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3rd International Conference on

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CONFERENCE PROCEEDINGS

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FOREWORD

The 3rd International Conference on Stability and Handling of Liquid Fuels followed two previous Conferences held in Tel Aviv, Israel (1983) and San Antonio, Texas, USA (1986). It was held in the Cavendish Conference Centre, London from the 13th to the 16th September 1988. The Conference was hosted by the Institute of Petroleum on behalf of the International Association for Stability and Handling of Liquid Fuels. The Conference was fully subscribed (more than 200 delegates) for all sessions. Financial support was provided by the US Departments of Defense and Energy, and the proceedings have been printed at the Royal Aerospace Establishment, UK.

56 papers presented at the Conference dealt with the storage and thermal stability of gasolines, jet fuels, diesel fuels, residual fuels and crude oils. Certain aspects of the handling of these materials were also considered, and a session was devoted to the problems of microbiological growth in liquid fuels. The largest group of papers was those associated with the stability of diesel fuels, closely followed by those dealing with jet fuels. Both subjects are highly complex and have been researched extensively over the last 30 years, but it is I think fair to state that significant advances were reported at the Conference. Examples are the oxygen overpressure technique for diesel fuel stability prediction and the fiber optic JFTOT modification. In addition to the verbal presentations 7 posters were displayed throughout the Conference and are represented in these proceedings by full written papers.

As in the previous conferences there were major contributions from the defence establishments of several nations, reflecting the military importance of high fuel quality after extended storage. It was encouraging to note, however, that commercial organisations were well represented both in papers and attendees.

For the written papers authors were invited to submit a maximum of 15 sides of print-ready copy, but observant readers may note that several authors exceeded this limit. The editors have been tolerant and not applied cuts, but this should not be taken as a precedent for the proceedings of future conferences.

As an aid to those seeking information on specific topics, 'Briefs' have been prepared for all the papers except the Plenary Lecture and are placed together ahead of the papers. The briefs are intended to be complementary to the author's own abstracts, where provided, and try to give specific indications of the work included in the paper. I am personally responsible for these briefs and apologise to any author who considers the brief of their paper to be inaccurate.

The Conference would not have been possible had the Institute of Petroleum not undertaken the onerous task of hosting. This was carried out with supreme efficiency by a small team led by Caroline Little and I thank them on behalf of the International Association for Stability and Handling of Liquid Fuels.

Financial support for the Conference was provided by the US Air Force European Office of Aerospace Research & Development, the US Army European Research Office (London) and the US Department of Energy. This is gratefully acknowledged.

I must personally thank the Royal Aerospace Establishment for permitting me to undertake the job of Conference Chairman, and for the support provided to me in this task by the UK Organising Committee.

Robin Hiley
Chairman of Organising Committee

BP Research Centre, Sunbury, UK
7 December 1988

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BRIEFS

Session 1. Stability of residual fuels

Residual fuel oil stability and compatibility studies [14]

N Por, R Brauch, N Brodsky, R Diamant

Following a study of the stability of residual fuel oils blended from visbroken and vacuum residues the authors conclude that asphaltene peptisation state values and hot filtration test results provide the best estimates of stability and compatibility. Residue from a visbreaker operating at milder conditions and equipped with a soaker yielded more stable fuel oils than those from a simple visbreaker operated under more severe conditions.

Prediction of storage stability and compatibility of residual fuel oils [21]

W C Rovesti, R P Anderson

A series of rapid stability/compatibility tests including Bureau of Mines Correlation Index (BMCI), Toluene Equivalence (TE) and hot filtration were evaluated. All could be performed to an acceptable degree of reproducibility in electric utility laboratories. The parameter BMCI-TE was found to give a valuable indication of stability reserve, values below 10 indicating potential problems. Reproducibility of the TE measurement requires improvement, and a less time-consuming procedure is desirable.

Coating systems for the internal lining of methanol and methanol-containing fuel storage tanks [73]

O C Vorster

The author outlines the properties desirable in coating systems for concrete and steel tanks used to store petroleum fuels, methanol and blends. Results of tests on a series of coatings based upon different binders and on a three-coat system combining desirable properties are reported. It is concluded that the three-coat system should give satisfactory performance in all respects.

Effects of storage on the stability of residual fuel oil [39]

C P G Lewis, F De Jonge

The stability of three residual fuels during storage in 20m^3 tanks, 50l drums and laboratory glassware (300ml) is discussed. Significant increases in viscosity and asphaltenes content were observed for fuels stored in the laboratory at 75°C, but the effects were less for drum storage at the same temperature. Results are discussed in terms of the ratio of flocculating tendency of the asphaltenes to the peptising power of the maltene phase. A beneficial effect from a dispersant additive is reported.

The influence of lubricating oils on the colloidal stability reserve of residual fuel oils [59]

W Pogonowska-Fabriek, P Holbrook

The stability reserve of some 20 fuel oil/lubricating oil blends is 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 fuels even at low concentrations. ^{13}C NMR aromaticity measurements on the fuels and lubricating oils are also reported, and the authors suggest that these may serve as a tool to assist in the prediction of residual fuel oil stability reserve.

Quality of fuels formed by severe hydrotreatment of vacuum residues [34]

T Hara, K Yanagida, A Okano

Infra-red spectrometry of dilute carbon disulphide solutions of vacuum residues is used to study heteroatom functionalities, particularly the distribution of acidic OH and NH groups. Severe hydrotreatment of petroleum vacuum residue in the presence of hydrodesulphurisation catalyst produced a dry sludge which was found to be mainly wax.

Session 2. Microbiological growth in fuels

Biodegradation of stored heavy fuel oil with production of methane in unlined rock caverns [8]

R Roffey, A Edlund

The production of methane by microorganisms during storage of heavy fuel oil on a waterbed in unlined rock caverns is described. Of four methods to inhibit the methanogenic bacteria investigated - aeration, increase of pH, addition of nitrate, isothiazoline biocide - addition of nitrate at 0.5g/l to the water phase was found to be most successful.

Studies on a U.S. military approved fuel preservative and stabiliser [23]

F T Klein

The characteristics and efficacy of a nitroalkyl morpholines biocide, approved as the biocidal component required by US specification MIL-S-53021, are reported and discussed.

A survey of the microbial contamination level of some Finnish fuel storage systems [24]

P Carlson, S Niemelä, E Tenhunen

Biannual sampling of jet fuels and light heating oils in rock caverns and steel tanks revealed generally sparse microbial growth in the jet fuels. In the rock caverns the constant low temperature tended to select an aerobic flora consisting predominantly of cold-tolerant gram-negative rods. Many of the bacteria were pseudomonads, which are especially difficult to eradicate with biocides. Low concentrations of C_2-C_{19} saturated aliphatic carboxylic acids found in water bottoms were not thought to be of microbiological origin.

The use of BNPD to control microbial growth in diesel fuel systems [48]

R Elsmore, W G Guthrie

The compound 2-bromo-2-nitropropane-1,3-diol (BNPD), already widely used as an antimicrobial in pharmaceuticals, cosmetics, etc, was assessed for possible application as a fuel biocide. The compound dissolved into distillate fuels in the presence of a cosolvent such as methoxyethanol, but partitioned strongly into the aqueous phase. Biocidal activity against fungi, aerobic and sulphate-reducing bacteria in fuel/water systems was quantified.

A biological monitoring and control strategy for large diesel fuel storage facilities [49]

M P Reynders, P Stegmann

19 bacterial and 4 fungal species isolated from fuel tank bottoms and blocked fuel filters were identified as primary hydrocarbon utilisers. The effectiveness of biocides (coded) against these organisms was evaluated and 4 of the 7 tested proved superior. Two water-soluble biocides were selected for use and their dose rate calculated on the basis of the tank water-bottom present, not the total volume of fuel. It was confirmed that the most effective biocide had no deleterious effects upon the fuel nor encouraged tank corrosion.

Microbiological test methods for fuels in the laboratory and on site [5]

E C Hill, G C Hill, D A Robbins

The various methods of test for microbiological contamination in aqueous and fuel phases, both in the laboratory and on-site, are discussed and many potential pitfalls pointed out. In particular the need is emphasised to neutralise any biocide present in the sample before growth assay techniques are employed. Methods of extraction of microorganisms from the fuel phase into water are discussed and a novel strategy involving the use of flocculant is described.

Biocides for microbiological contamination control in naval distillate fuel [56]

R M Morchat, A J Hebda, G M Jones, R G Brown

The efficacy of 5 biocide types - benzimidazoles, pyridinethiol-1-oxides, dioxaborinanes, morpholines, isothiazolones - against cultures of *Cladosporium resinae*, *Yarrowia lipolytica* and *Pseudomonas aeruginosa* in diesel fuel/water systems was assessed. Growth was estimated as the weight of cellular soluble protein measured using a spectrophotometric method. Only two biocide types, the pyridinethiol-1-oxide and isothiazolones, showed good efficacy against all three species, but the isothiazolones were ineffective against a mixed culture.

Evaluation and comparison of microbial growth in distillate fuels [57]

P J Miller-David, G G Pipenger

The results are reported of a large-scale (293 samples) survey of microbiological contamination, principally in diesel fuel storage tanks belonging to end-users. The extent of contamination of the mainly bottom samples was assessed visually, then quantified by plating on SMA. Organisms were subsequently isolated and identified. Gram negative and positive bacteria, molds and yeasts were found, the most populous organisms in each group being *Corynebacterium*, *Pseudomonas*, *Monosporium* and *Candida* respectively.

Session 3. Jet fuel stability

Nuclear magnetic resonance techniques for predicting thermal stability of jet and diesel fuel [3]

J A Russell, B K Bailey, J P Buckingham

The correlation between distillate fuel thermal stability, as assessed by JFTOT breakpoint, and structural parameters derived from NMR measurements is investigated. An attempted correlation for a set of 27 fuels having breakpoints in the range 375-725°F yielded a coefficient of determination of only 0.7034. Dividing the fuels into 3 subsets yielded better correlations, particularly for the very stable subset. The structural factor exerting the greatest influence was found to be total aromatic protons. Results are also 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.

Old and new ways of using the JFTOT for aviation fuel stability research [41]

G Datschefski

The use of the JFTOT in research is contrasted with its principle function as a specification tool. Examples of its research use taken from the literature are discussed and drawbacks of the standard method for research purposes stated, notably the effect of heater tube metallurgy and deficiencies in the tube deposit rater. Modifications to the apparatus and method which enhance its value as a research tool are considered, particularly the several novel methods of heater tube rating which are currently being evaluated. Methods of breakpoint estimation from single test results are discussed.

Comparison of JFTOT heater tube deposit rating methods for the evaluation of fuel thermal stability [7]

R E Morris, R N Hazlett, C Linden McIlvaine

Quantitative methods for the measurement of JFTOT heater tube deposits using carbon combustion, dielectric breakdown and optical interferometry are assessed and intercompared. A good correlation between total deposit volume given by the latter two techniques and carbon mass given by the first technique is demonstrated for deposits ranging from 50-900μg total carbon. The dielectric breakdown method became imprecise for very thin deposits, whilst the interferometric method was constrained for thin coatings by the wavelength of light employed and for thick coatings by light absorption in the coating.

Thermal stability measurements using the fiber optic modified jet fuel thermal oxidation tester [36]

R A Kamin, C J Novack, S Darrah

Details are given of modifications to the JFTOT which permit in-situ measurement of heater tube deposit thickness by optical interferometry. 8 fiber optic probes are attached in a helical pattern around a modified tube holder and yield data continuously during a test. A modified tuberator (TDR) employing a single probe is also described. Raw data from the probes show a series of of maxima and minima corresponding to constructive and destructive interference, from which successive increments of 0.14micron film thickness may be counted. Results for 6 fuels tested over a temperature range of 204-316°C are presented in the form of Arrhenius plots.

The role of alkylperoxy and alkyl radicals in fuel deposit and gum formation [32]

K T Reddy, N P Cernansky, R S Cohen

Fuel degradation mechanisms are hypothesised based upon the quantification and identification of soluble degradation products. The mechanisms propose that at temperatures below 300°C alkylperoxy radical reactions are most important, whilst between 300-400°C alkyl radical reactions become predominant. Data for the production of C5-C10 alkanes, alkenes, aldehydes, tetrahydrofurans, dodecanol and dodecanone from dodecane stressed in a modified JFTOT apparatus are presented.

Influences exerted by selected stabiliser additives on the thermal stability of jet fuel [6]

R E Morris, R N Hazlett, C Linden McIlvaine

The effectiveness is reported of hindered phenol, phenylenediamine, tertiary amine and metal deactivator additives in reducing oxidation and solids formation during thermal stress in a modified JFTOT apparatus. The additives were tested in 2 commercial Jet-A fuels. Oxygen and hydroperoxide concentrations were measured in samples of the stressed fuels, insolubles were assessed from filter pressure and heater tube deposits were quantified by carbon combustion. The hindered phenol additive was found to be ineffective, whilst the metal deactivator was very effective.

Further studies of the effects of polar compounds on the thermal stability of jet fuels [46]

R H Clark, L Smith

The deleterious effects of nitrogen and sulphur compounds, and of acidic species upon the thermal stability of sweetened jet fuel is investigated. Stability was determined using the JFTOT and a glassware flask oxidation test. Of the nitrogen compounds indole and 2,5-dimethylpyrrole were most deleterious whilst of the sulphur compounds disulphides and sulphonic acids gave the greatest deposits. No consistent relationship was found between the flask test and JFTOT results. On the basis of heat exchanger tube rig tests it is concluded that total acid content is a better predictor of thermal stability than sulphur content.

The role of metal deactivator in improving the thermal stability of aviation kerosines [47]

R H Clark

The beneficial effects of N,N′-disalicylidene-1,2-propanediamine (MDA) upon the thermal stabilities of 10 jet fuels are determined using glassware oxidation, the JFTOT and a heat exchanger tube rig. In the flask test MDA was found to chelate copper in almost unity mole ratio, reducing oxidation rate accordingly. In the heat exchanger rig MDA gave a reduction in fouling tendency for copper sweetened fuels but not for hydroprocessed fuels. In JFTOT specification tests MDA improved the performance of both sweetened and hydroprocessed fuels. The improved JFTOT results from hydroprocessed fuels are ascribed to heater tube deactivation by the MDA, and this 'overresponse' to MDA is discussed.

Jet fuel instability: organo-sulphur hydroperoxide interactions [4]

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

Reactions between tert-butyl hydroperoxide and several sulphur compounds are studied in tetradecane solution and deaerated benzene at 120°C. The major product observed from hexyl sulphide was the corresponding sulphoxide. Dodecyl disulphide was the major product from dodecanethiol with the sulphoxide also observed. Thiophenes did not yield simple compounds but tetrahydrothiophene gave the corresponding sulphoxide. Results from the storage at 65°C of jet fuels doped with various sulphur compounds are also reported and discussed in the light of the pure compound studies.

Hydroperoxide formation and reactivity in jet fuels [9]

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

Reduction in peroxide formation during the storage of 4 jet fuels at 65°C was observed when thiophenol was present. Shale-II-derived JP-5, Jet-A, hydrotreated and hydrocracked jet fuel blendstocks were studied and all showed marked reductions in peroxide content when thiophenol ws present. The effect was greatest at a thiophenol sulphur concentration of 0.1%, but still significant at 0.01%.

The chemistry of antioxidant additive depletion in jet fuels [17]

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

2 hydrocracked jet fuel components were aged at 60°C and 80°C, neat and with the addition of phenolic antioxidants. Color, insolubles and peroxide formation were monitored throughout

ageing periods ranging up to 68weeks. In the neat fuels peroxidation was first observed, but this peaked and fell at the same time that insolubles began to form. Two different phenolic antioxidants both delayed the onset of peroxidation. Aged fuels and insolubles from additive-free fuels were analysed using MS, GC/MS and IR spectroscopy. It is concluded that the insolubles arise primarily from the oxidation of alkyl-substituted indans, tetralins, indenes, dihydronaphthalenes and benzenes.

Effect of peroxide on the thermal stability of hydrocracked aviation fuel [35]

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

2 hydrocracked aviation fuels were aged at 60°C for 16weeks, neat and with the addition of 12ppm 2,4-di-tert-butylphenol. Samples taken after intermediate ageing times were analysed for peroxides, acidity and gum content, and subjected to the JFTOT test at 282°C. Severe peroxidation was observed, commencing after 3-6weeks for the neat fuels, but delayed in the presence of the antioxidant. JFTOT results showed two distinct regimes dependent upon peroxide content of the aged fuels. At low concentrations (0-150ppm) tube deposition was a dull brown lacquer, whilst at higher concentrations the deposit was whitish and began closer to the fuel inlet position.

Research on problems with the use of current fuel system icing inhibitors in jet fuels [18]

D W Brinkman, M L Whisman, K Q Stirling, C French, W Carley, H Dogrul

The use of fuel system icing inhibitors (FSII) in military jet fuels is outlined. Strategies for the removal of glycol ether FSII's from tank water bottoms before disposal are discussed. It is 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.

Session 4. Stability of gasolines

Stability properties of gasoline-alcohol blends [13]

N Por

Blends of 3 gasoline types - straight-run, aromatic (cat reformed) and olefinic (cat cracked) - with methanol, tert-butanol, methyl tert-butyl ether and combinations of these oxygenates were prepared and their stability characteristics assessed. The oxygenates had little effect upon the straight-run gasoline, but increased the formation of gums, peroxides and inlet system deposits in the olefinic gasoline. The addition of suitable phenolic and amine antioxidants improved the stability of the oxygenate blends. The results are discussed with reference to radical formation and reactions with alcohols.

Evaluation of motor gasoline stability [37]
D L Morris, J N Bowden, L L Stavinoha, M E LePera

Extensive data abstracted from an on-going evaluation of methods for the prediction of motor gasoline stability is presented, indicating that ASTM D525 is not viable as a predictor of gum formation during storage. A modified form of ASTM D873 is shown to be a superior predictor, correlating with both unwashed and existent gum formations of gasolines stored in excess of 2 years under ambient storage.

Storage stability of aviation gasoline [51]
R Dekel

Aviation gasoline conforming to MIL-G-5572 grade 100/130 was stored in 2001 steel drums under ambient conditions and in 1litre polythene bottles at 40-50°C. The same fuel was also blended with 5% lubricating oil and similarly stored. Specification test data together with UV and FTIR spectra are reported for various storage times up to 54weeks. Properties significantly altered during storage under both conditions were potential and existent gum, distillation and RVP. The higher temperature storage in polythene containers gave greater changes in properties. Two-stroke engine tests carried out before and after storage revealed no significant changes in performance.

Session 5. Stability of diesel fuels

Evaluation of commercial stability additives for naval distillate fuel [2]
D R Hardy, E J Beal, R N Hazlett, J C Burnett

The results of a large test matrix are summarised in which the effectiveness of 9 commercial stabilising additives was measured in 9 freshly refined fuels. The additives are coded but generic chemical names indicate that 6 of the 9 contained secondary or tertiary amines. The fuels detailed in the paper all contained 30% catalytically-cracked LCO and were thus unstable. Results of storage tests under a variety of conditions including ASTM D2274, 43°C bottle storage and the oxygen overpressure test described in paper 66 are reported. Two of the amine additives were generally effective in reducing insolubles formation.

Distillate fuel stabilisation in a major European refinery [71]
P B Mabley, G M Wallace

The use of an additive package (of unspecified composition) to optimise refinery economics in the production of distillate fuel is described. Results are presented showing that the additive reduced colour degradation and insolubles formation in blends containing 10% virgin LCO and 5% visbroken gas oil. The resultant levels were comparable to, or better than, hydrotreated distillate. Financial savings of approx $600,000pa are claimed as a result of additive use.

Middle distillates stability: composition and additive utilization effects on their aging at different temperatures [42]
C Bernasconi, A Chaffardon, P Charleux, J Denis, J Gaillard,
J P Durand

Results of storage tests at 120°C, 43°C and ambient are reported for straight-run and cracked gas oils of various types. Additives containing combinations of aliphatic amines, metal deactivators and dispersants were included in some of the tests. The stability of LCO fractions obtained by distillation is also reported, demonstrating that removal of 315°C+ material greatly improves stability. Analytical results for some fuels before and after ageing and gums resulting from instability are given. All results are discussed in the light of contemporary literature and many conclusions drawn.

Solid absorbents as distillate fuel stability agents [55]
W Arfelli, A J Power, R K Solly

This paper reports that the presence of polyurethane 'Fuel Stability Foam' (FSF) can reduce or eliminate the consequences of fuel instability. Straight-run/cracked distillate blends were aged at temperatures ranging from 43°C to 120°C in the absence and presence of 0.2%wt/vol FSF. The FSF greatly reduced insolubles and improved filterability. FSF is also shown to have a 'clean-up' effect upon already degraded fuels and to neutralise the effects of known instability promoters (chloroacetic acid, benzenethiol and copper naphthenate). Possible mechanisms of action accounting for the beneficial effects of FSF are considered.

Storage stability changes with commercially available diesel fuel winterizing additives in the United States [58]
G G Pipenger

29 commercially available winter additives (coded) were used to treat three ASTM No.2D fuels of differing stability. Results of ASTM D2274 and ambient storage tests on the blends are presented. It is concluded that most of the 'multifunctional' additives did not adequately protect fuels for long-term storage. Many of the additives were found to be deleterious to fuel stability.

Stability measurements of military and commercial marine fuels from a worldwide survey [65]

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

Results are presented of stability tests on 22 F-76 military and 26 commercial marine fuels using 43°C bottle storage, ASTM D2274 and the 90°C oxygen overpressure test reported in paper 66. The samples were obtained from a wide spread of geographical locations. The results indicate that the commercial fuels are quite stable, whilst the military F-76 fuels were not so stable. The oxygen overpressure test was found correctly to assess the stability of aged fuels.

Comparison of thermodynamics of nitrogen and sulphur compounds implicated in fuel stability problems [31]

F D Sutterfield, W V Steele, D G Archer, R D Chirico, M M Strube

The removal of sulphur and nitrogen compounds from fuels by hydrogen treatment is considered from a thermodynamic viewpoint. Compounds typical of the various N and S types present in fuels are selected and the Gibbs free energies for possible hydrodesulphurisation and hydrodenitrogenation reactions calculated at 100° intervals from 300°K to 1000°K. Compounds considered include pentane-1-thiol, benzenethiol, butyl sulphide, thiophene, butylamine, aniline, pyrrole and pyridine. The results are discussed and it is concluded that thiophenes, pyrroles and pyridines are the most resistant compounds to present hydrogenation practice.

Study of fuel degradation processes by UV laser technique [11]

M Rotel, J Zahavi, N Por, Y Ben-Asher

2 diesel fuels, composed of straight-run and partially-cracked stocks were irradiated with 193nm light from an excimer laser. The fuels were irradiated as drops flowing over a microscope slide. It is reported that the partially-cracked fuel produced darker, denser and heavier deposits on the slide than the straight-run fuel. Electron microscopy revealed differences in morphology between the two deposits. Analysis of the irradiated fuel revealed an increase in gum and peroxide content.

Investigation of 'sediment precursors' present in cracked gas oil [44]

J F Pedley, R W Hiley

Milligram quantities of two groups of compounds 'A' and 'B' were isolated from a degraded catalytically-cracked gas oil, using a sequence of chromatographic separations. Treatment of the compounds with acids yielded products which closely resembled the insoluble sediment produced during storage of the fuel, so they were regarded as 'sediment precursors'. Analysis of the compounds, using principally mass spectral techniques, suggested that they contained indole groups linked to a phenalene ring system. Detection of phenalene and the corresponding ketone, phenalenone, in the fuel is also reported. The relevance of these compounds to the stability of fuels containing cracked stocks is discussed.

Synthesis of 'sediment precursor' compounds and simulation of sediment formation in cracked gas oil using model systems [45]

J F Pedley, R W Hiley

The synthesis and characterisation of the compounds 2-methylindolylphenalene and bis(2-methylindolyl)phenalene is described and these compounds are compared with the 'sediment precursor' species dealt with in paper 44. From the observed close similarities it is concluded that indolylphenalenes play a major part in sediment formation. Model fuels containing phenalene, 2-methylindole and p-thiocresol singly and in combination were stored under ambient conditions for 6 months. Those containing both phenalene and 2-methylindole yielded the most sediment.

