a tremendous increase in the use of secondary containment coatings using Epoxies and Polyesters to protect the environment.

HANDLING AND STORAGE

Barbee and others (245), in 1986 published methods for evaluation of jet fuel cleanliness. Debris such as metal flakes, rust, fibers, and dirt are often encountered in JP-4 jet fuel and probably is introduced by debonding or delamination of the contaminant from handling, storage, and transportation equipment.

McVea and others (246) tested seven different filter media for their capacity to remove organic particulate, AC fine test dust, microbiological matter, water and combinations from fuels.

Dekel (247) also measured the contamination of fuel samples and filters taken from 20 aircraft stationed in regular and desert environments. Organic materials derived from the aircraft system were found to be major contributors to contamination together with siliceous materials from the environment.

Giles and co-workers (248) analyzed sludges, crude oils and brines collected from three crude oil storage caverns using a number of techniques. Sludges contained water and waxes formed a major component of the sludges. Paraffins up to n-C_{72} were identified. Viable anaerobic and aerobic bacteria were found in the sludges but no evidence for active microbiological degradation of the oil was found.

Westbrook and Stavinoha (250) have defined a set of guidelines which should enable users to avoid equipment malfunction caused by poor fuel quality or contamination. Topics covered include fuel system monitoring and cleaning. Sampling and specific practical recommendations were made.

HANDLING AND STORAGE CITATIONS

245. BARBEE, J. G., R. S. MCINNIS, K. B. KOHL AND L. L. STAVINOHA. ENHANCED METHODOLOGY FOR JET FUEL CLEAN AND BRIGHT EVALUATIONS. 2ND INTERNATIONAL CONFERENCE ON STORAGE STABILITIES OF LIQUID FUELS, SAN ANTONIO, TEXAS, USA. JULY 29 - AUGUST 1, 1986.

Debris encountered in JP-4 jet fuel included metal flakes, rust, fibers, dirt, etc. The flake-like organic debris was probably a man-made component and not a fuel product. It had a high melting point and was insoluble in most common solvents. The most likely source was an unpigmented paint or protective coating from one of the epoxy families. It could be introduced by debonding or delamination of the contaminant from any handling, storage, or transportation equipment containing that coating.

246. MCVEA, G. G., M. E. MEDWELL, A. J. POWER AND R. K. SOLLY. FUEL FILTRATION CHARACTERISTICS OF VEHICLE FILTER MEDIA. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Fuel samples containing naturally-produced organic particulate, AC fine test dust, microbiological matter, water and combinations of these were passed through seven different filter media and the rapidity of blockage measured. Many effects which run contrary to initial expectations were reported. For example vehicle filters blocked less rapidly than 2 µm glass fiber medium when charged with organic particulate but more rapidly when challenged with AC test dust. In several cases combinations of two types of contaminant had a greater blocking effect than simple summation would predict. It is concluded that many of the effects can be explained if the loosely agglomerated nature of organic particulates is borne in mind.

247. DEKEL, R.; PARTICULATE CONTAMINATION OF JET FUEL SYSTEMS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Fuel samples and filters were taken from 20 aircraft of two types stationed in regular and desert environments for examination. Contamination of the fuel samples was measured by filtration followed by gravimetric and visual assessment of the filters. The nature of particulate contamination on these filters and fuel filters taken from the aircraft was determined by FTIR and X-ray spectroscopy. Selected results from the whole study were presented in the form of summary tables. Organic materials derived from the aircraft system were found to be major contributors to the contamination together with siliceous materials from the environment. No correlation was found between visual and gravimetric assessment of filters. Significant increases in particulate contamination were observed after structural work on aircraft in spite of tank flushing.

248. GILES. H. N., P. W. WOODWARD AND R. A. NEIHOF. BIOGEOCHEMISTRY OF SLUDGE THAT FORMS IN SALT DOME CAVERNS USED FOR STRATEGIC STORAGE OF CRUDE OIL. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Sludges, crude oils and brines collected from three crude oil storage caverns near Freeport, Texas were analyzed using a wide variety of techniques. The sludges contained 5-40% water, some of which was in the form of a very tight emulsion which could not be broken by ultracentrifugation. Waxes formed a major component of the sludges and paraffins up to n-C_{72} were identified. The waxes were also found to contain isoparaffins, cycloparaffins and long alkyl chain substituted benzenes. Viable anaerobic and aerobic bacteria were found in the sludges but no evidence for active microbiological degradation of the oil was found. Stable isotopic ratio analysis of methane distilled from the samples indicated a thermogenic, rather than biogenic, origin.

249. BOCARD, C., G. ASTAING AND C. BERNASCONI. WATER SENSITIVITY OF DIESEL FUELS: EFFECTS OF COMPOSITION AND AGEING. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

Water was introduced into a number of straight-run/cracked diesel fuel blends, both by mechanical mixing and solution/condensation. The filterability of the water-containing fuels was reported and discussed. The effect aging at 43° C in contact with water was also studied. The fuel/water interfacial tensions, extents of emulsification in a standard test, water contents and filterabilities of the fuels as a function of aging time were reported. Various effects of the presence of water were found for the different fuels and these were presented.

250. WESTBROOK, S. R. AND L. L. STAVINOHA. USER GUIDELINES FOR DIESEL FUEL HANDLING AND STORAGE. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

This paper lays out a set of guidelines which if followed should enable users to avoid equipment malfunctions caused by poor fuel quality or contamination. Topics covered include fuel system monitoring and cleaning, sampling, user-defined fuel specifications, acceptance criteria and the use of additives. Each topic was dealt with in detail and specific practical recommendations were made.

251. BEN-ASHER, J., N. POR AND A. B. SHAVIT. ADDITIVE RESPONSE AND THE EFFECT OF THE CHEMICAL COMPOSITION ON STORAGE STABILITY OF DIESEL FUELS. 3RD INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS, LONDON, 13-16 SEPTEMBER, 1988.

The storage stability properties of five gas oil types, two of which contained catalytically-cracked gas oil, were studied after periods of ambient storage ranging up to 45 weeks. The storage properties were measured using ASTM D 2274, UV irradiation, the DuPont 150° C test and the Bureau of Mines Rapid Over Test at 110° C. The effects of two additives qualified to MIL-S-53021 are also reported. The results were discussed with reference to degradation mechanisms involving peroxy radical formation and free radical polymerization. It was concluded that the rapid over test at 110° C is applicable to the evaluation of diesel fuel stability and breakdown mechanisms. It was also proposed that a linear combination of oxygen consumption, soluble gums, and insolubles with appropriate weighting factors to form a 'stability index' may be a useful approach to interpretations.

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