Examination of fuel deposits from various sources by pyrolysis/field ionisation mass spectrometry [25]

R Malhotra, G A St.John

Sediments from a variety of fuels aged under differing conditions were examined using pyrolysis/field ionisation mass spectrometry. The technique yields mass spectra which consist essentially of molecular ions. Several of the sediments gave very similar mass spectra, characterised by strong peaks at 131,145,159daltons and containing other homologous series. A distinct second kind of spectrum was observed for other sediments. The 131 series of peaks have been ascribed to indoles by other authors but it is proposed in this paper that they might arise from a peroxide polymer of dihydroquinoline. The spectrum of a sediment derived from dimethylpyrrole-doped fuel was very different from 'natural' sediments, as was the spectrum produced by a JFTOT tube deposit.

Studies of fuel deterioration and additive inhibition mechanisms [62]

S R Westbrook, L L Stavinoha, D L Present, J P Hsu, J G Herrera

Straight-run diesel fuel, light cycle oil and a 50/50 blend of the two were aged at 80°C and the formation of insolubles and discoloration quantified. The effect of five additives, including N,N'-dimethylcyclohexylamine (DMCA), was also studied. Results from the analysis of insolubles formed by the LCO are presented, including pyrolysis/GC/MS, FTIR, and FIMS data. Two 'model' fuels were prepared, the second of which contained 2-methylindole and naphthalene sulphonic acid (NSA) amongst other components and yielded sediment in significant quantities. Acid/base neutralisation of NSA by DMCA added to the model system caused a marked reduction in sediment formation. It is concluded that the reaction of certain acidic compounds with nonbasic nitrogen compounds, such as indoles and carbazoles, appears to be one of the mechanisms by which fuel insolubles are formed.

The development of reference fuels for use with the ASTM D2274 test for fuel storage stability [67]

M D Klinkhammer, E W White, K W Flohr

Reference fuels consisting of trimethylpyrrole (TMP) dissolved in a mixture of n-dodecane (75%), t-amylbenzene (22.5%) and 1-dodecene (2.5%) were prepared and aged according to ASTM D2274. The total insolubles formed at TMP concentrations ranging from 11.4 to 91.4mg/100ml were determined by four different operators and a statistical analysis of these results leads to an equation relating total insolubles to initial TMP concentration. Total insolubles as a function of test time at 3 concentrations of TMP are also reported and the absence of an induction period noted. It is concluded that the 4-component TMP mixture can give repeatable and predictable levels of D2274 insolubles and might be used for reference purposes.

A study of precursors in the formation of insoluble products during the aging of middle distillate fuels [70]

M D Klinkhammer, E W White, K W Flohr

Three mid-distillate fuels were analysed before and after stressing at temperatures of 43°C, 65°C and 95°C, using gas chromatography. Three GC detectors - flame ionisation, electron capture and thermionic specific - were simultaneously employed. Peaks eluting late in the chromatograms were found to increase in intensity after stressing, the effect being most pronounced for the electron capture detector. The authors suggest that a refined version of the technique could be used as a supplement to accelerated stability tests, or as a predictive stability test in its own right.

Measurement of low levels of strong acids in gas oils [43]

S J Marshman

Conductometric and potentiometric titration methods for the quantification of low levels of strong acids in gas oils are described, and results from a variety of straight-run/cracked blends given. It is concluded that the conductometric method detects only strong acids and has a limit of detection of about 0.1mgKOH/1. The paper also describes the measurement of phenalene and its homologues in diesel fuels using a chromatographic technique with electrochemical detection. By selection of the correct detector oxidation potential response to phenalenes was greatly enhanced over that to the isomeric fluorenes.

Development of predictive tests for fuel stability [1]
N C Li, H Chang, S M Wang, P J Huang, J R Tzou

Light scattering measurements during aging of several fuels doped with compounds including dimethylquinoline, dimethylpyrrole, thiophenol and styrene are reported and discussed. Light scattering results from jet fuel (JP-5) containing added dimethylphenol and copper, aluminium or iron powders are also considered. A deposit formed from dimethylphenol in the presence of copper powder is shown to be a dimer of dimethylphenol. Electron spin resonance spectra of deposits formed from dimethylpyrrole in jet fuel are also presented and discussed.

Study of stability of diesel fuels under operational conditions [10]
E Zahavi, A B Shavit, J Ben-Asher, N Por

The condition of three diesel fuels before and after 7hrs exposure in the fuel system of operating buses is compared. The fuels were straight-run light, straight-run full range and a blend of catalytically cracked with straight-run. All were tested with and without the addition of a stabilising additive qualified to MIL-S-53021. Results of stability tests under various laboratory conditions are also reported. All three fuels were found to suffer a loss of stability on exposure to the bus fuel system, accompanied by increased formation of sediment, higher acidity and a reduction in filterability. The MIL-S-53021 additive improved the thermal stability of all three fuels.

Stability of motor diesel fuels and prognostication of their storage terms [75]
Zh Kalitchin, Sl Ivanov, S Tanielian, A Ivanov, P Georgiev, K Kanariev, M Boneva

The results of thermally accelerated storage stability tests on 22 model diesel fuels prepared from denormalizate, hydrogenizate, light diesel fraction and normal parafins are reported. Ageing was carried out at 368°K and 413°K in an apparatus with stirring. Results of some tests under an argon atmosphere are compared with those under oxygen. Several additives were found to have beneficial effects. A nephelometric method for the early detection of insolubles is described and was used in parallel with conventional insolubles determination. Two of the fuels were tested at a range of temperatures and an Arrhenius-type equation used to interpret the results.

Assessing distillate fuel storage stability by oxygen overpressure [66]

R Hardy, E J Beal, R N Hazlett, J C Burnett

A new procedure for the prediction of distillate fuel stability is proposed, based upon thermally accelerated ageing of 100ml samples under an oxygen overpressure of 100psia. Filterable and adherent insolubles are quantified using standard techniques. Experimental results are presented demonstrating a large increase in insolubles resulting from increasing oxygen overpressure and showing close correlation with atmospheric pressure tests at 80°C and 43°C run over longer times. It is concluded that the extra degree of acceleration provided by oxygen overpressure, the excellent precision obtained with replicate samples, and most importantly the ability accurately to predict insolubles formation of various fuels during ambient storage are significant advantages over previous methods.

A study of variables affecting results obtained in the ASTM D2274 accelerated stability test. Parts 2 & 3 - effects of selected chemical and physical factors [68]

E W White, R J Bowen

The effects of oxygen concentration, catalytic phenomena, oxidation vessel and constant temperature bath configuration, and filtered insolubles drying time on the results of D2274 tests are examined experimentally. Oxygen concentration, varied by using nitrogen, air and oxygen was found to exert a strong effect upon the results and the presence of metallic copper had a catalytic promoting effect. Exposure of the fuel to ultraviolet light before testing caused significant increases in result, as did air sparging before test. The geometry of the oxidation cell and its age were found to exert measurable, but minor, effects. The geometry and size of the heating bath determined its response to the addition of oxidation cells, causing a spread in results for different baths. The drying time of the filtered insolubles was found to be critical and an increase from 1hr to 2.5hrs is recommended. The significance of all the findings is discussed and many recommendations concerning the test procedure made.

Operability of automotive diesel engines with unstable fuels -accelerated stability tests relevance [60]

B Martin, X Montagne, C Bernasconi

Three fuels, one straight-run and two 70/30 straight-run/catalytically cracked blends were aged in 501 steel tanks at temperatures of 43°C, 65°C and 80°C. The generation of insolubles, particle morphology. filterability, vehicle filter plugging and injector fouling are reported for the aged fuels. Significant effects of ageing temperature upon particle morphology and filterability are reported and discussed. Injector fouling is reported to be worst with the cracked/SR blends but ageing these at different temperatures produced variable effects.

Session 6. Fuel storage, handling and filtration

Fuel filtration characteristics of vehicle filter media [54]

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

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 are reported and discussed, for example vehicle filters blocked less rapidly than 2μm glass fibre medium when challenged 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.

Particulate contamination of jet fuel systems [52]

R Dekel

Fuel samples and filters taken from 20 aircraft of two types stationed in regular and desert environments were examined. Contamination of the fuel samples was measured by filtration followed by both 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 are 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.

Biogeochemistry of sludge that forms in salt dome caverns used for strategic storage of crude oil [22]

H N Giles, P W Woodward, R A Neihof

Sludges, crude oils and brines collected from three crude oil storage caverns near Freeport, Texas were analysed 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 parafins up to n-C72 were identified. The waxes were also found to contain isoparafins, cycloparafins 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.

Water sensitivity of diesel fuels: effects of composition and ageing [27]

C Bocard, G Castaing, C Bernasconi

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 is reported and discussed. The effect of ageing 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 ageing time are reported. Various effects of the presence of water were found for the different fuels and these are discussed in detail.

User guidelines for diesel fuel handling and storage [61]

S R Westbrook, L L Stavinoha

This paper clearly 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 is dealt with in detail and specific practical recommendations made.

POSTERS

Additive response and the effect of the chemical composition on storage stability of diesel fuels [12]

J Ben-Asher, N Por, A B Shavit

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 45weeks. The storage properties were measured using ASTM D2274, UV irradiation, the DuPont 150°C test and the Bureau of Mines Rapid Oven Test at 110°C. The effects of two additives qualified to MIL-S-53021 are also reported. The results are discussed with reference to degradation mechanisms involving peroxy radical formation and free radical polymerization. It is concluded that the rapid oven test at 110°C is applicable to the evaluation of diesel fuel stability and breakdown mechanisms. It is 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 interpretation.

Analytical techniques for monitoring antioxidant depletion in jet fuels [15]

C D Pearson, J W Vogh, O K Bhan, D Sutterfield

The quantitation of 2,6-di-tert-butyl-4-methylphenol and 2,4-tert-butylphenol at low ppm levels in jet fuels using two techniques is described. GC/MS utilised a Carbowax 20M capillary column programmed from 50°C-220°C with selective detection of the molecular, m-15 and m-43 ions. Minimum detection level for the GC/MS method ranged down to 0.2ppm. The second method employed reverse-phase HPLC with selective electrochemical detection. 1% toluene added to the methanol/water/potassium acetate mobile phase reduced interference from hydrocarbon species. Detection limit for the HPLC method was 1ppm and agreement between the methods was observed to be very good.

Thermal instability mechanisms of jet fuels [16]

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

Six jet fuels were thermally stressed in a slightly modified JFTOT apparatus. Insoluble solids formed during stressing were collected on a 0.45micron nylon membrane, which replaced the original S/S mesh filter. Normal run time was 24hrs, the fuel reservoir being replenished several times. High resolution mass spectroscopy of tube deposits showed the presence of naphthalenes, phenols and some nitrogen and sulphur compounds. GC/MS and high resolution mass spectroscopy of the filtered insolubles showed a considerable diversity between the insolubles from different fuels.

Small-scale reactor for fuel oxidation testing [19]

K Q Stirling, D W Brinkman, F D Sutterfield

The merits of the oxygen overpressure test described in paper 66 are discussed and a novel glass pressure vessel suitable for the conduct of the test is described. The vessel is fabricated from 38mm borosilicate glass tube with a 15mm glass piston valve at one end, the other end being closed. The vessel is coated with chemically-resistant plastic and examples have been presure tested to 750psig. Each vessel holds a single 100ml sample and is encased in an aluminium outer housing. Results of a four laboratory, six sample round-robin are given demonstrating the good reproducibility of the oxygen overpressure method.

Characterisation of particulate matter in aged diesel fuel [53]

I J Baran, A J Power, R K Solly

The morphology of insoluble particles formed in diesel fuels during ambient and accelerated ageing is examined by scanning electron microscopy. In all cases the particles were spherical, about 1-2microns in diameter and showed a marked tendency to agglomerate into larger clusters. The presence of fuel stability foam (see paper 55) reduced the formation of particles considerably. Periodic observation of particles in a fuel ageing at 43°C showed an early preponderance of small particles, followed by a reduction in these whilst the number of larger particles increased. The morphology of Hormoconis resinae mycelia and spores is also briefly dealt with.

Fuel related problems at a nuclear power plant of the emergency diesel generator system [20]

H L Chesneau

This paper gives a technical summary of events following the discovery of contamination in the fuel tank supplying an emergency diesel generator at a nuclear power plant. Samples from the tank were found to contain water and sediment in excess of 0.05%, the acceptable limit. Although subsequent investigation demonstrated that the samples had been incorrectly obtained, and that fuel supplied to the generator would have been acceptable, it was decided as a precaution to clean the tank. The fuel contents were temporarily transferred to road tankers, the tank cleaned and the fuel returned to the tank through clay and a 0.5micron filter. Biocide and MIL-S-53021 stabiliser were added to the clean fuel.

Field trials illustrating the long term effectiveness of methylisothiazolones in the preservation of liquid fuels [74]

M M Dorris, D P Carmody, D G Pitcher

A brief summary of a poster displayed at the conference is given. The poster described the performance features of methylisothiazolones and illustrated two field trials. A single 2.8ppm dose of biocide protected stored fuel from microbiological contamination for at least two years.

Additional Paper

Inground concrete tanks for storage of petroleum products [76]

K J Duncan

The advantages are outlined of concrete storage tanks constructed in the ground for the storage of crude oil and refined products. Chief benefits to be gained are a reduction in 'breathing' evaporation losses and greater security.

Summary of Plenary Meeting of the International Association for Stability and Handling of Liquid Fuels

The plenary meeting of the International Association for Stability and Handling of Liquid Fuels was held on Wednesday, 14 September 1988, and chaired by Leo L. Stavinoha of Southwest Research Institute (chairman of the Association Steering Committee).

The International Association for Stability and Handling of Liquid Fuels was founded at the 2nd Conference in San Antonio, TX in 1986 as a nongovernmental, nonchartered organization sponsored by Southwest Research Institute. The association encourages cooperation in research and experimentation, through biannual newsletters and the sponsoring of periodic conferences. Honorary membership is open to all who are interested in stability and handling of liquid fuels, with a current mailing list of 450 individuals.

The Association Steering Committee is composed of the following 19 members:

Harry Giles
U.S. Department of Energy, USA
Dennis Hardy
Naval Research Laboratory, USA
Art Hartstein
U.S. Department of Energy, USA
Bob Hazlett
Consultant, USA
Cy Henry
E.I. duPont de Nemours, USA
Robin Hiley
Ministry of Defence, England
Amos Ishai
Paz Oil Company Ltd., Israel
Maurice LePera
U.S. Army Belvoir Research, Development and Engineering Center, USA
Alternate, **Jim Mengenhauser**
Rex Neihof
Naval Research Laboratory, USA
Bob Penfold
The Institute of Petroleum, United Kingdom
Nahum Por
Oil Refineries Ltd., Israel
Alan Roberts
Office of the Chief of Naval Research, USA
Michael Sinwell
Naval Sea Systems Command, USA
Alternate, **Richard Dempsey**
James Speight
Western Research Institute, USA
Leo Stavinoha
Southwest Research Institute, USA
Dexter Sutterfield
National Institute for Petroleum & Energy Research, USA
Ed White
David Taylor Research Center, USA

The purpose of this meeting was to have delegates fill out a questionnaire (Table 1) to help the association determine the location of the next conference and to get a general response as to whether a more formal association (with administration fees) should be formed.

A total of 141 completed forms were received from the 208 registered participants representing 30 countries as tabulated in Table 2.

Due to limitations on the size of the meeting room, additional participants were turned away at the door and approximately 35 were rejected by mail. Responses to the Questionnaire are summarized in Table 3.

In summarizing the responses, it was concluded that the attendees tended to choose Fall of 1990 or 1991 for a meeting in the U.S. or Canada with almost equal preference for Germany or Italy. A high preference was shown for Australia, but this represents a very long expensive trip for most attendees. A very favorable response was received for both planned attendance and attendance with paper presentation at the next conference. If a formal association is formed, a fairly high response (85) indicated willingness to pay an administrative fee of $25 U.S.

When it came to the question of hosting and organizing a conference, the best offer (pending approval of the Board of Directors) came from the Coordinating Research Council, Inc. (CRC) with Dr. Alan Zengel as managing director.

Under the auspices of CRC, there are no limits as to where a meeting could be held. Dr. Zengel was impressed with the conference, but thought that equipment/hardware people needed more representation; this is something that CRC can help with and promote for the next conference. A conference organizing committee would have to be formed that could operate in the city chosen for the conference. Otawa, Canada might be a logical location (using Canadian DOD facilities) for the next Conference, depending on developments during the following year.

TABLE 1. Questionnaire

3rd INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS

Questionnaire

(Please Print)

Name ______________________________

Title ______________________________

Representing ______________________________

1) Next Conference (circle preference):

Time of Year:	Spring	Summer	Fall	Winter
Year:	1989	1990	1991	1992
Where:	US	Canada	Japan	Australia
	Germany	Italy	Israel	☐

Comments: ______________________________

____

____

2) Concerning the next Conference, do you plan to (circle answer):

A. Attend	Yes	No
B. Present Paper	Yes	No

3) Would you like to be - a member of the International Association for Stability and Handling of Liquid Fuels paying an annual fee of US $25 for administration costs?

Yes No

4) Would you like to (circle answer):

A. Organize the next Conference	Yes	No
B. Host the next Conference	Yes	No
C. Assist with its business of the International Association between Conferences?	Yes	No

TABLE 2. Summary of Countries and Number of Delegates Represented at 3rd International Conference on Stability and Handling of Liquid Fuels

	Country	Number of Delegates
1.	U.K.	66
2.	USA	32
3.	Sweden	12
4.	Norway	8
5.	Denmark	8
6.	Finland	2
7.	Germany	11
8.	France	11
9.	Spain	7
10.	Holland	8
11.	Bulgaria	3
12.	Austria	2
13.	Hungary	2
14.	Belgium	1
15.	Switzerland	1
16.	Israel	5
17.	Italy	6
18.	South Africa	4
19.	Greece	1
20.	Bahrain	1
21.	Kuwait	1
22.	Australia	3
23.	Canada	4
24.	Brazil	2
25.	Venezuela	1
26.	Japan	1
27.	New Guinea	1
28.	Singapore	1
29.	Malaysia	1
30.	India	2
	Total	208

TABLE 3. Summary of Responses From Questionnaire
(141 Received)

1) Location of next conference:

Time		When		Where	
Time of Year	Responses	Year	Responses	Country	Responses
Spring	37	1989	9	U.S.	35
Summer	26	1990	60	Canada	24
Fall	54	1991	62	Germany	21
Winter	3	1992	2	Italy	20
				Britain	5
				Israel	6
				Japan	7
				Australia	13

2) Attendance at next conference:

Plan to attend ----------------------- 120
Plan to attend and present paper --- 51

3) Would like to be a member of International Association for Stability and Handling of Liquid Fuels paying an administrative fee of $25 U.S. if Association is formalized?

Yes ------------ 85
No ------------- 22
No Response --- 34

4) a and b) Would like to host and/or organize next conference?

Country	Positive Responses, Number of Delegates	
	Host	Organize
Israel	4	4
South Africa	3	3
Bulgaria	3	0
Greece	1	0
Australia (open to discussion)	1	1
Canada (open to discussion)	1	1
U.S.: San Antonio, TX	1	1
Washington, DC	If ACS Hosts	7
CRC Auspices*	1	1

c) Would like to assist with business of International Association between conferences?

Yes --- 36

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* CRC = Coordinating Research Council, Alan Zengel, managing director.

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

SUMMARY OVERVIEW

LONG-TERM STORAGE STABILITIES OF LIQUID FUELS

STABILITY AND HANDLING OF LIQUID FUELS A LOOK INTO THE PAST AND EXPECTATIONS FOR THE FUTURE

PRESENTED BY

LEO STAVINOHA
BELVOIR FUELS AND LUBRICANTS RESEARCH FACILITY
SOUTHWEST RESEARCH INSTITUTE
SAN ANTONIO, TEXAS

ABSTRACT

This presentation reviews the 1st and 2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels, intervening events, and expectations from this, the 3rd International Conference on Stability and Handling of Liquid Fuels.

DISCUSSION

In 1983, in Hertzalia, Israel, in the 1st International Conference on Long-Term Storage Stabilities of Liquid Fuels, we set a stage for the exchange of information and interaction among researchers in this important endeavor. The proceedings of this 1st Conference was edited by Nahum Por and published by the Israeli Institute of Petroleum and Energy.

The 2nd International Conference on the Long-Term Storage Stabilities of Liquid Fuels was held July 29—August 1, 1986 in San Antonio, Texas at the Hilton Palacio Del Rio Hotel. The conference was hosted by Southwest Research Institute (SwRI) and sponsored in principle by the United States Departments of Energy and Defense.

This conference discussed liquid fuels with respect to their quality and resistance to change in storage. The liquid fuels included gasoline, middle distillate (diesel, turbine, jet, and burner), residual fuel oil, and crude oil.

The Conference program encompassed 67 papers in 10 sessions, including a number of panel and poster presentations:

SESSION 1: Fuel Surveys and Long-Term Storage Studies
  Panel: Quality of Fuels in Storage
SESSION 2: Strategic and Emergency Fuel Storage
SESSION 3: Operational Storage and Fuel Systems
SESSION 4: Microbial Aspects of Fuel Stability
SESSION 5: Biocides and Microbiology of Fuels
  Panel: Biocides for Liquid Fuels
SESSION 6: Methods for Characterization, Analysis, and Testing
  Panel: Filtration
SESSION 7: Theoretical Aspects of Fuel Stability
SESSION 8: Test Method Development and Evaluation
  Panel: Accelerated Stability Test Error Sources
SESSION 9: Shale/Coal Liquids and Additive Chemistry
SESSION 10: Effect of Refinery Processing and Additives on Stability
  Panel: Refinery Processing and Additives for Diesel and Naval Distillate

The subject of long-term storage stabilities of fuels is complex, and the scope is best illustrated by the session topics. The increasing importance of this subject continues to be evidenced by considerable research effort in many countries. In keeping with the spirit of the first Conference held near Tel Aviv, Israel, in 1983, pooling of unclassified knowledge during this conference proved to be of benefit to all participants.

The proceedings of this Conference was edited by Leo L. Stavinoha and published by Southwest Research Institute.

Table 1 lists the titles of papers given at this Conference and demonstrates the large range of topics.

TABLE 1. PAPER TITLES OF 2nd INTERNATIONAL CONFERENCE

Storage Stability of Residual Fuel Oils

Fuel-Soluble Biocides for Control of Fungal Contaminants in Hydrocarbon Fuels

Consequences of Sulphur Compound Conversions in Storage of Jet Fuels

Enhanced Methodology for Jet Fuel Clean and Bright Evaluations

The Use of Dioxabornnanes to Control Microbial Growth in Liquid Fuels

Additive Evaluation for Shale *JP-4 Jet Fuel*

In Vitro Biodegradation of Crude Oils (Abstract Only)

Methodology for Evaluating Stability of Motor Gasolines

Causes of Color Changes and Particulate Formation in Navy Distillate Fuels

Fuel Filterability Problems After Storage

Update on Long-Term Distillate Fuel Storage Program From 1982. Problems With Internal Tank Corrosion

Effects of Shale-Derived Polar Compounds on Diesel Fuel Stability

Effect of Microbial Contamination in Storage Tanks on the Long-TermStability of Jet Fuel

The Impact of Microbial Activity on the Quality of Jet and Diesel Fuel Stored in Models

Development of a Test Method to Determine Potential Peroxide

Test Methods and Experience of Switzerland on Long-Term Storage Stabilities of Gasolines

A Recent Instability Occurrence With Naval Distillate (NATO F-76) (Abstract Only)

Long-Term Storage Stabilities of Crude Oil Reserved by Japan National Oil Corporation

Stability Measurements of Commercial Marine Fuels From a Worldwide Survey

The Role of Phenols in Distillate Fuel Stability

Acid-Base Phenomena in Distillate Fuel Stability

Assessment of Storage Stability Additives for Naval Distillate Fuel

Additives for Middle Distillate and Kerosene Fuels

Formation of Insolubles During Storage of Naval Fuels

Filterability of Degraded Fuels

Storage Stability of Coal-Derived Liquids (Abstract Only)

Application of the Filterability-Index Test Method to Evaluate Diesel Engine Operability

Storage Stability of Hydrotreated Residual Oils

Studies Relating to the Mechanism of Diesel Fuel Deterioration and Additive-Inhibition

Summary Overview of Sources of Error in Accelerated Stability Test Methods for Diesel Fuels

Storage Stability of Kerosene and a Jet Fuel

Field Tests on Storage Stability of Gasoline, Jet Fuel and Diesel Fuel

Gum and Deposit Formation From Jet Turbine and Diesel Fuels at 100°C

The Use of Isothiazolones in Contaminated Distillate Fuels

Influences of Sulfur, Nitrogen and Oxygen Bearing Compounds on Diesel Fuel Storage Stability

Liquid Phase Oxidation of Sulfur Compounds

Microbes in Fuels: An Overview With a Naval Flavor

Microbiological Studies in Rock Caverns With Jet Fuel, Heavy Fuel Oil and Crude Oil

Hydrotreatment of Light Cycle Oil for Stabilization of Automotive Diesel Fuel

Effects of Polymeric Coating Systems for Concrete Fuel Tanks on the Quality of Jet Fuel

The Role of Antioxidants in Improving Stability Properties of Shale Oil and Its Products

Developments in Handling Long-Term Storage Problems of Jet Fuels

Stability Properties and Compatibilities of Residual Fuels

Fuel Filter Plugging by Insoluble Sediment in Diesel Fuels

Effect of Nitrogen and Sulfur Containing Compounds on the Deterioration of Fuels at Elevated Temperatures

Effect of Microbial Contaminants on the Corrosion of Fuel Storage Tanks

Methods to Monitor Biodeterioration of Jet Fuel During Long-Term Storage in Rock Caverns

Automotive Diesel Fuel Stability--An Australian Viewpoint

Effect of Stability Additives Upon Distillate Fuel Filterability

Attempts to Standardize Fuel/Water Emulsions for the ASTM Coalescence Procedure

Thermal Stability Deposit Measuring Device

A Quality Control System for Diesel Fuel in Long-Term Storage

Fates of Heteroatoms When Processing Synthetic Crudes

In-Ground Crude Oil Storage Containers "FromWhence It Came"

Fuel System Design Considerations for Diesel and Gas Turbine Engine Powered MilitaryVehicles

Effectiveness of Antioxidants in JP-5

Storage Characteristics of Additive Treated Diesel Fuel

Application of a Field Fuel Quality Monitor to Surveillance of Prepositioned Fuel Stocks

Methodology for Identification of Diesel Fuel System Debris Related to Problems in the Field

A Study of Test Variables Affecting Results Obtained in the ASTM D 2274 Accelerated StabilityTest

Operational Problems With Marine Fuel Oils

Chemical Characterization of Fuel Sediments Using Analytical Supercritical FluidMethodologies

Chemistry and Mechanism of Distillate Fuel Stability

Microbiology of Hydrocarbon Fuels

Pyrolysis/Field Ionization Mass Spectrometric Analysis of Fuel Sediments

Microbiological Contamination Control in Naval Distillate Fuel

The Influence of Polar Compounds on the Stability of Jet Fuel

Thermal Stability of Diesel Fuels

Effects of an Unstable Diesel Fuel on Injector Coking and Vehicle Performance

Introductory Remarks to Session 9: Shale Coal Liquids and Additive Chemistry

Keynote Address

Introductory Remarks to Session 8: Test Method-Development and Evaluation

Of the 202 conference attendees, 70 were from 21 countries other than the United States. The technical input provided from investigators from other countries proved to be most enlightening to the U.S. research community as well as to all other attendees present at the conference.

For your consideration, I offer the following overall observations drawn from the Conference:

- In general, jet fuel long-term storage stability appears satisfactory. Heavily hydrotreated stocks require the addition of oxidation inhibitors, primarily hindered phenols, to prevent peroxide formation.

- The storage stability of middle distillates, such as gas oils, diesel fuels, and heating oils, depends upon the amount and type of cracked stocks included. Amine-type stabilizers, as opposed to primary amine-type antioxidants, appear most successful in preventing sediment formation, but the selection of additives still seems to be pragmatic and empirical rather than based on theory.

- Although sediment weight is used by most as a criterion of fuel suitability, several investigators emphasized the lack or correlation between sediment weight and fuel filtration characteristics. The ability of particles to settle or to stay suspended as a function of particle size appears to be a major factor. Several laboratory filtration tests are under development.

- The need for a short-term test for the prediction of storage stability continues, but no test which accelerates conditions by increasing test temperature is dependable over a wide range of fuels. In this connection, several investigations using oxidation accelerators at lower temperatures appear worthy of further study.

- Microorganisms can cause storage difficulties, particularly in wet caverns. However, available biocides can control the problems, except for wet cavern storage. Some biocides were reported to be effective at low parts per million concentrations in fuels.

- Several new, useful procedures are available to detect the onset of fuel corrosivity by techniques more sensitive than the standard corrosion tests.

- A new device for measuring lacquer-type deposits on thermal oxidative test tubes (ASTM D 3241) uses the principle of dielectric breakdown voltage. This method appears to be most useful in fuel thermal stability programs that are examining neat and storage changes as well as additive and metallurgical effects on deposit kinetics.

- New techniques utilizing mass spectroscopy and supercritical liquid chromatography are helping to understand the mechanism of sediment formation in middle distillate fuels.

At the 2nd Conference in San Antonio, the International Association for Stability and Handling of Liquid Fuels was founded as a nongovernmental, nonchartered organization sponsored by Southwest Research Institute. The association encourages cooperation in research and experimentation, through biannual newsletters and the sponsoring of periodic conferences. Honorary membership is open to all who are interested in stability and handling of liquid fuels.

Some highlights of activities since 1986 include:

- ASTM Methods issued:

–D4625-86	Test Method for Distillate Fuel Storage Stability at 43°C (110°F)
–D 4740-87	Test Method for Stability and Compatibility of Residual Fuels by Spot Test

- **ASTM Symposia**

–Distillate Fuel System Contamination–Handling and Storage; June 1987

–STP 1005, resulting from the symposium last June, is in typesetting. A dedication to Harvey Doering has been added.

- **Proposed Standard Guide for Evaluating Nonconventional Microbiological Tests Used for Enumerating Bacteria: ASTM Designation E35.15**

SCOPE:

In recent years, a variety of procedures, test kits, and instruments have been marketed to provide results of microbiological analyses in a shorter time period than the typical 48-hour incubation period required by the Heterotrophic Plate Count, formerly known as the Standard Plate Count Procedure. The purpose of this guide is to assist users and producers of such nonconventional tests in determining their applicability for processing different types of samples and in evaluating the accuracy of the results.

–Draft No. 6 is now in progress–

- **IP Code of Practice for Examination of Light Distillate Fuels for Viable Microorganisms: Designation IP 385/88**

–SCOPE:

The method is recommended for the examination of liqht distillate fuels for viable microbiological contamination

–SUMMARY OF METHOD:

After separation of any water phase, known volumes of fuel are filtered aseptically through membrane filters. The filters are washed with sterile dispersant and rinsed through with sterile saline solution. The membranes are then placed on the surface of agar growth media in Petri dishes and incubated. From the number of colonies observed after incubation, the count of molds, yeasts, and bacteria present in a given volume of the original fuel sample is calculated.

The method is suitable for light distillate fuels including:

- aviation turbine kerosine
- aviation turbine gasoline
- aviation gasoline
- high-speed diesel engine fuels
- central heating oils

- **Electric Power Research Institute**

–EPRI AP-5506, Interim Report, November 1987
"Stability and Compatibility of Residual Fuels Oils"

RESULTS:

Results indicated that fuel oils may exhibit sediment formation instability without accompanying viscosity instability. The Shell accelerated-dry sludge test correlated well with sediment formed in the baseline thermal stability test, which simulates tank storage. In contrast, viscosity increases occur without accompanying sediment formation. The presence of high levels of cokelike material, as determined by ASTM Test D 473, appeared to indicate viscosity instability.

Several variations of a test method comparing the solvency power of a blend of oils with contained-asphaltene solvent requirements appear to offer promise for predicting the compatibility of oil in a multicomponent blend. This test makes use of readily measured oil properties, such as specific gravity and viscosity. Straightforward correlations based on these properties and an experimental measurement of solvent requirement provide rapid results that utilities can use to make purchasing and end-use decisions.

–EPRI AP-5826, Vol. 1-4, Final Report
Residual Fuel Oil User's Guidebook
Volumes 1-4

This guidebook presents valuable information on using residual fuel oil of increasingly unpredictable quality in boilers, diesel engines, and gas turbines to generate electric power. It also contains a comprehensive bibliography on related topics.

–STORAGE AND HANDLING OF FUEL OIL FOR STANDBY DIESEL GENERATOR SYSTEMS

A GUIDE FOR NUCLEAR POWER PLANT MAINTENANCE PERSONNEL

Prepared by
STEVEN R. WESTBROOK
and LEO L. STAVINOHA
Southwest Research Institute
6220 Culebra Road
San Antonio, Texas 78284

July 1988

- Engine-Fuel Interaction: Development of Marine and Navy Fuels, SP667, has been published by:

Society of Automotive Engineers, Inc.
400 Commonwealth Drive
Warrendale, PA 15096

The special publication is based on a panel discussion presentation made at the 1986 Marine Propulsion Technology Conference, held May 14 in Washington, DC. According to Simon K. Chen, organizer of the Blue Ribbon Panel, the papers in this publication represent comments made by distinguished researchers, engineers, and experts in this field and reflect their views on present progress and future prospects.

- Energy and Fuels: A major new journal of the American Chemical Society. Premier Issue: January/February 1987. For further information, write:

AMERICAN CHEMICAL SOCIETY
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- **Microbial Problems in Fuels**
  Diagnosis and Control
  Produced for The Institute of Petroleum

The development of new diesel, gas oil, and fuel oil products involves the use of new additives and materials. Fuel-handling and distribution are also changing to suit the changing patterns of use. These two factors combine to create environments in which microbes may grow and live inside storage tanks and fuel systems, contamination resulting in increased costs, loss value, engine and system fouling, and in some acute cases, health and safety risks.

This 22-minute video program shows how such contamination occurs and describes the ways in which installations may be protected from such problems.

Available from: Ramillies House
1/2 Ramillies Street
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EXPECTATIONS

And now, what about the 3rd International Conference on *Stability and Handling of Liquid Fuels?*

During this 3-1/2 days, we will hear and discuss some sixty-seven (67) papers covering residual, gasoline, diesel, jet, and crude oils. Based on the abstracts, these papers, when combined as Proceedings from this 3rd Conference, will give us much information.

Table 2 summarizes the perception I have of what each paper will have as a highlight, based on the book of abstracts provided to each of you. Let's quickly take a look at what can be expected.

During the progress of this Conference, we will each have the opportunity to enlarge on these perceptions through the author's presentations. I wish you a good meeting here in London, and, when we part on Friday afternoon, I know we will have learned a lot more about this important subject.

TABLE 2. PERCEPTION OF HIGHLIGHTS OF PAPERS: 1988

STABILITY OF RESIDUAL FUELS

Por [14]: Peptization state phenomenon for stability and compatibility of residual fuels

Rovesti [21]: Simple tests predict or prevent residual fuel instability or incompatibility

Kassim [38]: Understanding storage life and sludging in blended fuel oils

Vorster [73]: Coating systems for lining tanks to store methanol and ethanol

Lewis [39]: Oil phase aromaticity and asphaltenic molecule flocculation tendency determines residual fuel stability

Pogonowska-Fabriek [59]: Impact of waste lubricating oil on bunker fuel oil quality and shipboard handling

Hara [34]: Effects of hydroprocessing severity on product stability

MICROBIOLOGICAL GROWTH IN FUELS

Edlund [8]: For microbiological control of inflowing cavern water, only nitrate gave satisfactory inhibition

Klein [23]: A mixture of two biologically active chemicals and a fuel stabilizer also inhibits formation of extracellular bacterial polymeric material

Carlson [24]: The low temperature in rock cavern fuel storage tends to promote presence of aerobic flora (mainly cold-tolerant) gram negative rods

Jones [30]: How to use light microscopy for assessing microbial growth in fuel, water, and interface samples

Elsmore [48]: Efficacy of BNPD shown for both inhibiting growth and killing microorganisms

Stegman [49]: Use of water-soluble biocides to control microbiological growth in large diesel fuel storage containers

Hill [5]: A simple on-site assay for determining biocide treatment effectiveness for microbial inhibition or kill

Morchat [56]: Five major types of commercial biocides are compared for application in ship fuel systems employing filter coalescers

Van Vleet [57]: By isolating organisms from a fuel, selection can be made of the most effective treatment method

JET FUEL STABILITY

Russell [3]: Aromatic, alpha hydrogen, methylene hydrogen, and methyl hydrogen composition from NMR have been correlated to JFTOT thermal breakpoint temperature

Datschefski [41]: Expanded application of JFTOT through carbon burnoff for quantitation, stainless steel tubes for high test temperatures, and a capillary tube heater section for turbulent fuel flow generation

Morris [7]: JFTOT deposits are quantitated by carbon burnoff, dielectric breakdown voltage, and light interference

Kamin [36]: Fiber optics measurement of JFTOT deposits allows deposition rate measurements at temperatures around the breakpoint temperature

Reddy [32]: Alkylihydroperoxides are mechanistically related to autooxidation while alkyl radical seem to be responsible for deposits at intermediate and pyrolysis range of temperature

Morris [6]: Evaluates various additives over the 200 to 310°C range using stainless steel tubes and quantitative analyses

Clark [46]: Compositional information predicts fuel degradation rates simulating jet engine oil-cooler

Kendall [47]: Metal deactivator additive binds copper and also passivates metal surfaces

Mushrush [4]: Type and concentration of sulfur compounds important in relationship to peroxidation

Watkins [9]: Refinery processing of jet fuel responsible for peroxide concentrations

Brinkman [17]: New analytical techniques allow study of antioxidant mechanism

Kamin [35]: Similarity of deposit composition shows similarities between storage and thermal oxidative temperature ranges

Brinkman [18]: New technology for EGME and DEGME removal from fuel water allows removal and *disposal*

STABILITY OF GASOLINE

Por [13]: How alcohols and ethers decrease gasoline stability

Morris [37]: Test methods and limits related to storage condition and time

Dekel [51]: Chemical changes for assessing storage life of aviation gasoline and lubricating oil treated gasoline

STABILITY OF DIESEL FUELS

Hardy [2: Effectiveness of commercial additives in freshly refined diesel fuels

Mabley [71]: Maximizing use of LCO with additives that inhibit color and sediment formation

Bernasconi [42]: Importance of olefins, polyaromatics, and heteroatomic hydrocarbons to color, gum and sediment formation

Arfelli [55]: Use of solid absorbants to minimize fuel deleterious effects in vehicle and storage systems

Pipenger [58]: Twenty-four commercially available multi-functional winterizing additives are evaluated for effectiveness and cost/benefit

Hardy [65]: Worldwide fuel survey evaluates quality related to fuel type and geographical location

Steele [31]: Removal of sulfur compounds by hydrodesulfurization is impeded kinetically as is nitrogen compound removal

Zahavi [11]: Laser irradiation is ideal to study susceptibility of chemical bonds to degradative influence at varying severities

Hiley [44]: Precursor compounds may be formed by condensation of oxidation products of polycyclic aromatic hydrocarbons with indoles

Hiley [45] Model systems simulate sediment formation

Malhotra [25]: Pyrolysis/field ionization mass spectrometric analysis combined with thermal evolution profile of selected peaks elucidates between adduct and pyrolysis products of sediments

Westbrook [62]: Acidic, basic, and neutral fractions of sediment are analyzed to characterize formation of insolubles

Klinkhammer [67]: Reference fuel development for training and apparatus qualification encouraging

Klinkhammer [70]: "Tholins" (after the Greek word mud) defined by GC concentration and complexity may be the key to improved test procedure

Marsham [43]: New analytical methods for type and quantity of acids related to fuel instability

Li [1]: Thiophenol, alkylphenol, and alkylpyridine are added to accelerate fuel aging

Zahavi [10]: Filter clogging and deposit formation in city bus fuel systems correlated to fuel composition, stability additive, and thermal stability

Juvarajan [33]: Development of correlation between accelerated aging and ambient storage to develop better ways to evaluate fuel stability in Malaysia

Ivanov [75]: Predicting diesel fuel storage life

Hardy [66]: A new precise accelerated method for diesel fuel stability predicts stability for 3 years at ambient conditions

White [68]: Summary of physical and chemical effects responsible for poor precision of D 2274

Martin [60]: Severity of aging test determines particle size and relationship to filtration characteristics

FUEL STORAGE, HANDLING, AND FILTRATION

Baran [54]: Compares filtration rates with gravimetric particulates for aged fuels

Dekel [52]: Definition of critical dirt amount with the use of particle counters on jet aircraft systems

Giles [22]: Crude oil sludge/emulsion layer in solution mined salt caverns found to be natural settling out of colloidal constituents

Bocard [27]: Water enhancement of fuel gum filter plugging capability

Westbrook [61]: Summary of fuel storage and handling practices for quality assurance of standby emergency electrical generators

POSTERS

Ben-Asher [12]: Evaluation of additive effects on straight run and catalytic-derived diesel fuels

Brinkman [15]: Analytical methods for hindered-phenol antioxidant in jet fuel stability studies

Brinkman [16]: Analytical methodology for reaction pathways leading to thermal instability in jet fuels

Stirling [19]: Device for accelerated stability testing of diesel fuels

Hebda [29]: Microbiological involvement in furnace oil tank failures

Salleh [40]: Stability and handling of methyl esters of palm oil as diesel fuel

McVea [53]: Relation of particulate in aged fuel to engine malfunction

Chesneau [20]: Procedures for critical fuel system cleanup at emergency standby generator sites

Pitcher [74]: Methylisothiazolones provide long-term biocidal effectiveness

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3rd International Conference
on Stability and Handling of Liquid Fuels
London, 13–16 September, 1988

RESIDUAL FUEL OIL STABILITY AND COMPATIBILITY STUDIES

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ABSTRACT

Following the introductory study on residual fuel oil stability properties and compatibilities reported at the 2nd International Conference on Long Term Storage Stabilities of Liquid Fuels which took place in San Antonio, Texas in July 1986, further work regarding this subject has been carried out at the Oil Refineries Ltd. Research Laboratory in Haifa.

The present work covers an investigation of the relation between the chemical characteristics of residual fuels and their stability and compatibility properties, with emphasis given to the mechanisms of the processes associated with degradation product formation during storage and use.

Data reported in this work facilitate the operation of visbreaker processes, not only with respect to their severities but also regarding the visbreaker technologies involved; this study has been made possible by using data concerning intermediate as well as final samples of the products obtained in the recently employed soaker operations and comparing them with similar samples obtained in the formerly used conventional visbreaking process. All the samples have been subjected to conventional as well as specially devised tests and laboratory processes. Data obtained show the advantages of using the asphaltene peptization state phenomenon as an indication of the stability and compatibility properties of the residual fuels; this can also be useful as a controlling parameter for the desired optimized severity of visbreaker operations.

INTRODUCTION

The present study on stability properties and compatibilities of residual fuels is a continuation of the former work on this subject described in a paper delivered at the Second International Conference on Handling and Stabilities of Fuels which took place in San Antonio, Texas in August 1986.

In the past study emphasis has been given to observation of degradation product formation in fuels of various chemical characteristics (straight run, cracked), to the effect of storage time and storage conditions on the degradation product formation rate in the various fuel oil types, to the effect of temperature and exposure to air and, finally, to the suitability of the various estimates of fuel oil instabilities.

In the present work the effect of visbreaker operating conditions and visbreaking technology on residual fuel oil stability has been emphasized and effective process control, based on modified stability estimates, has been investigated.

VISBREAKER OPERATION CONTROL

The tendency of visbreaker operators is to employ severities ensuring an increase of distillate gains by reducing viscosities of the residual product. Economic considerations indicate therefore an increase in visbreaker severities, while fuel oil quality considerations indicate the necessity of limiting these severities to reasonable levels. In order to achieve an optimization between the opposing economic considerations and fuel oil quality requirements, some sort of estimates must be defined; these estimates should serve as an effective control of visbreaker operating severities, optimizing economics and fuel oil quality requirements, by reaching a compromise between these two opposing goals.

Fuel quality estimates must be both reliable and relevant to the visbreaker operation control. Among the more conventional procedures for fuel oil stability and compatibility determinations are the following :

* The hot filtration test (SMS 742)
* The centrifuge test (Mobil Method 1006)
* Asphaltenes content (I.P. 143)
* The compatibility spot test (ASTM D 2781)
* The xylene equivalent test
* Viscosity changes during storage at ambient and at elevated temperatures, with and without exposure to air.

The less conventional procedures, investigated in this work, are the following ;

- Accelerated oxidation (see appendix 1)
- U.V. irradiation (see appendix 2)
- Peptization state of asphaltenes (SMS 1600 and Martin & Bailey Method).

DISCUSSION OF RESIDUAL FUEL STABILITY ESTIMATES

In the following, an analysis of the results obtained by using the various procedures for visbreaker operation control, with respect to optimizing economics and residual fuel quality, is described in some detail.

For the purpose of this study the following residual products have been drawn and backblended with a one-to-one mixture of straight run and catalytically cracked middle distillate to obtain a standard fuel oil (175 cs at 50°C):
a. Visbroken fuel oil obtained without soaker operation;
b. Visbroken fuel oil obtained with soaker operation;
c. Vacuum tower bottoms.

The standardized fuel oil samples have been stored for 12 weeks at ambient temperature and at 50°C, with and without exposure to air .
Samples have been drawn periodically and subjected to accelerated oxidations and U.V. irradiations. Changes in viscosities, asphaltene contents, asphaltene peptization states, carbon residues, hot filtration tests, xylene equivalents and compatibility spot test have been established.

Table 1 summarizes results obtained with two types of visbreaker residues, one produced by a visbreaker operating at more severe conditions and the second employing a soaker and thus operating at milder conditions.

Table 2 compares results obtained with two types of residues: A straight run residue originating in vacuum tower bottoms and a cracked residue obtained in a visbreaker.

The results show an increase in viscosities of fuels in storage, especially when exposed to heat, accelerated oxidation processes or ultraviolet irradiations. The viscosity increase rate during storage is higher for cracked fuels as compared to straight run fuels, but the exposure to heat, and even more so to air, is much more pronounced.
Diagram 1 illustrates the fuel oil viscosity increases when exposed to the above-mentioned prevailing conditions.

Asphaltene peptization state values have been found to have a good correlation to the stability and compatibility properties of fuel oils and can therefore serve as a suitable estimate for production control as well as for product quality monitoring (diagram 2).

Asphaltene contents have increased by accelerated oxidation processes as well as by U.V. irradiations, but correlation with production severities or stability tests others than accelerated oxidation or U.V. irradiation has not been observed to be sufficiently reliable.
It seems therefore that asphaltene peptization state values would be preferable to asphaltene concentration values in this respect.

Results of hot filtration tests are well in line with viscosity increase rate values and are also suitable estimates for fuel oil stability properties.

Carbon residue and compatibility spot test results do not correlate well with the other stability estimating parameters.

The role of asphaltene peptization state as an estimate for residual fuel instability is discussed in more detail in the following.

Analyses of numerous data obtained for establishing correlations between residual fuel oil stability properties and the various quality estimates have led to the following conclusions: Gaestel's approach (6) defining a colloidal instability index as the ratio of the sum of asphaltenes and saturated oils to the sum of the peptizing resins and aromatic solvents, can be adapted also for residual fuel oil instability estimates. This approach, which is not based on the asphaltene concentrations alone, but on the peptization state of the asphaltenes, can be considered as valid keeping in view the colloidal nature of the residual fuel oil system. In this system the micelles form the dispersed phase in the colloidal solution by which the residual fuel oil is characterized. The solid asphaltene core, surrounded by a viscous resin film, which transforms continuously into a high aromatic media, forms thus the dispersed phase floating in a dispersing phase of the mineral oil. In the case that this system is of a sufficiently continuous character, the asphaltenes are considered to be well peptized and the residual fuel displays a satisfactory degree of stability.

The equilibrium of a well-peptized asphaltene system, as described in the foregoing, can be easily disturbed; application of heat, oxidation, ultraviolet irradiation, or addition of a paraffinic solvent thus altering the chemical composition and decreasing the aromatic reserve, – each of these are capable of disrupting the equilibrium of the colloidal system representing a particular residual fuel oil type. As a result asphaltene particles are deprived of their enveloping layers, which previously merged continuously with the consecutive layers. The micelle system becomes non-continuous and the asphaltene cores are prone to agclomeration. This process leads to an instability of residual fuel oils, taking the form of sludge and deposit formation at the bottoms of storage tanks, and of degradation formation resulting in products clogging fuel the lines, filters etc.

Tables 1 and 2 and Diagrams 1 and 2 show some of the results obtained in the present investigation. The subjects of the above discussion are supported by these laboratory results.

CONCLUSIONS

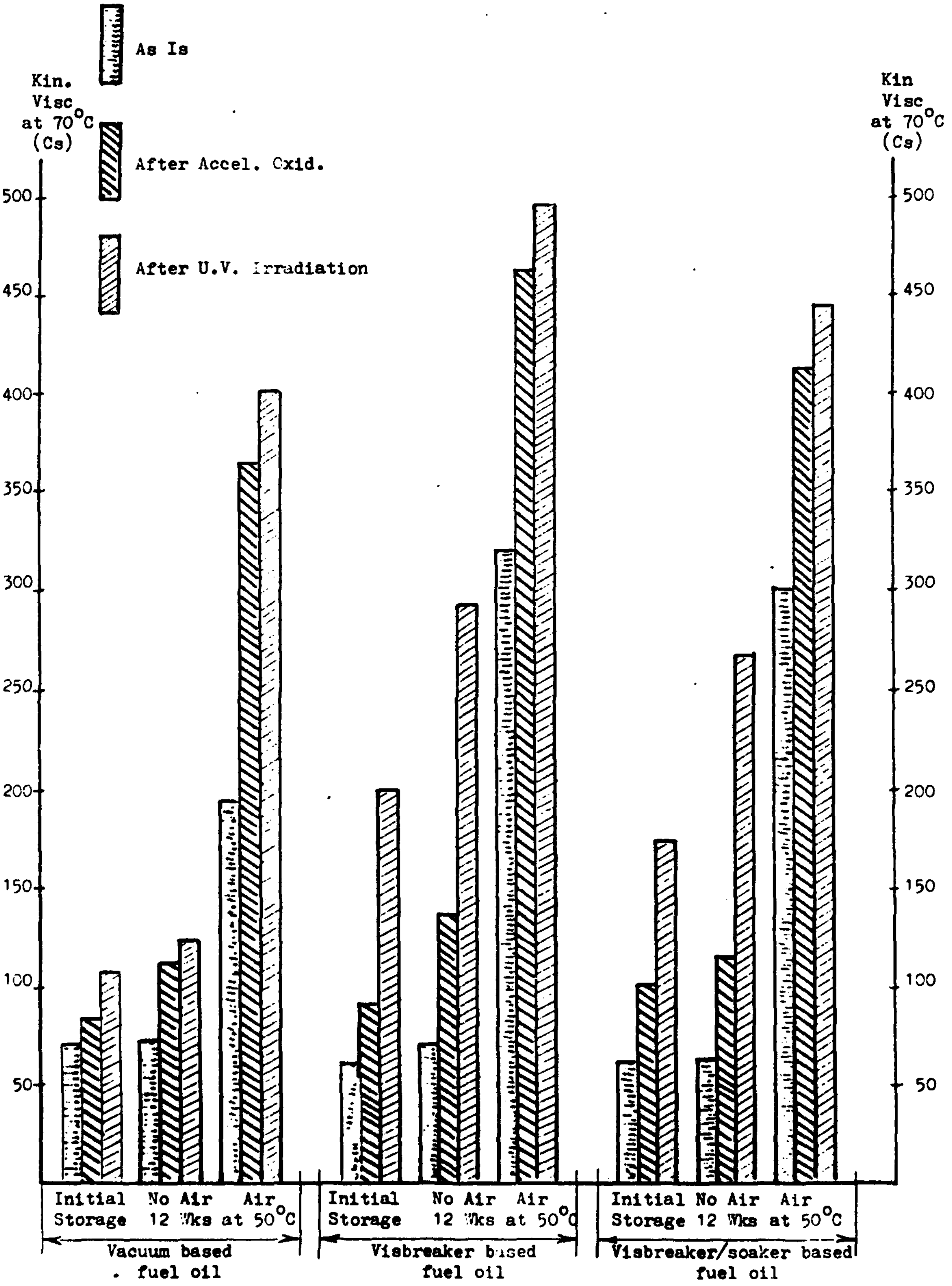
In principle it can be said that visbreakers employing soakers yield fuel oils of better stability properties than visbreakers operating without soakers, and therefore at higher temperatures. In respect of stability and compatibility estimates, the preference for asphaltene peptization state determinations and hot filtration test values has been shown.

T A B L E   1

VISBREAKER BOTTOMS BASED MEDIUM FUEL OIL	Density 15^{o}C	Kin. Viscosity		Asphaltenes	Carbon Residue	Hot Filtration		Spot Test	Compatibility		Asphaltenes Peptization State
	g/ml	50^{o}C cs	70^{o}C cs	%wt	%wt	Exist. mg/100 ml	Pot. mg/100 ml	Xylene Eq.	Cold	Hot	
INITIAL											
With Soaker:											
Original	0.9760	174	63	10.2	15.5	0.38	0.45	80	5/4	5/4	2.0
Accel. Oxid.			101	12.8		0.52		100			1.8
U.V. Irrad.			173	11.7				70	5/3	5/3	1.7
Without Soaker:											
Original	0.9822	182	61	10.4	14.9	0.40	0.53	75			1.7
Accel. Oxid.			91	11.4		1.65		85			1.6
U.V. Irrad.			200	11.4							1.6
STORAGE, 50^{o}C, 12 wks											
With Soaker, exp. to air:											
Original	0.9944	1,349	300	12.3	17.3	0.67	0.78	90	5/3	5/2	1.7
Accel. Oxid.			412	15.5				80			1.6
U.V. Irrad.			435	13.7				70			1.6
With Soaker, no air:											
Original	0.9757	189	65	10.1	16.4	0.46	0.50	65	5/4	5/4	1.7
Accel. Oxid.			116	13.5		0.69		100			1.6
U.V. Irrad.			268	12.0				95			1.6
Without Soaker, exp. to air:											
Original	0.9949	1,400	320	12.4	17.5	1.12	1.34	100	5/4	5/4	1.6
Accel. Oxid.			461	15.8		2.01		100			1.5
U.V. Irrad.			497	15.1				100			1.5
Without Soaker, no air:											
Original	0.9770	202	71	10.3	16.5	0.50	0.57	70	5/4	5/4	1.6
Accel. Oxid.			138	13.6		0.87		100			1.5
U.V. Irrad.			293	12.6				100			1.5

TABLE 2

	Density 15°C	Kin. Viscosity		Asphaltenes	Carbon Residue	Hot Filtration		Spot Test Xylene Eq.	Compatibility		Asphaltenes Peptiz. State
		50°C	70°C			Exist.	Pot.		Cold	Hot	
	g/ml	cs	cs	%wt	%wt	mg/100 ml					
VACUUM RESIDUE BASED MEDIUM FUEL OIL											
Original	0.9640	181	71	6.2	12.7	0.35	0.37	55	5/5	5/4	2.2
Accel. Oxid.			84	6.3		0.46		60			1.9
U.V. Irrad.			108	6.6		0.41		50			1.9
VISBREAKER BOTTOMS BASED MEDIUM FUEL OIL											
Original	0.9760	174	63	10.2	15.5	0.38	0.45	80	5/4	5/4	2.0
Accel. Oxid.			101	12.8		0.52		100			1.8
U.V. Irrad.			173	11.7		0.49		70			1.7
Storage, 50°C, 12 wks											
VAC. RES. BASED MED. FUEL OIL EXP. TO AIR:											
Original	0.9810	743	195	8.9	13.7	0.50	0.54	55	5/5	5/4	1.9
Accel. Oxid.			364	10.8		0.48		55			1.9
U.V. Irrad.			402	10.6		0.48		50			1.9
WITHOUT AIR:											
Original	0.9684	194	73	7.8	11.9	0.35	0.37	55	5/5	5/4	1.9
Accel. Oxid.			113	10.6		0.38		60			1.9
U.V. Irrad.			125	8.1		0.41		55			1.9
VISB. BOTTS. BASED MED. FUEL OIL EXPOSED TO AIR:											
Original	0.9944	1,349	300	12.3	17.3	0.67	0.78	90	5/3	5/2	1.7
Accel. Oxid.			412	15.5		0.61		80			1.6
U.V. Irrad.			435	13.7		0.54		70			1.6
WITHOUT AIR:											
Original	0.9757	189	65	10.1	16.4	0.46	0.50	65	5/4	5/4	1.7
Accel. Oxid.			116	13.5		0.69		100			1.6
U.V. Irrad.			268	12.0		0.56		95			1.6



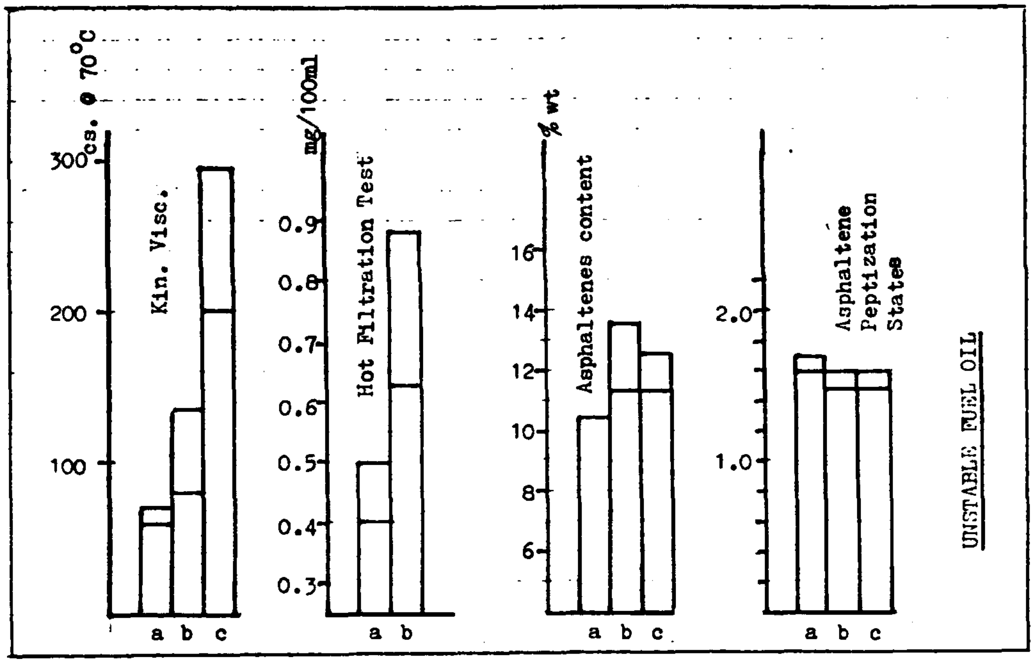
As Is
After Accel. Oxid.
After U.V. Irradiation
Kin. Visc at 70°C (Cs)
Kin Visc at 70°C (Cs)
500
450
400
350
300
250
200
150
100
50
Initial Storage
No Air 12 Wks
Air at 50°C
Vacuum based fuel oil
Initial Storage
No Air 12 Wks
Air at 50°C
Visbreaker based fuel oil
Initial Storage
No Air 12 Wks
Air at 50°C
Visbreaker/soaker based fuel oil

DIAGRAM 1

	cs at 70°C		Hot Filtration		Asphaltenes		Asphaltene Peptization State	
	before storage	after storage	before storage	after storage	before storage	after storage	before storage	after storage
UNSTABLE FUEL OIL								
Initial	61	71	0.40	0.50	10.4	10.3	1.7	1.6
After accel. oxidation	91	138	0.65	0.87	11.4	13.6	1.6	1.5
After U.V. irradiation	200	293			11.4	12.6	1.6	1.5
STABLE FUEL OIL								
Initial	71	73	0.35	0.46	6.2	10.1	2.2	1.9
After accel. oxidation	84	113	0.46	0.69	6.3	13.5	1.9	1.9
After U.V. irradiation	108	125	0.41	0.56	6.6	12.0	1.9	1.9

Storage conditions: 12 weeks, 50°C, not exposed to air

TABLE 3



a - Initial values
b - after accelerated oxidations
c - after U.V. irradiations

Lower values: Before storage) Except for Asph. Pept. States,
Upper values: After 12 weeks, 50°C.) where opposite is true.

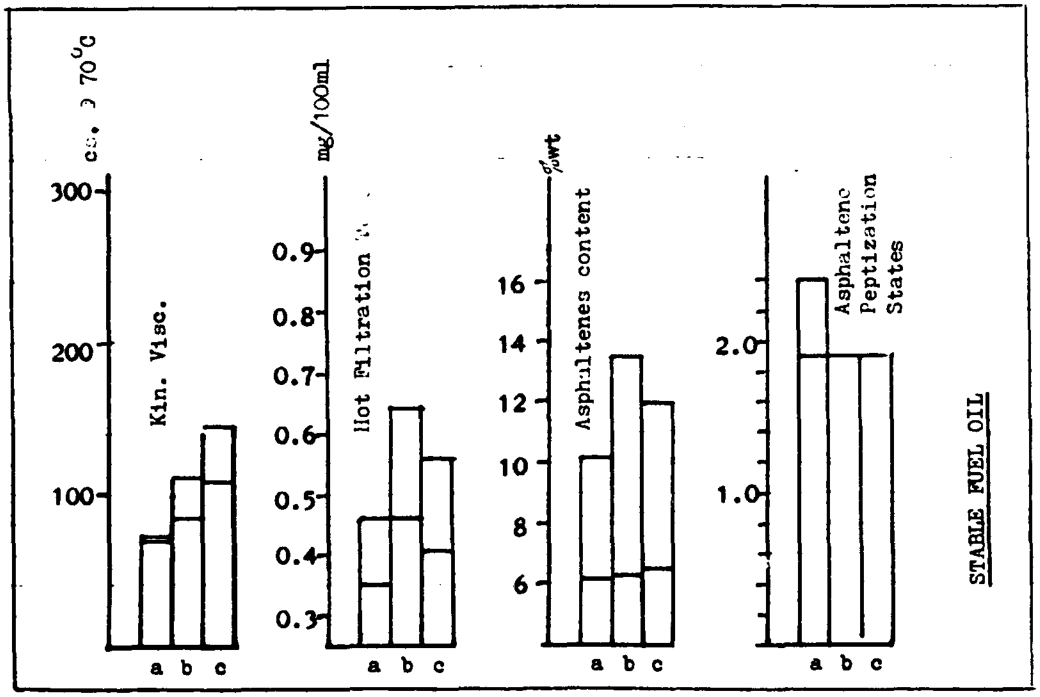


DIAGRAM 2

APPENDIX 1 - ACCELERATED OXIDATION OF RESIDUAL FUEL OILS

The method for accelerated oxidation of residual fuel oils used in the present investigation, is briefly described in the following:

A weighed sample of fuel oil is exposed to oxygen in a bomb, filled initially with oxygen at 100 psi (689 kPa or 7 bar), at a constant temperature of 100 ± 2 °C.

The pressure in the bomb is monitored continuously until a drop in the pressure is noted. A break point is reached when the pressure drop of 2 psi (13.8 kPa or 0.14 bar) within 15 minutes is succeeded by a similar pressure drop within the succeeding 15 minutes.

Alternately, the fuel oil is exposed to oxygen at similar conditions, but for a specified period, say 600 minutes, and then removed from the bomb and subjected to the relevant tests: viscosities, hot filtration, asphaltene contents and asphaltene peptization state determinations before and after the accelerated oxidation test.

The apparatus and materials used in this test are the same as those used in the ASTM D 525 or IP 40 method.

APPENDIX 2 - ULTRAVIOLET IRRADIATION OF RESIDUAL FUEL OILS

The ultraviolet irradiation of fuel oils, as performed at ORL, is briefly summarized in the following:

A weighed quantity of fuel oil is placed into a metallic pan in a form of a thin film (similar to that as used in the Thin Film Oven Test of Asphalts, ASTM D 1754). The pan is placed under an ultraviolet lamp and irradiated for three hours, the distance between the lamp and the fuel oil surface being about 10 cm.

During the irradiation the whole assembly must be wrapped in black, non transparent paper, cardboard or foil, in order to prevent damage to the eyes and skin.

An ultraviolet source of a wavelength of about 360 nm and power of 180 W has been used in the present work.

The change in viscosities, hot filtration test results, asphaltene contents and asphaltene peptization states before and after the irradiation is recorded and evaluated.

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THIRD INTERNATIONAL CONFERENCE ON STABILITY
AND HANDLING OF LIQUID FUELS
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PREDICTION OF STORAGE STABILITY AND COMPATIBILITY OF RESIDUAL FUEL OILS

by

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ABSTRACT

The occurrence of problems in the storage and handling of residual fuel oils in the United States Electric Utility Industry has increased with the increased use of lower quality crudes and with the increased severity of refining which refiners have used to convert residual materials to distillate products. Conventional residual fuel oil specifications and test methods were found to be inadequate to predict or prevent problems due to instability (tendency to form sediment on storage or thermal stress or to undergo other changes such as changes in viscosity) or to incompatibility (tendency to form sediment on blending with a diluent or with another fuel).

In the 2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels, we reported on simple rapid test methods which showed promise for the prediction of stability and compatibility characteristics of residual fuels. These tests have been further evaluated. The results of the rapid test methods correlate with baseline laboratory tests for stability and compatibility. The more promising predictive tests are undergoing implementation in selected electric utility laboratories as part of an overall program to relate the test results to actual plant performance relative to heavy fuel oil blending, storage and handling. This report discusses some of the initial results of this "field evaluation" of the rapid test methods.

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INTRODUCTION

The late 1970's and early 1980's were marked by a sharp decline in the quality of residual fuel oils available to the United States Electric Utility Industry. This decline in quality is due to a combination of factors including the refining of lower quality crudes (lower gravity, higher heteroatom, metal, and asphaltene contents), a decreased demand for residual fuels which has caused the refiner to resort to more severe processing to convert resid into distillable products, and the growth of the spot market at the expense of long term supply contracts. Although the frequency of occurrence of problem fuels may have declined during the current "oil glut", the potential for problem fuels will increase as the long-term trends toward severe processing of lower quality feedstocks continue.

Utilities currently have inadequate means of preventing or even predicting problems with instability or incompatibility. Instability of residual fuel oils is demonstrated by its tendency to produce sediment on long-term storage or on heating. Instability can also be exhibited by other changes in the fuel such as increases in viscosity on storage or on heating. Incompatibility is the formation of a deposit when one fuel is blended with another fuel or a cutter stock. Incompatibility usually results from precipitation of asphaltenes (asphaltenes are defined as the fraction soluble in an aromatic solvent such as benzene but insoluble in a paraffinic solvent such as pentane or heptane) when a fuel of high asphaltene content is mixed with a more paraffinic fuel (or cutter stock) which is of inadequate aromaticity to keep the asphaltenes in solution. Both phenomena can manifest themselves in operational problems such as pluggage in transfer lines and strainers, stratification and settling in storage tanks, and pumping/flow disruptions which can even impact combustion of these fuels. In response to the need for improved means of preventing or minimizing problems arising from the blending, storage and handling of residual fuel oils in utility boiler systems, a multi-phase project whose overall objective was to provide validated, rapid laboratory test methods for predicting oil compatibility and storage stability was initiated.

In earlier phases of the project, a number of rapid, simple tests were developed or evaluated for their potential for practical electric utility application. Requirements for the tests were that they be single enough to run in utility quality control laboratories and rapid enough to be useful in fuel acceptance/disposition decisions (meaning an analysis must be accomplished in a few hours). Details of this earlier work are given elsewhere (1, 2). Since the publication of the results of the earlier phases of the project, a further investigation of the relationships between the predictive tests and the results on long-term aging and/or blending was conducted. This work, which has led to an improved understanding of certain stability/compatibility phenomena, is briefly discussed in this paper.

The predictive tests investigated earlier had only been correlated against controlled laboratory simulation of utility blending and storage environments. This included accelerated thermal aging. Furthermore, the predictive tests had not been employed routinely in electric utility oil laboratories. Neither had the rapid tests undergone evaluation as to their ability to predict problems involving the use of residual fuel oil in actual power plant environments. The current "field evaluation" phase of the project, the early results of which are also discussed in this paper, is aimed at addressing these issues.

SUMMARY OF PRIOR WORK

Key conclusions (based on work with a large number of fuel oils) of the earlier phases of the work are summarized below:

- Specifications and laboratory tests commonly employed by the electric utility industry are inadequate to predict or prevent problems arising out of residual fuel instability or compatibility.

- Residual fuel oils may be differentiated as to their relative stability through long-term aging at elevated temperature. This involved contacting the fuel in the presence of air at 100°C (212°F) and measuring changes in sediment formation and viscosity after 4 and 8 weeks. This accelerated thermal aging test can be used as a <u>baseline test</u> to evaluate rapid, predictive tests of fuel stability.

- The quantitative determination of the presence of "sludge" in residual fuel oils, or the formation of "sludge" due to blending or thermal aging of these fuels, may be made through measurement of hot filtration sediment (IP-375). This test can be used as a <u>baseline test</u> for assessing the incidence of oil blend incompatibility or sludge formation instability.

- The presence of significant levels of coke, as measured by the ASTM D473(Sediment by Extraction, with toluene) is indicative of severe thermal cracking of the residual portion of the oil, may indicate that the fuel is subject to viscosity instability. However, the absence of coke does not insure viscosity stability.

- The accelerated dry sludge test reported by Shell (<u>3</u>) correlates well with sediment formation resulting from accelerated thermal aging, at least for a fuel oil blend that may be "borderline" with regard to it ability to solubilize contained or formed asphaltenes.

- Residual oil blend-compatibility may be predicted by a simplification of a method first proposed by EXXON (<u>4</u>) that compares solvent quality (actually a measure of aromaticity) with solvent quality demand. Solvent quality of a resultant oil blend is obtained from the Bureau of Mines Correlation Index (<u>5</u>) of the individual blend components while solvent quality demand of the resultant oil blend is obtained from the Toluene Equivalences (TE) of the individual blend components. TE is obtained from the percent of toluene in a toluene: n-heptane mixture required to completely solubilize the asphaltenes.

- The new ASTM spot test (ASTM D4740-87) has utility for the simple and rapid determination of the presence of problematic levels of sediment or sludge in residual oils.

ADDITIONAL INSIGHTS INTO STABILITY/COMPATIBILITY PHENOMENA

Relationships Between Sediment Formation and Viscosity Increases

It was reported previously that there is not a correlation between instability as indicated by sediment formation and instability as indicated by viscosity increases, i.e., a sample may form a large amount of sediment on aging but undergo only small increases in viscosity, or conversely, show a large increase in viscosity but form no sediment. This is illustrated in Table 1.

Table 1

COMPARISON VISCOSITY INSTABILITY WITH SEDIMENT FORMATION
(4-Week Baseline Stability Test)

A. Low Sediment - Large Viscosity Increase

	HFS	% Viscosity Increase	BMCI-TE
A-5	0.11	312	34
A-9	0.00	169	46
A-11	0.06	244	14
C-27	0.00	200	37
D-5	0.00	204	39
D-9	0.00	1299	39
		Avg.	35±11

B. High Sediment - Small Viscosity Increase

	HFS	% Viscosity Increase	BMCI-TE
C-10	0.90	68	6
C-11	0.59	39	13
D-4	1.05	72	8
D-7	NF	52	1
		Avg.	7±5

NF= Not Filterable

Por, et al. (6) have also studied the increase in viscosity of fuels on aging. They commented that fuels which undergo viscosity increases without sedimentation have sometimes mistakenly been considered stable. They indicated that if the chemical characteristics of the fuel are favorable for dissolving degradation products formed on aging, then viscosity increases will be observed. Conversely, if the chemical characteristics are not favorable, then formation of sediment will be observed.

An examination of the solvency characteristics of the residual fuels exhibiting these two different manifestations of instability shows that our results are consistent with Por's explanation for sediment formation versus viscosity increases. These results are summarized in Table 1. The quantity, BMCI - TE, may be taken as a measure of the excess solvent capacity of the fuel. For the fuels undergoing large increases in viscosity but little or no sediment formation, the average BMCI - TE of 35 indicates a reasonable excess solvency. However, for the fuels which underwent only small increases in viscosity but formed large amounts of sediment, the average BMCI - TE of 7 indicates no excess solvent capacity. Thus Por's explanation is in agreement with our observations.

Behavior of Blends on Aging

In contrast to stability of a fuel which is defined by the changes which occur in the fuel on long-term aging, compatibility is defined by the changes (sediment formation) which may occur essentially instantaneously on blending of a fuel with another fuel or with a cutter stock. The compatibility of a blending of a fuel with another fuel or with a cutter stock. The compatibility of a blend can be predicted by consideration of the BMCI and TE of the blend. When BMCI - TE is less than about 10, incompatibility of the blend is indicated. The BMCI and TE of a blend are calculated from the BMCIs and TEs of the components. Results of an earlier study of the compatibility of two-component blends are summarized in Figure 1. For the two series of blends studied, sediment begins to form when BMCI - TE decreases to about 10.

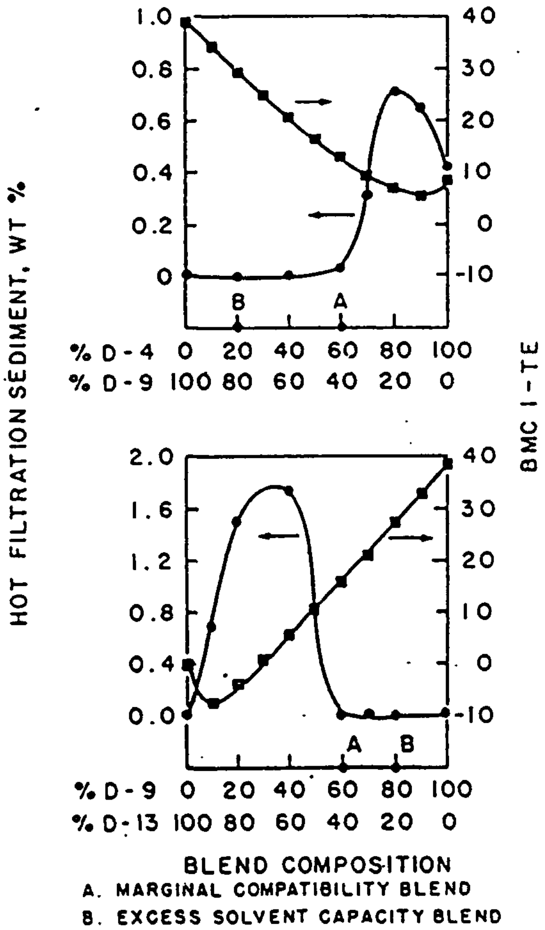

Figure 1 [BMCI-TE] and Hot Filtration Sediment for Two Component Blends

Two components may be blended to form a compatible blend but compatibility (a more or less instantaneous phenomenon) does not imply that the blend will be stable on long-term aging. A study of the stability of two sets of blends has been completed. Two blend compositions (shown as points A and B in Figure 1) for each set of blends were studied. Compositions of the "A" blends were selected to represent "borderline" compatibility; i.e., sediment does not form on mixing but BMCI -TE is only slightly greater than 10. Compositions of the "B" blends were selected so that the blend had excess solvent capacity; i.e., BMCI - TE is substantially greater than 10.

Table 2 summarizes the results for the blends which were subjected to the baseline stability test (aged for 4 and 8 weeks at 100°C with fresh air supplied above the surface of the fuel). All four blends were essentially free of sediment before aging. However, after 4 weeks of aging, the borderline compatibility blends had formed large amounts of sediment (3 and 8%) while the excess solvent capacity blends were still sediment free. After 8 weeks of aging, sediment levels in the borderline compatibility blends has reached 4 and 12%. One of the excess solvent capacity blends remained essentially sediment free but the other had begun to form sediment (1%).

These runs indicate that a comparison of BMCI and TE of blends is useful not only for predicting compatibility on blending but also for predicting behavior on aging of the blends. Blends with BMCI - TE only moderately greater that 10 more readily form sediment on aging than blends with excess solvent capacity as demonstrated by a higher BMCI - TE.

Table 2

AGING OF BLENDS

			Hot Filtration Sediment After Aging , Wt.%		
(A)	Borderline Compatibility	BMCI-TE	0 weeks	4 weeks	8 weeks
	60% D4, 40% D9	13	0.03	3.02	3.73
	60 D9, 40% D13	16	0.00	8.50	20.52
(B)	Excess Solvent Capacity				
	20% D4, 80% D9	29	0.00	0.01	1.16
	80%, D9, 20% D13	27	0.00	0.00	0.08

UTILITY FIELD EVALUATION OF TEST METHODS

Based on the studies reported previously, it was concluded that simple tests which could be conducted in utility laboratories showed promise for prediction of fuel problems due to instability or incompatibility. Consequently, the next phase of the project was implemented; in this phase, which is in progress, the efficacy of the tests in field operation is being determined. Both the ability of quality control laboratories (either utility or oil test labs) to obtain accurate and reproducible results with the proposed methods and the correlation of these rapid predictive tests with behavior of the fuels in actual utility power plant operation are undergoing evaluation.

The field evaluation is comprised of two main elements: (1) Fuel Oil Analysis and Documentation and (2) Logging of Design/Operating/Maintenance Data. The second element involves systematic record keeping by participating utilities for periods of 6-9 months in order to document how the oils perform in service. The data base generated will be used to examine cause-effect relationships between fuel properties and plant performance. These results are beyond the scope of this paper.

Some of the recommended procedures are standard methods, some are in the standardization process, and some are still evolving. A training session was held prior to the start of the field evaluation to provide training of utility or test lab personnel in the test methods. This was followed by analysis of a set of round-robin samples. Analyses which are being run at the test sites are shown in Table 3 (on Page 8) which summarizes the results of the round-robin analyses. Analyses are also being run on shipments as received ("A" samples), and on fuel remaining in the tank ("B" samples) before the transfer of the new shipment. In addition, periodic samples ("C" samples) are obtained from the tank during drawdown as are profile samples drawn from various depths within the tank.

The individual analyses are discussed below. Round-robin data for utility C are not presented as complete data are not yet available and the available data indicate there are some problems to be resolved. This will be followed by a brief presentation of typical data being generated by the utilities.

Spot Test

The spot test procedure was originally proposed by Nippon Oil Corporation (NOC) and was approved by ASTM in late 1987 and was first published in April of this year as ASTM D 4740-87, "Standard Test Method for Stability and Compatibility of Residual Fuel Oils by Spot Test". The method is quick and easy; it involves only placing a drop of the preheated fuel on a filter paper and heating at 100°C for one hour.

The appearance of the spot is compared (Table 3) with a set of standard spots and assigned a numerical rating of 1 to 5 (6 in the original NOC method). A dark inner ring indicates the presence of suspended solids. A 1 or 2 rating (no or faint or poorly defined inner ring) indicates a minimum of suspended solids. Ratings of 3 or higher (well-defined thin inner ring to very dark solid inner ring) indicate excessive suspended solids and likely operating problems.

In this test, "stability" simply indicates the absence of suspended solids and does not mean that suspended solids will not be formed over a period of time.

There is usually agreement between laboratories as to whether the fuel is rated as satisfactory (1 or 2) or unsatisfactory (3 or higher). Most commercial fuels receive 1 or 2 ratings; reproducibility of higher spot ratings needs, and is receiving, further attention.

Bureau of Mines Correlation Index

The original BMCI was calculated from gravity and average boiling point. In earlier work in this project, the average boiling point was determined by ASTM D 1160 distillation or by simulated distillation by chromatography (proposed ASTM crude oil method). As utilities usually do not have these capabilities, they are determining kinematic viscosity at 210°F which can be used to calculate the Watson K factor and subsequently the average boiling point and BMCI by means presented earlier (2). Hand calculation of BMCI by these methods would be tedious but simple PC programs (basic and spreadsheet programs) have been written.

Utility B is measuring Saybolt Universal viscosity at 210°F and converting to kinematic viscosity via conversion tables in ASTM D 2161.

The second measurement needed for BMCI determination is gravity; it would not be expected that there would be any difficulty in gravity determination. However, data in Table 3 show that sample E, the hydrometer method (ASTM D 287) indicated a lighter fuel than the other methods. This is a waxy fuel which appears to have some heterogeneity. It is probable that lighter components rise to the top of the fuel samples and affect the density determination by hydrometer.

The range in BMCI values determined in different laboratories is small (Table 3). Prior work (2) indicated good agreement between BMCIs based on simulated distillation with those based on viscosity measurements.

Toluene Equivalence

Toluene equivalence (TE) is of key importance. It is a measure of the solvency requirement of a fuel; i.e., how aromatic the fuel must be to keep asphaltenes in solution. It is expressed as the percent of the toluene required in a toluene/heptane mixture to completely dissolve the asphaltenes. Complete solubility is determined by spot test.

The TE is used in combination with BMCI to predict whether incompatibility (precipitation of asphaltenes) may occur on blending. Reproducibility of the TE measurement is of key importance. Although the method is not complex, it is time consuming and has been the most troublesome of the proposed analyses. Although the range in TE measurement was greater than desired, reasonable reproducibility was obtained for the round-robin analyses (Table 3). However, large discrepancies have been observed between measurements made at various laboratories. It was recognized earlier that wax in the fuel could interfere with the determination and a modified procedure was used when wax interference was recognized. Some of the discrepancies were attributed to interference of minor levels of wax and the procedure was modified to include a mandatory heating of the spotted filter paper which eliminates an inner ring due to the presence of wax. Problems in reproducibility have continued to occur; most seem to have been resolved but this method is still in need of further improvement.

Sediment by Hot Filtration

The sediment by hot filtration procedure was recently adopted by the Institute of Petroleum as IP-375 and is expected to be adopted by ASTM this year. The method determines the level of insoluble material which can be separated from a *residual fuel* by filtration at 100°C. Excessive levels of insolubles can lead to fuel handling and combustion problems. The organic insolubles included in the hot filtration method may include precipitated asphaltenes which would not be included in the sediment by extraction procedure discussed below.

Some difficulties were initially experienced in determination of hot filtration sediment but most of the difficulties appear to have been resolved. Reproducibility (Table 3) leaves much room for improvement but improvements may be difficult due to problems in sampling/handling of hetergeneous residual fuels.

We have arbitrarily defined sediment levels >0.1 wt% as excessive and possibly problem causing. The level which may cause problems will undoubtedly vary with individual installations and may also vary with other characteristics of the fuel.

Table 3

ANALYTICAL RESULTS, ROUND-ROBIN SAMPLES

	A	B	C	D	E	Stated Repeatability of Method	Stated Reproducibility of Method
Modified Spot Test							
NIPER[1]	1,1	2,1,1	4,2,2	1,1,1	4,3,3		
Utility A	1,1	1,1	2,2	1,1	3,3		
Utility B	1	1	2	1	2		
API Gravity							
NIPER (ASTM D 4052)	11.2	21.9	19.6	7.4	26.8,27.3[2]		
NIPER (ASTM D 287)[3]		21.4,22.1			31.1		
Utility A (ASTM D287)	11.4	22.8	20.3	7.4	30.9	0.2	0.5
Utility B (ASTM D 287)	11.3	22.6	20.1	7.4	30.7		
Viscosity, cSt @ 210° F						0.35%	0.70%
NIPER (ASTM D 445)	9.48	19.83	13.94	46.71	4.03		
Utility A (ASTM D 445)	9.23,9.20	19.88,19.75	14.30,14.25	48.41,48.37	3.98,3.94		
Utility B[4]	10.10	20.50	14.79	50.95	4.26		
BMCI[5]							
NIPER	81.6	45.1	53.0	88.7	28.8		
Utility A	81.1	42.2	50.8	88.6	29.4		
Utility B	81.0	42.6	51.3	88.5	29.3		
Toluene Equivalence (vol. %)							
NIPER	52	0	60	52	49		
Utility A	52	6	60	54	52		
Utility B	53	0	54	50	50[6]		
Asphaltene Content (wt %) ASTM D 3279						1.51%[7]	2.78%[7]
NIPER	3.7	0.07	2.9	14.1	0.08		
Utility A	4.2,3.6	0.07,0.04	2.2,2.4	13.8,13.5	0.22,0.23		
Utility B	4.2	0.10	2.5	13.0	0.14		
Sediment by Hot Filtration (wt %)						$0.123\sqrt{x}$[8]	$0.341\sqrt{x}$[8]
NIPER	0.14,0.16,0.16	0.00	0.09,0.09,0.06	0.01	0.01		
Utility A	0.08,0.09	0.01,0.01	0.07,0.06	0.03,0.02	0.01,0.01		
Utility B	0.16,0.17	<0.01	0.05	<0.01	0.04,0.05,0.06		
Accelerated Dry Sludge (wt %)							
NIPER	0.12,0.15,0.14	0.01	0.18,0.18	0.04	0.03		
Utility A	0.17,0.18	0.01,0.01	0.09,0.09	0.02,0.02	0.06,0.06		
Utility B	0.16,0.16	0.02	0.17,0.18	0.04,0.03	0.10,0.11		
Sediment by Extraction (wt %) ASTM D 473						$0.017 \pm 0.255S$[9]	$0.033 \pm 0.255S$[9]
NIPER	0.14	0.00	0.01	0.01	0.01		
Utility A	0.14,0.12	0.01,0.01	0.02,0.01	0.03,0.03	0.02,0.02		
Utility B	0.11	0.05	0.04	0.03	0.01		

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[1] The National Institute for Petroleum and Energy Research, Contractor to the Electric Power Research Institute.

[2] ASTM D 4052 gave 26.8; direct determination by pycnometer (in triplicate) gave 27.3. The discrepancy between these methods and the hydrometer may be due to sample inhomogeneity and settling.

[3] Hydrometer method.

[4] SUS converted to kinematic viscosity via ASTM D 2161.

[5] Calculated from kinematic viscosity at 210° F and API gravity (via hydrometer method where available, otherwise via D 4052) via equation 5.

[6] One operator originally determined TE to be 20; a reevaluation of the spots gave a TE of 50. This is an unusual fuel. The change in appearance of the spot between 20 and 50% toluene is small.

[7] Acceptable range of two results for n-heptane insolubles between 4.0 and 25.0%.

[8] x = average result of duplicate tests in wt %.

[9] S = average result in percent.

Accelerated Dry Sludge

Sediment by hot filtration measures existent sludge; the accelerated dry sludge test determines "potential" sludge; i.e., the dry sludge test is a measure of the potential of the fuel for forming sludge on aging. It involves addition of one part of a poor solvent (cetane, n-C_{18}) to 10 parts of residual fuel. After 1 hour at 100°C, the fuel is filtered by a procedure similar to the hot filtration procedure. A good correlation between the accelerated dry sludge determination and sediment on long-term aging has been observed (Table 3). As with the sediment by hot filtration, we have arbitrarily assigned 0.1 wt% as the dividing line between a good and potential problem fuel. This value is subject to change as more data are accumulated.

Initially, some difficulty in quantitative reproducibility of the dry sludge measurement was experienced with the five round-robin samples. The problem has now been resolved and satisfactorily reproducibility has been achieved in most cases. No reproducibility studies have been reported for the accelerated dry sludge test. The round-robin values are within the reproducibility range reported for the sediment by hot filtration test.

Sediment by Extraction

In this procedure, the sample is extracted with refluxing toluene. Precipitated asphaltenes which are included in the sediment by hot filtration are not included in this method. High levels of sediment by extraction may be due to organic (coke) or inorganic matter (catalyst fines, dirt, rust, etc.). Whether the sediment by extraction is organic or inorganic can be determined by ashing which leaves only the inorganic matter. The presence of coke has been correlated with severe thermal processing and high levels of viscosity instability.

Sediment by extraction is a standard ASTM method (D 473) and no difficulty in reproducibility has been experienced.

Analysis Utility Samples

A selection of typical data reported by utility A for as-received fuels is summarized in Table 4. Although these are high sulfur fuels and are of moderately high asphaltene content (up to 9.3%), they are all considered high quality fuels by the criteria of this project. In all cases, spot test ratings are 1, and sediment by extraction, sediment by hot filtration, and accelerated dry sludge are all negligible. TEs are usually low (in the 12 to 42 range) with BMCIs exceeding TE by

Table 4

UTILITY A, "A" SAMPLES

Spot Test	API Gravity	Viscosity 210°F cSt	BMCI (Eq. 5)	TE	Asphaltenes	Sediment by HF, Wt%	Accelerated Dry Sludge, Wt%
1	11.6	38.25	74.8	28	6.50	-	-
-	12.5	38.25	71.8	28	-	-	-
1	12.1	46.95	72.5	25	8.74	<0.01	<0.01
1	11.7	18.94	76.8	65	6.88	0.03	0.05
1	12.1	23.60	74.7	58	5.35	0.03	0.04
1	12.3	43.05	72.0	30	7.58	0.01	0.01
1	12.3	22.00	74.2	38	5.12	0.02	0.03
1	11.4	31.45	76.0	42	6.00	0.02	0.03

a comfortable margin. In two cases, TE exceeded the TE range cited above, but in those cases BMCI - TE was still greater than 10. Using the mathematical methods for predicting compatibility from the BMCIs and TEs of the components, it does not appear to be possible to prepare an incompatible blend from any combination of the utility A fuels.

A problem sample was received from another utility A generating site. The problem was associated with combustion of the fuel but it is of interest that the criteria of this project indicate that the problem fuel is of very low quality. Analyses are summarized in Table 5. The spot test rating of 5 indicates a high level of insolubles. BMCI - TE is -10 to -15; this indicates an inadequate solvent capacity to maintain the asphaltenes in solution; the presence of sediment is thus anticipated. The sediment by hot filtration and accelerated dry sludge analyses (1.3-2.7 wt%, and 1.4-3.5 wt%, respectively) indicate the presence of high levels of insolubles. These high levels of suspended solids would be expected to lead to problems in handling (and combustion if the solids reach the burner). The low sediment by extraction values indicate that the solids are asphaltenes and not foreign contaminants. The analyses indicate that this is an improperly blended fuel.

Representative data for utility B as-received fuels are summarized in Table 6. Values within parentheses were determined at NIPER; this utility initially had difficulties in the determination of TE. These represent a wider range of properties that was observed at utility A. Note that there is one high sediment fuel (3rd row). This is noted by the 5 spot test rating and the high sediment by hot filtration and accelerated dry sludge. A low sediment by extraction indicates that the insolubles are precipitated asphaltenes. Incompatibility is predicted by the low BMCI -TE (58 - 67 = -9). No problems associated with this fuel were reported by the utility. All other fuels are high quality by the criteria of this project.

Data for initial samples in storage at utility C at the initiation of the program are summarized in Table 7. By the criteria of this project, these are all very low quality fuels. All contain significant loadings of suspended solids as shown by high spot test ratings, high sediment by hot filtration, and high accelerated dry sludge. The low BMCIs (56-58) and high TEs (81-95) indicate that asphaltene precipitation should be expected. Sediment by extraction values (0.14-0.23 wt%) are higher than observed at the other utilities; these indicate the presence of contaminants which we have not yet classified. The utility, however, has not reported problems with the handling of this fuel. This indicates that specifications must be set for a specific installation and operation; it is believed that in many situations that fuel of this nature would lead to significant operating problems.

Table 5

UTILITY A, PROBLEM SAMPLE

Spot Test	BMCI (Eq. 5)	TE	BMCI-TE	Asphaltenes	Sediment by HF, Wt%	Accelerated Dry Sludge, Wt%	Sediment by Extraction Wt%
5	58.4	68	-10	5.10	1.33	1.74	0.01
5	60.2	75	-15	5.91	2.7	3.5	0.03

Table 6

UTILITY B, "A" SAMPLES

Spot Test	API Gravity	Viscosity 210°F cSt	BMCI (Eq. 5)	TE	Asphaltenes	Sediment by HF, WT%	Accelerated Dry Sludge, Wt%
1	11.8	39.20	74.0	58	2.40	0.04	0.02
1	15.3	27.6	63.7	26	1.80	0.01	0.02
5	16.8	35.04	58.2	49(67)	2.51(5.60)	0.51	0.37
1	10.2	34.50	79.8	49	7.10	0.04	0.01
1	16.6	34.5	58.9	52(0)	3.20(4.30)	0.02	0.01
1	10.9	37.05	77.2	50	5.50	0.03	0.02
1	10.1	23.45	81.4	34	5.95	0.02	0.02
1	11.6	34.15	75.1	18	5.04	0.01	0.01
1	12.0	31.96	73.9	35(32)	3.44	0.14(0.01)	0.09
1	10.4	29.25	79.7	24(24)	4.15	0.01	0.02
1	12.2	32.6	73.3	10(21)	3.01	0.03	0.02
1	12.6	37.0	71.6	15(24)	2.16	0.01	0.01

Table 7

UTILITY C, "B" SAMPLES

Spot Test	API Gravity	BMCI (Eq. 5)	TE	Asphaltenes	HFS, Wt%	ADS, Wt%	Sed. by Ext., Wt%
6	17.1	57.3	83	6.45	0.25	0.70	0.16
6	17.4	57.6	81	6.10	0.23	0.72	0.14
6	17.2	58.3	83	5.62	0.22	0.69	0.14
6	17.2	58.3	84	6.68	0.70	0.23	0.14
6	17.6	56.5	87	6.38	0.26	0.73	0.15
6	17.1	58.7	91	5.53	0.81	0.29	0.23
6	17.4	57.7	95	5.51	0.75	0.29	0.19

CONCLUSIONS

These preliminary results indicate that the proposed test methods can be carried out in utility laboratories and satisfactorily reproducible results can be obtained. There are, however, difficulties in reproducibility with some of the determinations. Determination of toluene equivalence which is a key measurement has been particularly difficult and an improved procedure would be highly desirable. This is being pursued.

Most of the fuel shipments received during the period of the field evaluation have been of high quality by the criteria of this project. The analyses were successful in picking out one fuel with which severe combustion problems were experienced. On the other hand, samples which the proposed analyses point out as problem samples have been handled without difficulty by one utility. It is apparent that specifications must be set for a specific operation.

Although utility participation in the field evaluation has ended, substantial oil property and operating/maintenance data remains to be incorporated into the computer data base. Project completion will involve further data workup and analysis and issuance of a final report. The final report is intended to be a working document for utilities. It will recommend what tests should be used and in what situations and will provide aid in interpreting test results. Purchasing decisions will be only one part of the knowledge derived from the test procedures. For example, they should indicate whether a fuel should be suitable for long-term storage or if it should be used immediately. They should also be useful for making informed blending decisions, i.e., what fuels may be blended without fear of incompatibility and what samples must be kept segregated.

The importance of these test methods should increase as the long-term trend toward more severe processing of lower quality feedstocks continues.

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

by

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INTRODUCTION

In the past, coating systems were extensively used to coat the insides of steel and concrete crude oil as well as refined liquid fuel storage tanks.

These coatings were however not resistant to the methanol/fuel or crude methanol mixtures being stored at present.

In this paper an attempt is made to asses the problems associated with the storage of methanol and methanol containing fuel mixtures in both steel and concrete storage tanks.

PROBLEMS ASSOCIATED WITH THE COATING OF STEEL STORAGE TANKS

When refined products are to be stored in steel storage tanks,they need to be coated on the inside, This prevents corrosion and also ensures that the products do not become contaminated by corrosion products.

The only feasable method of preventing corrosion in steel storage tanks is to coat the inside surface with an impermeable layer of a surface coating that has a high inherent resistance to the stored fuel and also is resistant to contaminants present inside the tank e.g. acids or sulphate reducing bacteria.

Methanol and methanol containing fuels are hygroscopic and absorb moisture and combined with the above-mentioned problems, this can lead to premature failure of the coating.

What is therefore needed is a coating system that is impermeable, has good adhesion to steel coupled to excellent inherent resistance to the stored products.

Needless to say, this coating should also be easy to apply and the costs of application should not be prohibitive.

PROBLEMS ASSOCIATED WITH THE COATING OF CONCRETE STORAGE TANKS

Concrete is a widely used material for the storage of liquids such as oil and other hydrocarbon products.

The main disadvantage of concrete is its poor tensile strength. This can however br overcome by reinforcement with steel. This steel can only function successfully if it is free from corrosion. Provided the cover is adequate the steel will not corrode, but as hair cracks are inherent to a concrete structure as a result of shrinkage, water can reach the steel reinforcement and with time the alkalinity of the concrete surrounding the steel will decrease and corrosion will take place.1) It is therefore necessary to protect the concrete against the ingress of liquids that may cause corrosion of the steel.

It may also be necessary to protect the concrete itself from the liquids stored in the tanks, especially if the liquids are acidic.

The natural porosity of concrete is another factor to be considered. The consequence of leakage of petroleum products can be disasterous. An incident has been reported where an underground tank used to store about 1000 litres of petrol leaked, causing the loss of several thousand litres of fuel, resulting in the permeation of dangerous fumes into basements within a radius of some 100 metres.2)

According to Closner3) the product also needs protection against contamination due to reaction with the concrete.

The surface of concrete is usually covered with a layer of laitance, resulting in a weak layer of non-durable material on the surface. Freshly cured concrete is alkaline and coatings that are saponifiable should be avoided.

Shrinkage cracks of up to 0,12mm can be expected and coatings should have the correct rheology to bridge these cracks.

Various oils and other compounds used as shutter release and curing agents are also present on the surface.

A further complicating factor is that apart from existing cracks, coatings will have to bridge cracks that may form after application of the coating. Crack widths of 0,15 to 0,2mm have been predicted.[4]

In summary it can be said that a coating system used in a concrete storage tank should have the following requirements:

- Resistance to fuel being stored.
- Be impermeable to the fuel.
- Should be able to bridge existing cracks as well as cracks that form after commisioning of the tank.
- Adhesion to the concrete as well as intercoat adhesion in the event of a multilayer system being used.
- Abrasion and scratch resistance.
- Resistance to sulphate reducing bacteria.
- Coating should not contaminate the stored fuels.
- Acceptable application properties.

COMPARISON OF DIFFERENT COATINGS

The following coatings were evaluated:

CODE	DESCRIPTION OF BINDER	PVC%	MAIN PIGMENT
A	ACR/AN COPOLYMER	25	RED IRON OXIDE
B	ACR/AN COPOLYMER BLEND	25	RED IRON OXIDE
C	ACR/AN COPOLYMER/DBP	25	RED IRON OXIDE
D	POLYESTER/VINYL/ISOCYANATE	25	RED IRON OXIDE
E	POLYVINYLIDENE/ VINYLCHLORIDE	15	RED IRON OXIDE
F	EPOXY (ARALDITE GY250/XB3731-1/HY943	20	RED IRON OXIDE

I RESISTANCE TO FUELS

The resistance of the abovementioned coatings after an immersion period of one year was determined. The criteria used for measuring the resistance properties was a shift in the glass transition temperature of the polymer as measured by TMA.

The following fuels were used:

- HIGH OCTANE PETROL (HOP)
- LOW OCTANE PETROL (LOP)
- DIESEL FUEL (D)
- JET FUEL (JF)
- A 10% ADMIXTURE OF METHANOL (M) WITH EACH OF THE ABOVE-MENTIONED FUELS
- CRUDE METHANOL (95% METHANOL, 3% FORMIC ACID AND 2% WATER) (CM)

RESULTS

CODE	HOP	+M	LOP	+M	D	+M	JF	+M	CM
A	+	o	+	o	+	o	+	o	-
B	+	+	+	+	+	+	+	+	o
C	+	o	+	o	+	o	o	o	o
D	+	o	+	o	+	o	+	o	-
E	+	+	+	+	+	+	+	+	+
F	+	+	+	+	+	+	+	+	+

+ = Indicates excellent resistance

o = Indicates satisfactory resistance

- = Indicates poor resistance

From the above it can be seen that there are a number of coatings that are resistant to most of the fuels and fuel combinations. They can be made up into a coating system (hereafter called IPT) as follows:

Topcoat = Very rigid and hard - Epoxy Coating (F) 0,4mm DFT

Undercoat = Soft and flexible - Rhoplex combination (B) 0,3mm DFT

Primer = Intermediate rigidity - Vinyl coating (E) 0,025mm DFT

A coating system made up of these coatings were then applied to tin plate and the various fuels brought into contact with the topcoat. After one year immersion no breakdown of the underlaying layers could be detected.

II PERMEABILITY

The permeability to the various fules and fuel mixtures was determined using a modified Gardner-Park cup. The cups were kept at a temperature of 25°C and 50 per cent relative humidity. Values are reported as $g.day^{-1}.0,1mm^{-1}$.

The epoxy based coating showed a permeability of less than 0,05 while the lowest value measured with the other coatings was 3,52 with coating D. (Diesel was used for this measurement)

This indicates that only the epoxy coating is acceptable as far as permeability is concerned and that the epoxy could be used as a coating on steel.

In concrete storage tanks, the epoxy will have to be used as a topcoat to provide the necessary impermeability.

III CRACK BRIDGING PROPERTIES

Marijs and Bonafont5) evolved a theory which allows membrane stresses and strains to be calculated as a function of the mechanical properties of the constituent materials and the associated substrate movement.

The following expression relates joint movement to the physical properties of the membrane constituents:

$$g = 2\sigma\sqrt{\frac{h}{EG}}$$

where g = joint movement (mm)

h = thickness of adhesive between membrane and substrate (mm)

E = elastic modulus of membrane ($N.\ mm^{-1}$)

G = shear modulus of adhesive ($N.\ mm^{-2}$)

σ = tensile strength of membrane ($N.\ mm^{-1}$)

Figure 1 shows the ideal model of a single layer membrane system before and after substrate movement.

The IPT coating system when applied to concrete, was found to be able to withstand the formation of cracks with a width of up to 0,5mm.

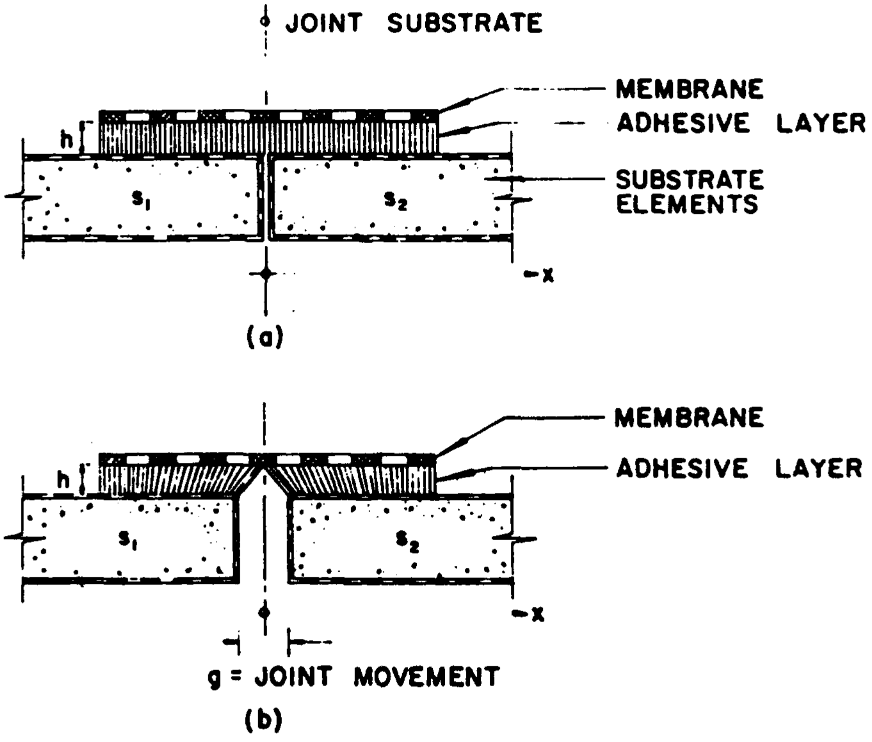

FIG 1. IDEAL MODEL OF A MEMBRANE SYSTEM

IV ADHESION TO CONCRETE

The adhesion of all the coatings as well as the IPT coating system to concrete was determined both before and after immersion in the various fuels for one month. The Erichson direct pull-off method was used.

Coatings A,C and D exhibited an adhesion failure after immersion.

All of the other coatings showed very good adhesion and the failure was observed in the substrate indicating a substrate cohesive failure.

No adhesion or intercoat adhesion failure was observed with the IPT coating system.

As only the epoxy coating can be considered for application to steel, only this coating was tested for adhesion to steel both before and after immersion for one month in the various fuels.

The adhesion was found to be excellent and values of more than 35kg.cm^{-2} were obtained.

V ABRASION AND SCRATCH RESISTANCE

In the event of a floating roof being employed, the coatings will have to withstand a fair amount of scratching, as sand or other abrasive material may be entrapped between the wall and the floating roof.

The only coating with a high degree of scratch resistance was the epoxy coating. It exhibited high scratch resistance even after prolonged immersion in the various fuels.

VI ABILITY TO BRIDGE CRACKS

In order to form a continuous film over the high and low points on any substrate, the coating should preferably exhibit rheopectic rheological behaviour. This was achieved by the used of suitable rheology modifiers.

An attempt was made to determine the minimum film thickness at which the coating system would bridge an existing crack in the surface of the concrete. For this purpose the IPT coating system was applied to a pre-cracked concrete beam, and sections through the crack were examined by means of a microscope. The maximum crack width at which the coating would cover the crack was determined as well as the coating thickness at that point

The results of these tests indicated that the coating system, when applied at a total film thickness of 0,5mm to existing cracks of 1,0mm width, would adequately bridge the crack resulting in a continuous film.

VII BACTERIOLOGICAL RESISTANCE

After exposure to the bacteria Desulphovibris Desulphuricans and Facultative mucoid bacilli for a period of six months at 25°C, no breakdown of the polymeric components in the various coatings could be detected.

VII EFFECT OF COATING ON STORED FUEL

After exposure for a period of one year no contamination of the various fuels by components emmanating from the surface coatings could be detected.

VIII APPLICATION AND RECOATING PROPERTIES

Tests indicated that if the epoxy coating needs to be overcoated with another layer of epoxy this should be done within 24 hours of application of the first layer. The other coatings were all ready for overcoating after 24 hours.

These tests were all carried out at 25°C and 50% relative humidity.

Two component spray equipment has to be used with the epoxy coating and care should be taken to ensure that the correct mixing ratio is adhered to. For this purpose a method based o the residue remaining after decomposition in Oxygen using Thermogravimetric analysis has proven very successful.

The other materials can easily be applied by conventional airless spray techniques.

In the event of high humidity prevailing during the application period the emulsion based materials can still be applied but care should be taken with the epoxy coating.

In the event of damage taking place after application of the coating, the epoxy coating has to be removed by means of sandblasting and a key area on the adjacent undamaged epoxy sandblasted before repairs commence.

Tests were also carried out on concrete soaked in the fuels to determine if tanks that were damaged in use could be repaired.

After exposure to for instance diesel fuel, the surface should be washed down with a volatile solvent such as petrol, scrubbed with a soap/water mixture, left to dry and then recoating can commence without any fear of adhesion problems occuring.

CONCLUSIONS

This investigation showed that coating systems does exist that can be used to coat the insides of steel and concrete storage tanks that are to be used for the storage of petrol, diesel fuel, jet fuel and crude methanol. In the event of any of the abovementiod fuels containing methanol the suggested coating systems will also withstand the fuel mixture.

Steel and concrete tanks should however be coated using different coating systems.

SUGGESTED COATING SYSTEM FOR STEEL TANKS

Steel should be sandblasted to SA 3 before application of any paint commences.

Two coats of the XB3731-1/HY943 cured epoxy coating should then be applied at a total dry film thickness of 0,4mm with a maximum interval of 24 hours between coats.

This intercoat time may be difficult to achieve but is necessary in order to get good intercoat adhesion and therefore a good quality coating system.

Care should be taken to ensure that the two components are mixed in the correct mixing ratios and that a smooth continuous film without any pinholes or other defects are obtained.

SUGGESTED COATING SYSTEM FOR CONCRETE TANKS

The concrete should be tooled free from any projections and then lightly sanblasted to remove laitance and any traces of shutter release and curing agents. In the event of any holes or cracks being opened they should be filled using a suitable polymer modified mortar.

The concrete should then be cleaned from any dust or debris, preferably by means of vacuum cleaning.

The vinyl primer (E) can then be applied in a thin layer, followed after 24 hours by the water-based undercoat (B) and then after a further 24 hours the epoxy topcoat (F) can be applied as a topcoat. The latter should be applied in two layers to avoid possible pinholing.

The total dry film thicknesses for the various coatings are as follows:

- Primer = 0,025mm
- Undercoat = 0,3mm
- topcoat = 0,4mm

More than 24 hours may elapse between the application of the primer and undercoat as well as between the undercoat and topcoat, but caution should be excersised with intercoat times on the epoxy topcoats.

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PAPER No. 39

EFFECTS OF STORAGE ON THE STABILITY OF RESIDUAL FUEL OIL

by

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Abstract

A stable fuel oil is defined as a fuel that will not throw down significant quantities of carbonaceous sludge during use, even when stored and handled at elevated temperatures. Sludge formation will not take place if the oil phase has sufficient aromaticity to prevent the asphaltenes from flocculating. Asphaltenes are large, complex and highly aromatic molecules that can be distinguished from coke or other contaminants by their solubility in highly aromatic solvents. The stability is governed by a balancing mechanism, which depends on the chemical nature of the asphaltenic molecules present and of the oil surrounding them. This balance is described in terms of the required aromaticity (flocculation tendency) for the asphaltene molecules to remain in solution, and the available aromaticity (peptizing power) of the oil phase.

This paper presents the results of investigations into the effects of storage on stability. It has been found that the stability of a stable residual fuel composed of normal refinery streams does not deteriorate perceptibly during storage for two years at temperatures up to 75°C. However, a significant change in the viscosity and in the asphaltenes content is observed as a result of the conversion of resins into newly formed (peptized) asphaltenes due to oxidation/polymerisation reactions. The rate of change depends markedly on the scale and temperature of storage. On a laboratory scale and at elevated temperature (75°C) the increase is significantly more pronounced than in large tanks at more realistic storage temperatures (up to 50°C). A marginally unstable fuel clearly shows additional flocculation of asphaltenes, the extent of which increases with storage temperature. The significant role of oxygen in the flocculation process has been demonstrated, i.e. in its absence flocculation is strongly delayed. The possibility of flocculation inhibition by chemical compounds is discussed. The state of the art of detection of flocculated aphaltenes in opaque media is reviewed. For field measurements a test kit has been developed, based on the Shell Spot Test, and recently obtained experience is presented.

1.0 INTRODUCTION.

As a result of the ongoing trend towards a further upgrading of the barrel the properties of residual fuel oil streams, produced from more severely thermally cracked residual material, will tend to move close to their specification limits. Upon storage further deterioration of product properties, often referred to as ageing, is a phenomenon that can jeopardize product quality. Obviously, good quality control is essential and should be given maximum attention.

A residual fuel oil can be looked upon as a dispersion of asphaltenes in an oily medium (the continuous phase), known as maltenes. When a fuel is diluted with a paraffinic solvent a brown or black precipitate can be produced. The portion of this precipitate that is soluble in a highly aromatic solvent is defined as asphaltenes; the remainder is generally non-carbonaceous material, e.g. grit, rust. The part soluble in the paraffinic solvent is defined as the maltenes. In the early 1950's Van der Kerkvoort et al. (ref. 1) extensively studied the stability behaviour of residual fuel oil. These studies resulted in an appreciable know how on the presence of asphaltenes and their flocculation behaviour on the basis of which the Shell concept for residual fuel oil stability and compatibility has been developed (refs 2,3). According to the model the stability of a residual fuel oil is governed by a balancing mechanism that depends on the physical and chemical nature of the asphaltenic molecules and of the maltenes surrounding them. This balance is described in terms of the aromaticity available in the oil phase (peptizing power, Po) and the required aromaticity (flocculation tendency, FT) for the asphaltene molecules to remain in solution. The ratio of these two parameters, ie. Po/FT, is defined as the P-value. When the P-value is >1, the fuel is said to be stable, on the other hand when the P-value <1, the fuel is unstable and the throw-down of significant quantities of flocculated asphaltenes, known as sludge, is possible.

We have studied whether prolonged storage of a residual fuel would change the stability parameters and could render a residual fuel oil unstable, ie. produce flocculated asphaltenes. The regular measurement of the stability parameters of the stored fuel oil in the programme also enabled us to study the effects of storage on other properties such as flash point, viscosity, asphaltenes content and density. The storage conditions covered both the laboratory-scale and the commercial-scale conditions and included the assessment of the effects of temperature and blanketing with either air or nitrogen. The stability parameters Po and FT were determined by applying in-house developed microscopic techniques; the amount of flocculated asphaltenes (dry sludge) was measured by the Shell Hot Filtration Test.

2.0 EXPERIMENTAL.

2.1 Storage trial.

The storage experiments were conducted on three heavy residual fuel oils obtained from West-European refineries. The fuels were of different crude origin and had different compositions, with P-values ranging from 1 to 1.5. Bunker fuels A and B had P-values of 1.5 and 1.2 respectively, whilst fuel oil C was deliberatedly manufactured with borderline stability, i.e. a P-value of 1.05. For the storage test programme the following conditions were selected.

1. LARGE SCALE: Two tanks of 2500 and 20 m^3 capacity were filled to 70-80%v with fuel and maintained at 50°C for storage periods of up to 4 months and one year respectively. After one year the temperature of the 20 m^3 tank was increased cyclically to 75 - 100°C.

2. SMALL SCALE: 0.3-, 1- and 50-litre samples were stored (flasks or drum) at temperatures of 35, 45 and 75°C; they were either vented to air or stored under a nitrogen blanket.

3. PRESSURIZED: Storage was conducted according to the Standard Test Method for Oxidation Stability of Gasoline, Induction Period Test Method (ASTM D525-80, modified). An amount of fuel was exposed to oxygen or nitrogen (our modified procedure) at an initial pressure of 100 psi (690 $kN.m^{-2}$) and at a temperature of 100°C for 96 hours.

2.2 Dispersant trial.

To test the activity of a dispersant type additive as a potential stability improver we selected a fuel oil consisting of a blend of two stable fuels, one based on a cracked residue and the other on a straight-run residue. By careful selection of the blending ratio, on the basis of the Po and FT parameters, a fuel was obtained which upon storage formed a significant amount of flocculated asphaltenes. With a treat rate up to 0.5%m the following storage conditions were selected:

40 mℓ fuel in 60 mℓ glass cylinders under air or nitrogen at temperatures of 45, 75 and 100°C (small scale) and 200 l drums with a vent to air at room temperature and at 80°C (semi large scale).

3.0 RESULTS.

3.1 Large scale storage tests.

The storage test in the 2500 m^3 tank was carried out with the borderline stable residual fuel oil C. At regular time intervals top and bottom samples were collected and analysed (Table 1). A comparison of the properties of the fuel at the time of filling the tank with those sampled after two months storage revealed no significant differences except possibly from a slight increase of the kinematic viscosity. After four months storage a small decrease was observed in the value of a number of properties such as density, asphaltenes content and Ramsbottom Carbon Residue, but the stability (P-value) had not changed.

Residual fuel oil A had been stored for one year in the 20 m^3 tank at a temperature of 50°C. The analyses (Table 2) indicate hardly any differences between top and bottom samples. In the course of time only small increases in density, viscosity, flash point and asphaltenes content were observed, with no change in Ramsbottom Carbon Residue. The stability parameters of the fuel (P-value, Po, FT and the existent/potential dry sludge) had not changed at all. After the subsequent thermal cycling of this fuel to 75°C (1x) and 100°C (2x) a further small increase in viscosity, flash point and asphaltenes content was observed.

3.2 Small scale storage tests.

In the 50 litre scale storage tests conducted for one year at 35, 45 and 75°C (Tables 3 and 4) no significant differences between the properties of top and bottom samples were observed either. During 52 weeks, however, the viscosity of both fuels increased significantly, particularly at the temperature of 75°C. This increase was accompanied by an increase in asphaltenes content and density, while flash point, Ramsbottom Carbon Residue and stability (P-value, Po and FT) had not changed. The dry sludge content (existent and potential) was somewhat higher after the storage period, but this is likely due to excessive adsorption of oil to the filter paper as a result of the higher viscosity.

The recently introduced modified method, in which the amount of dry sludge is compensated for oil adsorption by the use of two stacked glass fibre filters, would most likely have excluded this increase. The borderline stable fuel oil C prior to and upon storage on a one litre scale (Tables 5 and 6) already had an existent and potential Hot Filtration Test (HFT), each of approximately 0.20%. The fuel, however, was free of flocculated asphaltenes and the high HFT can be due to oil adsorption on the filter paper, although the presence of finely dispersed coke particles cannot be excluded either. After three weeks storage at 50°C under air the first formation of very finely dispersed asphaltenes was microscopically detected. For the nitrogen blanketed samples this occurred after five weeks storage. During further storage the amount only marginally increased and surprisingly the size did not increase either. Particularly the latter observation is contradictory to our experience with regard to asphaltene flocculation from unstable fuels. If such a fuel is stored at 100°C, i.e. the standard test temperature, not only the number but also the size of the particles increases. For clarification we carried out a limited additional storage programme in which the fuel was stored at temperatures of 50, 65 and 100°C. After 3, 7, and 28 days the samples were microscopically observed for the presence and size of flocculated asphaltenes, while in addition the dry sludge content was determined (after 28 days). The results (Table 6) reveal that the storage temperature has a very pronounced effect on the amount and size of the flocculated asphaltenes formed. Storage at 50°C resulted in such small particles that they were hardly visible under the microscope (size approximately 1 µm). After storage at 100°C the fuel showed a significant amount of asphaltenic flocs under the microscope. With regard to the other fuel oil properties (Table 5), neither the asphaltenes content nor the Ramsbottom Carbon Residue was significantly affected during the main part of the storage tests. Only, after about 4 months had the viscosity increased, particularly that of the fuel stored under air.

With 0.3 litre scale storage no top or bottom samples were drawn, but after homogenization the whole quantity of 0.3 litre was used for analysis (Tables 7 and 8). All changes of the properties showed similar trends to those found in the previous storage tests. The magnitude of the increase in viscosity and asphaltenes content, however, was far larger on this small 0.3-litre scale, in particular at the highest storage temperature, i.e. 75°C.

3.3 Activity of dispersant.

In the small-scale storage tests in 60 mℓ glass cylinders the fuel oil samples were analysed (after homogenization) for their dry sludge content and microscopically examined for the presence of flocculated asphaltenes. The analyses (Table 9) show that the flocculation of asphaltenes in the (undoped and doped) fuel oils is much more pronounced under air than under nitrogen. Further, at lower storage temperatures less severe flocculation of the asphaltenes was observed. Additive treatment decreased the rate of asphaltene flocculation, both under nitrogen and under air. Also in semi-large scale storage tests (200 litres, 80°C, air) the additive showed a definitely positive effect on the flocculation tendency (Table 10). 3.4 Induction Period Test Method (ASTM D 525-80, modified).

The bomb for the induction test period was pressurized to 100 psi (690 kN.m^{-2}) at room temperature and subsequently heated to 100°C. As a result, the pressure at the start of the test was higher (125 psi; 860 kN.m^{-2}).

In the tests under oxygen a pressure decrease started immediately and no breakpoint or induction period was observed with either of the two fuels. With nitrogen no pressure decrease was observed. It should be noted that the properties of the fuels (Table 11) prior to the test were slightly different from the initial properties for the long-term tests, due to a slightly different thermal history. In the test under oxygen the properties changed dramatically. The viscosity tripled and the asphaltenes content (pentane insolubles) increased significantly by 4 - 7% (m/m). Moreover the stability balance between offered (Po) and required aromaticity (FT) changed dramatically and fuel B even became unstable. Microscopic inspection of the stored sample clearly showed the presence of flocculated asphaltenes. The properties of the fuels stored under nitrogen did not change significantly.

4.0 DISCUSSION.

4.1 Viscosity increase.

In all the experiments the viscosity increased, as shown in Figures 1 and 2. The effect strongly depends on the scale and temperature of storage and can increase the viscosity to a level beyond the specification limit for this residual fuel oil grade (for all three test fuels 420 mm^2/s at 50°C). A possible factor involved is the loss of light, low-viscous components by evaporation during storage, which will be larger at higher temperatures. However, the observed viscosity increases would require such a significant loss of light components that other properties (density, flash point, initial boiling point, etc.) would have been affected as well. Assuming a viscosity for the light components of 1.5 mm^2/s at 50°C, the loss would have to be 7% m/m to give the viscosity increase for the 0.3 l scale test at 75°C. This would have been noticed from a distinct increase in the flash point, as demonstrated with blends of a short residue and kerosine. Evaporating 5%m of kerosine from a 80/20 (%m/%m) blend of short residue and kerosine results in an increase of the flash point by 15°C. Such an increase of the flash point was not observed in our storage experiments. The largest increase in flash point was for fuel A stored for one year at 50°C and on 20 m^3 scale and amounted to approximately 10°C; it was accompanied by a relatively small viscosity increase from 390 to 440 mm^2/s. This flash point increase may be partly due to the precision of the determination (± 5°C), but there are also indications that upon storage low molecular weight hydrocarbons such as methane and ethane are formed. The existence of these molecules has been confirmed by Head space analyses.

The fuels stored in the Induction Period test with oxygen show the largest viscosity increase even though this storage test is carried out in a closed bomb. Here evaporation of light components can hardly have occurred and contributed to the viscosity increase. Therefore it is concluded that the predominant cause of the viscosity increase of fuels upon storage is not the evaporation of light, low viscous components.

4.2 Generation of asphaltenes.

In most tests the content of asphaltenes (heptane and pentane insolubles) increased and these high molecular weight components will contribute significantly to a higher viscosity of the fuel. The viscosity increase was largest for the fuels stored at the highest temperatures and on the smallest scale (Figures 1 and 2). The increase of the asphaltenes content cannot be explained by loss of light components, as this would in some cases have meant an unrealistically high loss of approximately 30% (m/m). More likely, the formation of asphaltenes is the result of chemical and/or physical reactions of resin-like constituents.

These components are part of the maltenes but, although still soluble in a paraffinic solvent, have a chemical structure resembling that of the asphaltenes. Although we have no definite proof, the formation of asphaltenes seems to be the result of an oxidation-initiated polymerisation. This would not be reflected in the oxygen content of the fuels during storage, because the amount of oxygen in such a mechanism could be very low. Indeed, hardly any increase of the oxygen content was observed; in a number of cases even a decrease was found (Table 2 and 4), possibly due to loss of small amounts of water through evaporation and/or settling. This is evidence in support of the proposed oxidation/polymerisation mechanism, in which the temperature effect would be related to the rate of oxidation/polymerisation and the scale effect to the availibility of oxygen, e.g. surface/volume ratio, diffusion.

4.3 Dispersant.

To simplify the interpretation of the results of the dispersant tests we compiled Table 12, giving the times required to reach a dry sludge content of 0.1%m maximum, both for the small-scale and the semi-large-scale storage tests. With undoped fuel this criterion is met after 2-5 days; with doped fuels and concentrations of 0.2 and 0.5%m it is met after approximately 40 and 160 days, respectively. The dispersant decreases the flocculation tendency of the asphaltenes (FT) and, apparently, doped fuel requires less aromaticity to keep the asphaltenes in a peptized form and it is clear that the dispersant has a positive effect in abating the flocculation of asphaltenes. The effect is also observed in smaller scale tests, even with the rather severe storage condition of 100°C under air.

5.0 CONCLUSIONS.

Long term storage experiments of residual fuels under air indicate that the primarily affected properties are the viscosity and the asphaltenes content and to a far lesser extent the flash point and density. The rate of changes depends markedly on the storage scale and the storage temperature. Both viscosity and asphaltenes content increase with time, which cannot be fully explained by evaporation losses. This phenomenon is more likely due to an increase of the amount of asphaltenes as a result of oxidation/polymerisation of the resins in the maltenes fraction, as is confirmed by the strongly reduced effects when nitrogen blanketing is applied.

The stability (P-value, Po and FT) of fuel does not change during large-scale storage and when the storage temperature is kept as low as possible any changes in properties will be minimized. In small- scale storage tests with a larger surface/volume ratio and better availability of oxygen the chemical reactions are more severe and changes in properties are generally larger. Still no flocculation of asphaltenes occurred in a fuel with a P-value of 1.2 during storage, even after one year at 75°C. Only a borderline stable/unstable fuel with a P-value of about 1 did form flocculated asphaltenes at 50°C in a few weeks time under air, which is most likely related to an acceleration of the physical growth of the flocculated asphaltenes. The quantity and moreover the size of the flocculated asphaltenes are largely increased by an increase in storage temperature.

Addition of dispersant does not result in a repeptizing of flocculated asphaltenes, but it prevents or at least restricts further flocculation.

6.0 FURTHER TEST DEVELOPMENT.

In the laboratory the presence of particulate matter in residual fuel can be well observed through a microscope, but one has to use very thin layers of oil to obtain enough light transmission. Often this results in an undefined layer thickness (glass slides) and particularly improper focussing could lead to serious misinterpretations. Quite often fibres, sand or coke like material is classified as flocculated asphaltenes and the fuel is stated incorrectly to be unstable. To study the flocculation process of asphaltenes an interesting alternative is offered by the use of light transmission (ref. 4). When introducing light of suitable wave length, eg. IR, Mercury, Halogen via a bunch of glass fibres through a small inspection window, called optrode, the relative change in light absorbance, recorded as a function of time, reflects the formation of asphaltenes. An advantage of the fibre technique is that the signal from the optrode can be linked to a computer, which opens up the possibility for unattended monitoring and automization of test methods.

To avoid the use of the highly subjective microscopical inspection, and for a fast assessment of the stability of residual fuel oils in the field we have developed the portable Shell Spot Test Kit (ref 3). The test features an accelerated ageing procedure in which the oil is diluted with 10%v hexadecane and heated to 100°C for one hour. This corresponds to a small decrease in peptizing power of the fuel and as such could result in the flocculation of asphaltenes (Po/FT ratio <1). The presence of the flocs is studied by adsorbing a drop of fuel oil on a filter paper. If the spot, after washing with heptane to remove excess oil, shows a dark inner ring, the oil apparently could not withstand the dilution with hexadecane and is reported unstable. The test kit provides a simple method to measure both stability and compatibility of residual fuel oil in terms of a go/no go assessment.

7.0 REFERENCES.

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TABLE 1

Properties of Fuel C stored in 2500 m^3 tank at 50°C

Storage, months Sampling point	0 -	2 Top	2 Bot.	4 Top	4 Bot.
Density , kg/m^3 15°C	1003	1003	1001	1001	-
Viscosity, mm^2/s 50°C	412	508	493	474	484
100°C	42	42	42	39	40
Ramsb. Carbon Residue, %m	15.4	15.6	15.3	14.6	14.5
Heptane insolubles , %m	10.2	10.0	10.1	8.8	8.6
Pentane insolubles , %m	12.5	12.6	12.9	12.3	11.9
P-value	1.05	-	-	1.05	1.05

TABLE 2

Properties of Fuel A in 20 m^3 tank

Storage, weeks	0	52		73	
Storage, temp. °C	-	50		50 - 100	
Sampling point		Top	Bot.	Top	Bot.
Density, kg/m^3 15°C	993	995	995	995	994
Viscosity, mm^2/s 50°C	390	418	420	439	442
100°C	36	45	44	41	40
Flash point, PMcc °C	91	94	96	101	102
Ramsb. Carbon Residue, %m	14.6	14.4	14.6	14.1	14.5
Heptane insolubles , %m	8.2	8.5	8.6	8.5	8.2
Pentane insolubles , %m	9.9	11.9	11.7	12.4	12.8
Oxygen content , %m	0.4	0.41	0.39	0.28	0.29
HFT existent , %m	0.07	0.06	0.06	0.07	0.07
HFT potential , %m	0.07	0.09	0.09	0.09	0.08
P-value	1.5	1.6	1.6	1.6	1.6
Peptizing Power , Po	64	-	-	-	65
Flocc. tendency , FT	46	-	-	-	46

TABLE 3

Properties of Fuel A stored on 50-litre scale

Storage, weeks	0	52					
Storage, temp. °C	-	35		45		75	
Sampling point	-	Top	Bot.	Top	Bot.	Top	Bot.
Density , kg/m^3 15°C	993	993	994	994	995	995	995
Viscosity, mm^2/s 50°C	390	444	431	463	458	546	542
100°C	36	41	42	44	-	48	-
Flash point, PMcc °C	91	88	90	90	88	90	88
Ramsb. Carbon Residue, %m	14.6	-	14.3	-	14.2	-	14.5
Heptane insolubles , %m	8.2	-	8.8	-	9.1	-	10.2
Pentane insolubles , %m	9.9	12.6	12.9	12.9	13.1	14.2	14.0
Oxygen content , %m	0.40	0.45	0.45	0.45	0.46	0.48	0.46
HFT existent , %m	0.07	-	0.06	-	0.06	-	0.09
HFT potential , %m	0.07	-	0.10	-	0.12	-	0.19
P-value	1.5	-	1.5	-	1.5	-	1.5
Peptizing Power , Po	64	-	-	-	-	-	65
Flocc. tendency , FT	46	-	-	-	-	-	46

TABLE 4

Properties of Fuel B stored on 50-litre scale

Storage, weeks	0	52					
Storage, temperature °C	-	35		45		75	
Sampling point	-	Top	Bot.	Top	Bot.	Top	Bot
Density , kg/m^3 15°C	989	989	989	989	989	991	991
Viscosity, mm^2/s 50°C	418	465	461	480	485	633	629
100°C	36	41	42	42	44	49	52
Flash point, PMcc °C	91	88	90	88	88	88	92
Ramsb. Carbon Residue, %m	13.5	-	14.0	-	13.8	-	14.2
Heptane insolubles , %m	8.8	-	9.1	-	9.3	-	10.6
Pentane insolubles , %m	9.7	12.0	11.6	12.0	11.9	13.5	13.6
Oxygen content , %m	0.84	0.55	0.57	0.40	0.41	0.51	0.48
HFT existent , %m	0.09	-	0.10	-	0.18	-	0.17
HFT potential , %m	0.08	-	0.12	-	0.13	-	0.17
P-value	1.2	-	1.2	-	1.2	-	1.2
Peptizing Power , Po	63	-	-	-	-	-	58
Flocc. tendency , FT	55	-	-	-	-	-	52

TABLE 5

Properties of Fuel C stored on 1-litre scale (at 50°C)

Storage, days	3		35		112		147	
Blanketing	air	N_2	air	N_2	air	N_2	air	N_2
Density , kg/m^3 15°C	1003	-	-	-	-	-	1006	1002
Viscosity, mm^2/s 50°C	418	413	455	424	593	474	799	552
100°C	-	-	-	-	-	-	56	43
Ramsb. Carbon Residue, %m	15.0	14.7	14.9	14.8	15.6	15.1	16.3	15.3
Heptane insolubles , %m	10.1	9.8	10.0	9.8	11.1	10.5	11.6	10.9
HFT existent , %m	0.21	0.20	0.23	0.18	0.44	0.32	0.54	0.32

TABLE 6

Fuel C stored on 1-litre scale at different temperatures

Storage condition		Microscopic	Dry sludge,
Temp. °C	Days	Inspection	%m
-	0	o	0.16
50	3	o	-
50	7	o	-
50	28	+	0.19
65	3	o	-
65	7	+	-
65	28	+++	0.37
100	3	++	-
100	7	+++	-
100	28	++++	1.7

TABLE 7

Properties of Fuel A stored on 0.3-litre scale

Storage, weeks Storage, temperature °C	0 -	13 75	52 35	52 45	52 75
Density , kg/m^3 15°C	993	-	994	994	999
Viscosity, mm^2/s 50°C	390	503	466	490	892
100°C	36	45	45	46	-
Flash point, PMcc °C	91	94	90	90	94
Ramsb. Carbon Residue, %m	14.6	14.4	14.1	14.4	15.4
Heptane insolubles , %m	8.2	9.7	9.2	9.3	11.6
Pentane insolubles , %m	9.9	13.8	13.1	13.1	14.9
Oxygen content , %m	0.4	0.4	0.42	0.47	0.55
HFT existent , %m	0.07	0.07	0.12	0.13	-
HFT potential , %m	0.07	0.07	0.18	0.25	-
P-value	1.5	1.5	1.5	1.5	1.5
Peptizing Power , Po	64	64	-	-	68
Flocc. tendency , FT	46	46	-	-	48

TABLE 8

Properties of Fuel B stored on 0.3-litre scale

Storage, weeks Storage, temperature °C	0 -	52 35	52 45	52 75
Density , kg/m^3 15°C	988	991	991	995
Viscosity, mm^2/s, 50°C	418	513	549	1035
100°C	36	43	45	66
Flash point, PMcc °C	91	92	88	94
Ramsb. Carbon Residue, %m	13.5	13.4	14.1	14.7
Heptane insolubles , %m	8.8	8.9	9.3	11.6
Pentane insolubles , %m	9.7	12.0	12.4	15.0
Oxygen content , %m	0.8	0.9	0.9	0.6
HFT existent , %m	0.09	0.10	0.12	NF*
HFT potential , %m	0.08	0.15	0.17	NF
P-value	1.2	1.2	1.2	1.2
Peptizing Power , Po	63	-	-	59
Flocc. tendency , FT	55	-	-	52

* Not filterable within one hour

TABLE 9

Effect of fuel oil additive on flocculation (60 mℓ scale)

Storage conditions days	Dry sludge content 0.1%m					
	45°C		75°C		100°C	
	Air	N_2	Air	N_2	Air	N_2
Undoped						
0	0.06	0.06	0.06	0.06	0.06	0.06
5	-	0.04	0.15	0.12	0.47	0.10
21	0.08	0.07	0.37	0.13	-	0.34
64	0.15	0.07	-	0.28	-	-
140	0.23	0.10	-	-	-	-
0.5%m dispersant						
0	0.06	0.06	0.06	0.06	0.06	0.06
5	0.02	0.01	0.05	0.02	0.05	0.02
21	0.02	-	0.05	-	0.16	0.02
64	0.06	0.04	0.22	0.05	-	0.08
140	0.08	0.05	-	0.09	-	-

TABLE 10

Effect of fuel oil additive on flocculation
(200 litre-scale, air, 80°C)

Storage conditions days	Dry sludge content 0.1%m					
	Undoped		0.2%m dope		0.5%m dope	
	Top	Bot.	Top	Bot.	Top	Bot.
0	0.06	0.06	0.06	0.06	0.06	0.06
1	0.09	0.09	-	-	-	-
2	0.10	0.07	0.02	0.02	0.04	0.04
5	0.08	1.53	0.03	0.04	0.05	0.02
14	-	-	0.06	0.08	0.04	0.03
28	-	-	0.06	0.06	0.04	0.03
64	-	-	0.06	0.27	0.06	0.06
140	-	-	0.08	0.36	0.07	0.08
189	-	-	-	-	0.10	0.16

TABLE 11

Properties of Fuels stored according to Induction Period Test

Sample	Fuel A			Fuel B		
Storage, hours	0	96	96	0	96	96
Storage atmosphere	-	O_2	N_2	-	O_2	N_2
Initial pressure, psi *	-	125	125	-	125	125
Final pressure, psi	-	81	125	-	72	125
Microscope	o	o	o	o	+	o
Viscosity, mm^2/s 50°C	487	1419	515	421	1268	433
Heptane insolubles , %	9.2	13.9	9.6	8.8	12.8	8.5
Pentane insolubles , %	13.3	18.4	13.5	9.7	16.9	11.1
P-value	1.5	1.3	1.5	1.2	<1	1.2

*) 1 psi = 6.89 $kN.m^{-2}$

TABLE 12

Effect of fuel oil additive on flocculation

Storage conditions		Time to exceed dry sludge content of 0.1%m, days		
		Undoped	0.2%m dope	0.5%m dope
Small scale:				
Storage at 100°C,	**Air**	<1	1-5	14-21
	Nitrogen	5-8	28-49	63-98
Storage at 75°C,	**Air**	1-5	14-21	28-49
	Nitrogen	<5	63-98	>140
Storage at 45°C,	**Air**	28-49	98-140	>140
	Nitrogen	>140	>140	>140
200 litre scale, 80°C:				
Top sample		>5	>140	>189
Mid sample		2-5	>140	>189
Bottom sample		2-5	28-49	140-189

Figure 1
Fuel A viscosity increase at
different storage scales/temperatures

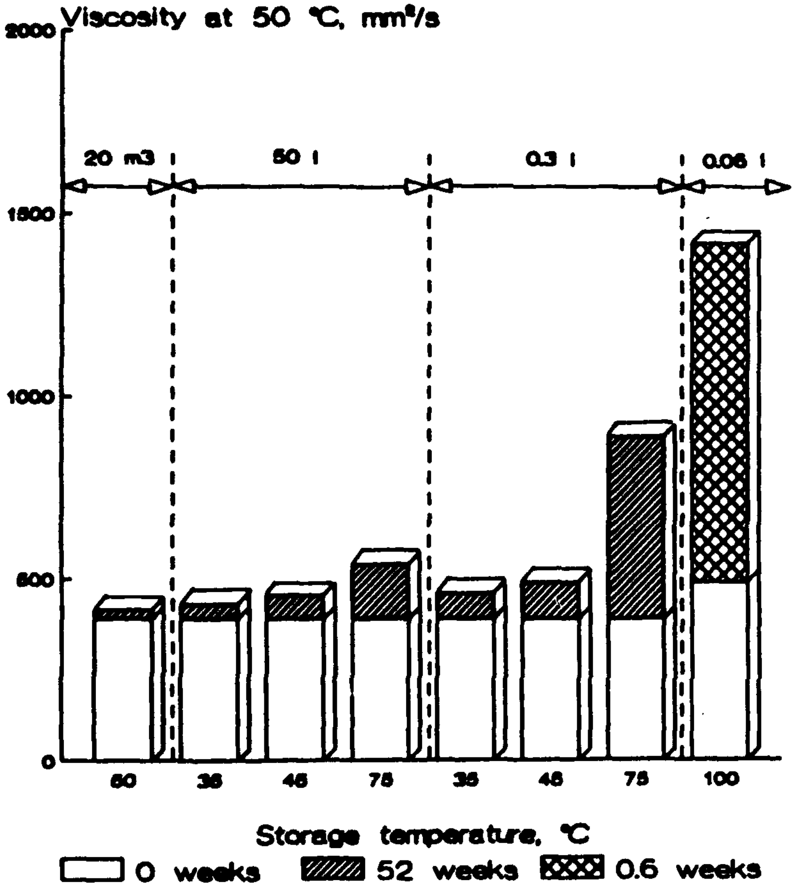
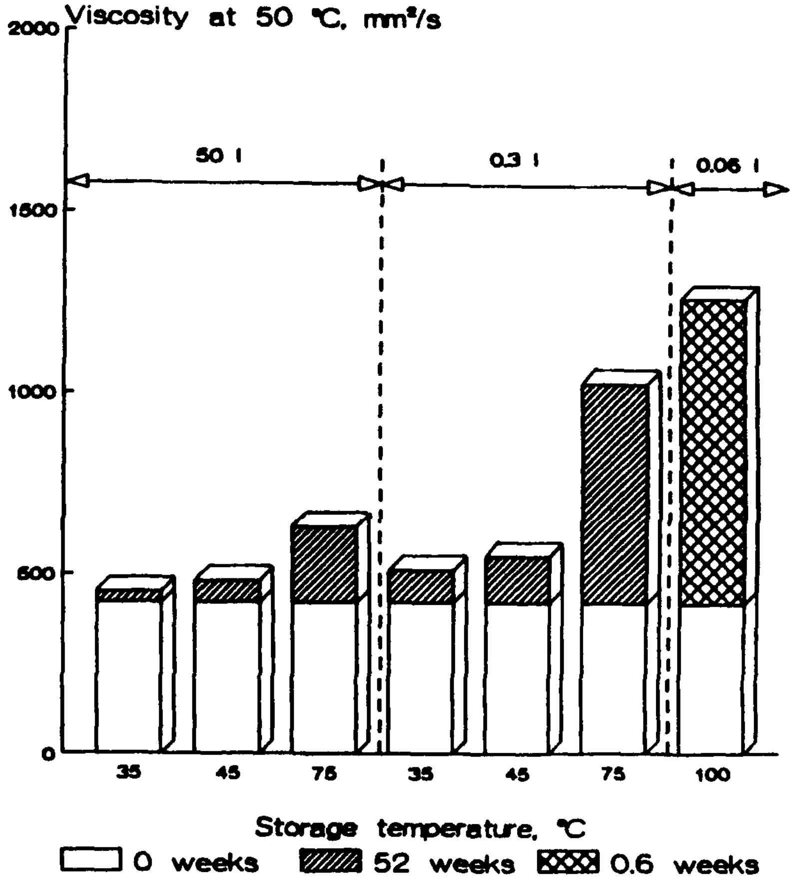


Figure 2
Fuel B viscosity increase at
different storage scales/temperatures



The Influence of Lubricating Oils on the Colloidal Stability Reserve of Residual Fuel Oils

by

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SUMMARY

In total some 200 blends of 5 residual fuel oils and 4 lubricating oils were prepared and over 500 Total Sediment determinations were carried out. The fuel characteristics covered a wide range of kinematic viscosity from 14.52 to 45.08 mm^2/s at 100° C, a variety of asphaltene contents from 0.94 to 12.21 % m/m and aromaticity levels from 22.3 to 45.2 mole % aromatic carbon.

The lubricating oils had viscosity indices ranging from 75 to 96 with aromaticity levels from 0 to 16.3 mole % aromatic carbon. The choice of lubricating oils also included varying amounts of TBN additives ranging from less than 0.05 to 28.23 mg KOH/g.

The blends prepared for F1 and F5 fuels proved totally compatible and stable, whereas blends of fuels F2, F3 and F4 showed incompatibility as determined by TOTAL SEDIMENT EXISTENT (TSE), POTENTIAL (TSP) and ACCELERATED (TSA) test methods. The analysis revealed that the margin between stability and instability relied on a very small blend concentration, with the addition of 1% by mass being sufficient to cause a sharp increase in the Total Sediment content.

It was quite clear that where incompatibility of blend components occurred, the sudden change from stability to instability was always initiated by the chemical ageing method at surprisingly low blend concentrations, followed by the thermal ageing method. It was significant that for blends recording TSP and TSA results above the 0.10% m/m maximum limit, TSE values remained acceptable until much higher concentrations of lubricating oil were reached.

A number of additional exercises were carried out to study the relationship of oil adsorption by the upper and lower filter media, the spread of the aged Total Sediment results at various levels and the extent of lubricating oil additive deposition on Whatman GF/A filter media. Also the rate of sediment change was studied at 1% increments, until the stability reserve of the blend was totally exhausted. In order to create as full a picture as possible, the blends with high concentrations of lubricating oil i.e. 50% and above, were also analysed.

The work has proved extremely promising in respect of the possible use of aromaticity factors determined by the NUCLEAR MAGNETIC RESONANCE (NMR) technique as a tool to assist in the prediction of residual fuel oil stability reserve.

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INTRODUCTION

Waste lubricating oils have been traded as fuels for some considerable time, initially as cheap fuel for use in boilers. In order to maintain the maximum price differential over the corresponding grades of residual fuels, only very basic attempts were made at removing the heaviest forms of contamination and extraneous dirt.

The rapid escalation in the standard of living in the developed countries after the second World War, principally in the area of private car ownership, meant a corresponding increase in the volume of waste lubricating oils. In addition industrial wastes in the form of cutting, transformer and hydraulic oils, were also introduced. These waste oils containing appreciable levels of heavy metals and toxic substances had embarrassing environmental characteristics. This eventually led to a total ban on their disposal on land either by ground fill or incineration.

Such restrictions gave strong impetus to the development of recycling processes aimed at recovering reusable lubricating oils, which commanded a much higher price in the market place, thus making the cost of collection and processing commercially viable. Present day recycling plants use sophisticated processes of filtration, chemical coagulation and vacuum distillation to produce reclaimed base oils of high purity, which with additive replenishment can achieve many of the properties of the original product.

In recent times the marine industry has also seen the proliferation of pollution restrictions, with the one notable exception of air pollution from combustion products. Marine bunkers have therefore become an acceptable and efficient outlet for using high sulphur fuels, and this may have led to the increasing practice of disposing waste and recycled lubricating oil effluents as a blend component of marine residual fuel oil.

It appears that to date very little information is available to define the limiting blend proportions of residual fuels with lubricating oils or how this affects the quality of the fuel oils from the end user need to treat and use the product.

Attempts to define any typical characteristics of waste lubricating oils have so far proved difficult for a number of reasons. The authors have therefore compromised in this initial investigation by using new lubricating oils having known and consistent properties.

EXPERIMENTAL DETAILS

Characterisation of Residual Fuel Oils and Lubricating Oils

The residual fuel oils were chosen on the basis of viscosity and Total Sediment content as the major variables. The selection also included variation in the refining processing route and crude oil origin to give a range of aromaticity, asphaltene types and content.

From the initial screening of approximately 25, five fuels originating from various sources were finally selected for the investigation.

Fuel No	Origin
F1	North Sea Atmospheric Residue (Forties Field)
F2	Middle Eastern Cracked Residue and Light Cycle Oil Blend
F3	North Sea Cracked Residue and Atmospheric Gas Oil Blend
F4	North Sea Cracked Residue and Light Cycle Oil Blend
F5	Heavy Stock from Deasphalting Unit and Light Cycle Oil Blend.

Particular attention was paid to the fuels' stability and cleanliness by determining the Existent, Potential and Accelerated Total Sediment. The results as set out in Table No.1 indicate that all the fuels were both stable and clean.

The four lubricating oils were new oils, which were perfectly clean as shown by the Existent Total Sediment results in Table No.2.

The individual fuels and lubricating oils, i.e. the components of the blends, were initially characterised by a series of physical and chemical analyses as shown in Tables No.3 and No.4.

Blend Preparation

Ten litre quantities of each fuel and lubricating oil were obtained. Prior to blending, fuel oil sample F1 was preheated to 47°C and the other fuel oil samples to 65 °C. Each sample was thoroughly homogenised using a high speed mixer for 30 seconds. The lubricating oil samples were similarly homogenised but without preheating.

Each blend was prepared on a mass/mass basis immediately after homogenising and remixed by a high speed mixer for 30 seconds. Blends were prepared in sufficient numbers to be analysed each day, avoiding any possibility of precipitation of asphaltenic material by prolonged storage.

Apparatus

The filtration apparatus used was not as specifically described in IP 375, but a modified version of the Stanhope-Seta Total Sediment Tester. The vacuum connections have been rearranged to provide two totally separate filtration systems with individual vacuum controlling vessels, gauges and separate outflow Buchner flasks. This modification has improved the repeatability and extended the capacity of the apparatus particularly when dealing with high volume sample through-puts.

Method and Procedures

Total Sediment Existent (TSE)

The assessment of existent stability as determined by the Total Sediment content was carried out by the Institute of Petroleum Total Sediment Method Designation IP 375/86.

IP 375 defines the Total Sediment as the sum of the organic and inorganic material separated from the bulk of a residual fuel after filtration through a Whatman GF/A filter medium, and which is insoluble in a predominantly paraffinic solvent. The scope of the method covers the determination of the total sediment up to 0.50% m/m in residual fuel oils having a maximum viscosity of 130 mm^2/s at 80°C. For the purpose of this paper the scope has been modified since it is the authors intention to show the actual extent of the instability created by the blends containing from 0 to 100% of lubricating oil. The Total Sediment measured on the unaged sample is reported as 'Existent'(TSE).

In accordance with IP 375 if filtration is not completed in 25 minutes using a 10±0.5g sample, the test should be discontinued and a further test carried out using a 5±0.3g sample. If filtration is still not completed in 25 minutes, the results should be reported as 'filtration exceeds 25 minutes'. In terms of tabulated results the authors have inserted (a) where a 5g sample was used and the symbol 'NF' (not filterable) to express the fact that filtration of 5g sample has exceeded the 25 minutes allowed.

Total Sediment Potential (TSP) and Total Sediment Accelerated (TSA)

In practice residual fuel oils undergo some thermal ageing during their storage, treatment and preheating prior to combustion. In order to rank fuels and to assess those which are likely to give potential problems during their normal lifespan two techniques are used: thermal and chemical ageing. The detailed procedures are contained in IP Proposed Method Designation BA in 1988 issue of IP Standard Methods for Analysis and Testing of Petroleum and Related Products.

Thermal ageing involves heating and maintaining the temperature of a sample at 100±0.5°C for a period of 24 hours±15 minutes.

In chemical ageing, a continuously stirred sample is diluted with 10% of hexadecane (cetane) at a maximum rate of 1 ml per minute. The sample is then heated and the temperature maintained at 100±0.5°C for a period of 60±2 minutes.

After thermal and chemical ageing each blend was tested in accordance with IP 375/86 and the Total Sediment results calculated. A correction factor for the diluent effect of the hexadecane used in the chemical ageing was applied to all test results above 0.05% m/m. The error created due to this dilution effect is not considered significant below this value.

The Total Sediment measured after thermal ageing is reported as 'Potential' (TSP) and after chemical ageing as 'Accelerated' (TSA). The objective of thermal ageing is to bring residual fuel after manufacture to full equilibrium and to subject it to an ageing process, which the fuel may receive during handling and treatment prior to use. Chemical ageing is used to assess the actual reserve of stability. This reserve can be defined as the maximum heat treatment which can be absorbed or the maximum paraffinic hydrocarbon to fuel oil ratio that can be tolerated by a particular blend, without causing asphaltene flocculation.

As the reserve of stability of a fuel oil blend is a function of the available aromaticity of the asphaltene-free oil phase and the required aromaticity of the asphaltene molecules, the residual fuel oils and lubricating oils were selected with different aromaticity levels as determined by Nuclear Magnetic Resonance (NMR) Spectroscopy. This is a fairly new technique to be applied to residual fuel oils, however, in recent years interest in the use of NMR technique for analysis of petroleum products has grown rapidly.

Carbon-13 NMR analyses were carried out on 5 fuels and 4 lubricating oils using Bruker WH400 Spectrometer and Pulse Fourier Transform (PFT) technique with a resonance frequency of 100 MHz.

For the analyses, small quantities of samples were diluted with Deuterochloroform. The inert relaxation agent, i.e., chromium (III) trisacetylacetonate was also introduced in small amounts to remove the Nuclear Overhauser Entrancement (NOE) and to reduce relaxation time. The chemical shifts were measured relative to the Deuterochloroform solvent signal taken to be at 76.9 ppm from TMS (tetramethylsilane assigned at 0 ppm). The chemical shift region for the aromatic carbons lies in the 110 - 160 ppm range and the aliphatic carbons in the 5 - 60 ppm range.

The aromatic carbon content is the ratio of the area obtained from integration of the signal between 110 - 160 ppm to an area corresponding to the total integration of aliphatic and aromatic carbons and is expressed as mole % aromatic carbon. The higher values of aromatic carbon indicate greater aromaticity.

In view of the link between the stability reserve and aromaticity of the oil phase, samples of all 5 fuels were deasphalted using the conventional technique. The aromaticity of the extracted asphaltenes was determined and the aromaticity of the asphaltene-free oil calculated. It would appear that the NMR technique allows direct measurement of the available aromaticity of the oil phase.

The aromaticity of the blend is the sum of the aromaticity of the components multiplied by their proportion in the blend. For each blend therefore, the extent of the available aromaticity can be determined.

The determination of the required aromaticity is not as simple, because it is a measure of the aromaticity needed to keep all the asphaltenes in solution. This is a function of the activity of the asphaltenes and their content. With this in mind, the aromaticity of the asphaltenes was determined.

DISCUSSION OF RESULTS

Before discussing the actual results it is thought instructive to provide details of several additional exercises which have been carried out.

Variations in Oil Adsorption Upper and Lower Filter Media

An assessment of oil adsorption was carried out on a random selection of prefiltered clean blends. The difference in the recorded weights did not exceed 1mg, which taking into account the sample size of 10g, is less than 0.01% m/m Total Sediment content. The amount of the oil adsorbed by the upper and lower filters can therefore be considered the same.

Spread of Aged Total Sediment Results

A number of duplicate determinations on aged sediment were carried out, some of which are shown below:

Blend	Test	Results %m/m
90%F2:10%L4	TSA	0.21, 0.25
95%F3: 5%L2	TSP	0.07, 0.08
95%F3: 5%L2	TSA	0.31, 0.36
86%F3:14%L3	TSA	0.24, 0.25
90%F4:10%L1	TSP	0.09, 0.08

Lubricating Oil Additive Deposition on Whatman GF/A Filter Medium

An evaluation of the retention of oil additives on the filter medium used in IP375 was carried out by determining the levels of calcium, zinc and phosphorus as set out below:-

	L1=TBN 27.82 mgKOH/g		L3=TBN 28.23 mgKOH/g	
Element mg/kg	Before Filtration	Residue on Filter (Note 1)	Before Filtration	Residue on Filter (Note 1)
Calcium	10,418	6	10,930	7
Zinc	319	3	316	3
Phosphorus	242	<1	241	<1

The residue on the filter media following TSE determination of blends F2: L1, and F3:L1 is also shown. The trace element contents of fuels F2 and F3 is given in brackets for comparative purposes:-

Element mg/kg	78%F2:22%L1 TSE 0.06% m/m Residue on Filter (Note 1)	100%F2	84%F3:15%L1 TSE 0.31% m/m Residue on Filter (Note 1)	100%F3
Calcium	14	(3)	19	(12)
Zinc	6	(<1)	4	(<1)
Phosphorus	<1	(<1)	<1	(<1)

The above indicates that no lubricating oil additives were deposited on the filter media.

Note 1 The filter media were washed in accordance with the procedure laid down by IP375, the residue was ashed and acid extracted. The resulting solution was subjected to Plasma Emission Spectrometric analysis for the determination of elements.

TEST RESULTS

F1 Blends (Table No.6)

In spite of the totally paraffinic nature of the lubricating oil L1, all the test results showed the F1 blends to be stable before and after ageing. Similar results of <0.01% m/m were obtained for lubricating oils L2, L3 and L4.

Only at concentrations of 50% did the results show actual values of 0.01% m/m and in one instance 0.02% m/m.

F2 Blends (Tables No.7 & No.8. Figs.1, 2, 3 & 4)

Blends of F2 with lubricating oils L1, L2 L3 and L4 all showed TSA results close to the limit of 0.10% m/m at concentrations of 9, 7, 22 and 9% respectively. The TSP results all reached the limiting value of 0.10% m/m at 1% to 5% higher concentrations of lubricating oil than the TSA results.

F2:L3 blends reached a maximum TSE result of only 0.02% m/m indicating existent stability at all blend proportions. The TSE results for F2 with L1, L2 and L4 exceeded the limit of 0.10% m/m at concentrations of 23, 20 and 30% respectively.

'Not-filterable' results were obtained on blends of F2 for both TSA and TSP, with the exception of F2:L3 TSP, at concentrations from 23% to 70% with the largest sequence of 'not-filterable' results recorded for F2:L2 between 10% to 75% lubricating oil concentrations.

It was also observed that all blends of F2 had lower TSP than TSA results with concentrations of up to approximately 50% lubricating oil, whereas above these concentrations the TSP exceeded the TSA results.

With the exception of TSE results for F2:L3, all other TSE, TSP and TSA results obtained on blends having lubricating oil concentrations higher than 50% did not fall below the limiting value, until the blends were essentially 100% lubricating oil.

For potentially stable blends of F2 with L1, L2, L3 and L4 the difference between TSA and TSP results did not exceed 0.07% m/m, for a given blend.

With the exception of F2:L3, all the remaining F2 blends reached the TSE limiting value at maximum of 15% and 20% higher concentrations of lubricating oil than the TSP and TSA results.

<u>F3 Blends</u> (Table No.9 & No.10. Figs. 5, 6, 7 and 8)

All blends of F3 showed incompatibility at certain proportions and in some cases the deposition of asphaltenes exceeded the capacity of the filter media, producing 'not-filterable' results after ageing.

F3 blends with L1, L2, L3 and L4 produced TSA results close to 0.10% m/m at very low concentrations of 5.5, 3, 11 and 3% respectively. The TSP results reached the limiting value at 1% to 6% greater concentrations of lubricating oil than the TSA results.

F3 blends with L3 exhibited the same behaviour as the blends of F2 with this lubricating oil, i.e. all TSE results were well below 0.10% m/m. All TSE results on F3 blends with L1, L2 and L4 exceeded the limit at concentrations of 15, 15 and 21% respectively.

'Not-filterable' results were obtained on blends of F3 for both the TSA an TSP results, at concentrations from 19% to 62%, with the greatest spread of 'not-filterable' TSA results recorded for F3:L1 between 19% and 58% lubricating oil concentrations.

As with the previous fuel, the same pattern continued in blends containing less than 50% of lubricating oil, all TSP results were lower than TSA results, and in blends having greater concentrations of this component, the TSP exceeded the TSA results.

Only with the blends of F3:L3, having lubricating oil concentrations of 80% and above, did the TSP and TSA results drop below 0.01% m/m.

The other acceptable TSA and TSP results were obtained for F3:L2 blends at lubricating oil concentrations above 90% and for F3:L1 and F3:L4 above 95%.

For potentially stable blends of F3, the maximum difference between the TSA and TSP results did not exceed 0.06% m/m for a particular blend.

With the exception of F3:L3 blends, all other F3 blends produced TSE results above the limiting value, at a maximum of 11 and 17% higher concentrations of lubricating oil than the TSP and TSA results.

F4 Blends (Table No.11 & No.12. Figs. 9, 10, 11 & 12)

All blends of F4 showed instability at certain proportions but were filterable throughout, before and after ageing.

Blends of F4 with L1, L2 , L3 and L4 showed TSA results close to 0.10% m/m at concentrations of 9%, 7%, 19% and 5.5% respectively. The TSP results reached the limiting value at 1% to 5% higher proportion of lubricating oil than the TSA results.

All TSE results on blends F4:L3 reached a maximum value of only 0.03% m/m and were perfectly stable before ageing. All other TSE results on F4 blends exceeded the limit of 0.10% m/m at concentrations of 21%, 16% and 26% respectively.

It was again observed that all blends of F4 had lower TSP than TSA results at concentrations of lubricating oil up to 50% . Above these concentrations, the TSP exceeded the TSA results.

With the exception of F4:L3 and F4:L4 TSE results all the results of F4 blends did not fall below the limiting value, until the concentration of lubricating oil in the blend exceeded 95%.

For potentially stable blends of F4 with all four lubricating oils, the maximum difference between TSA and TSP results did not exceed 0.05% m/m for a given blend.

With the exception of F4:L3 blends, all other F4 blends achieved TSE results above 0.10% m/m, at a maximum of 15% and 20% higher concentrations of lubricating oil than the TSP and TSA results.

F5 Blends (Table No.6)

Similarly to F1 blends, all F5 blends were stable before and after ageing.

With the exception of F5:L1 and F5:L2 blends at concentrations higher than 60%, results less than 0.01% m/m were obtained. These proved to have a high reserve of stability at all blend proportions.

CONCLUSIONS

The work has confirmed that the use of lubricating oil as a blend component of residual fuel has an influence on the colloidal stability of the blend. Flocculation of asphaltenes is always first indicated by the chemical ageing method at surprisingly low lubricating oil proportions in blends, followed by the thermal ageing method at 1 to 6% higher concentrations of lubricating oil.

The results clearly show the large differential, in the blend proportions, 15% and 20%, for the TSE results to reach the limiting values as compared with TSP and TSA results. Therefore it is clear that quality control procedures relying solely on TSE results are not sufficient if severe end user problems caused by instability are to be avoided. A good example of this is illustrated by the consistently low TSE results of all L3 blends.

For stable blends the maximum difference between the TSA and TSP result was 0.07% m/m, whereas for unstable blends the differences were much larger.

In all cases where the blends approached the margin of stability the addition of 1% lubricating oil created a sudden increase in the Total Sediment content.

Much more work is required to establish the relationship between the aromaticity level and the stability resevere of residual fuel oils, by NMR. However it would appear significant that fuel F1, having a low content of asphaltenes with a higher aromaticity, and fuel F5, having an average content of asphaltenes of a much lower aromaticity, both produced totally compatible aged and unaged blends.

A recent study of the characteristics of fuel samples received world wide shows a slow but progressive increase of the blending of waste and effluent lubricating oils with marine bunkers. Recent comments by suppliers attempting to justify this practice would tend to support this and even suggest an escalation of this practice in the future.

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TOTAL SEDIMENT RESULTS

RESIDUAL FUEL OILS

TEST	F1	F2	F3	F4	F5
TSE	<0.01	0.01	0.01	0.01	<0.01
TSP	<0.01	0.03	<0.01	<0.01	<0.01
TSA	<0.01	0.05	0.04	0.01	<0.01

TABLE No.1

LUBRICATING OILS

TEST	L1	L2	L3	L4
TSE	<0.01	<0.01	<0.01	<0.01

TABLE No.2

Fuel Oil Characteristics

PROPERTY	METHOD	F1	F2	F3	F4	F5
PHYSICAL DATA: Density @15°C kg/l	IP 160	0.9295	0.9900	0.9863	09965	1.0164
Viscosity @100°C mm^2/s	IP 71	14.52	45.08	30.04	35.05	36.67
Viscosity @ 50°C mm^2/s	IP 71	90.00	618.61	649.11	418.56	467.00
Micro Carbon Residue %m/m	ASTMD4530	3.95	17.15	13.87	13.32	17.20
Ash Content %m/m	IP 4	0.014	0.029	0.015	0.013	0.027
Pour Point °C	IP 15	+ 32	+ 2	+ 5	+11	- 19
Water Content %v/v	IP 74	0.05	0.10	0.09	0.08	0.05
Sediment Content %m/m	IP 53	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Asphaltenes Content %m/m	IP 143	0.94	12.21	6.50	6.39	5.63
ELEMENTAL DATA: Carbon %m/m	ELEMENTAL	86.98	85.73	88.07	88.37	86.10
Hydrogen %m/m	ELEMENTAL	11.88	10.70	10.52	10.32	9.40
C/H ratio	—	7.3	8.0	8.4	8.6	9.2
Sulphur Content %m/m	IP 336	0.74	3.20	0.89	0.83	4.10
Nitrogen Content %m/m	KJELDAHL	0.40	0.37	0.52	0.48	0.40
AROMATICITY: 1) Before deasphalting Aromatic Carbon mole%	NMR	22.3	33.4	34.6	39.4	45.2
2) After deasphalting Aromatic Carbon mole%	NMR	22.0	29.1	33.0	37.5	45.1
3) Asphaltenes Aromatic Carbon mole%	NMR	60.5	67.1	66.6	67.6	46.7

Table No. 3

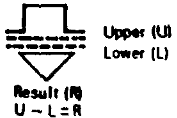
Lubricating Oil Characteristics

PROPERTY	METHOD	L1	L2	L3	L4
PHYSICAL DATA: Density @15°C kg/l	IP 160	0.8941	0.8893	0.9306	0.9139
Viscosity @40°C mm^2/s	IP 71	98.45	104.25	116.71	123.90
Viscosity @100°C mm^2/s	IP 71	11.00	11.36	11.29	11.53
Viscosity Index	ASTMDS 39B	96	95	78	75
Water Content %v/v	IP 74	< 0.05	< 0.05	< 0.05	< 0.05
Total Base Number mgKOH/g	IP 276	27.82	9.10	28.23	< 0.05
ELEMENTAL DATA: Carbon %m/m	ELEMENTAL	83.28	84.98	82.30	84.90
Hydrogen %m/m	ELEMENTAL	13.52	13.53	12.56	12.89
C/H ratio	—	6.2	6.3	6.6	6.6
Sulphur %m/m	PES*	0.40	0.40	2.06	1.80
AROMATICITY: Aromatic Carbon %mole	NMR	0	7.2	14.8	16.3

* PES - Plasma Emission Spectrometry

Table No. 4

Test Results



F 1

Lube oil No.	Test	Blend Lubricating oil:Fuel, % m/m 5	10	20	30	50	90	95
L1	TSE	<0.01				0.01	<0.01	
	TSP					0.01		
	TSA					0.02		
L2	TSE					0.01		
	TSP					0.01		
	TSA					0.01		
L3	TSE					0.01		
	TSP					0.01		
	TSA					0.01		
L4	TSE					0.01		
	TSP					0.01		
	TSA					0.01		

Table No. 5

F 2

Lube oil No.	Test	Blend Lubricating oil:Fuel, % m/m 5	10	20	30	50	90	95
L1	TSE	0.01	0.01	0.01	6.10 (a)	6.33 (a)	0.45	0.42
	TSP	0.01	0.02	1.84	NF	NF	2.19	0.45
	TSA	0.02	0.45	1.91	NF	NF	1.75	0.20
L2	TSE	0.01	0.01	0.11	1,97 (a)	3.36 (a)	0.71	0.25
	TSP	0.01	0.03	NF	NF	NF	2.43	0.42
	TSA	0.02	NF	NF	NF	NF	0.91	0.21
L3	TSE	<0.01	<0.01	<0.01	0.02	0.02	<0.01	0.01
	TSP	0.01	0.01	0.02	0.23	2.10	0.01	0.02
	TSA	0.02	0.01	0.02	NF	NF	0.01	0.02
L4	TSE	0.02	0.01	0.01	0.29	1.76 (a)	0.03	0.05
	TSP	0.01	0.01	NF	NF	NF	0.41	0.33
	TSA	0.02	0.21	NF	NF	NF	0.28	0.22

a - Sample size 5g NF = Not filterable

Table No. 7

F 5

Lube oil No.	Test	Blend Lubricating oil:Fuel, % m/m 5	10	20	30	50	90	95
L1	TSE	<0.01					0.05	0.04
	TSP						0,06	0.08
	TSA						0.04	0.06
L2	TSE						0.05	0.01
	TSP						0.08	0.06
	TSA						0.07	0.05
L3	TSE							
	TSP							
	TSA							
L4	TSE							
	TSP							
	TSA							

Table No. 6

F 2

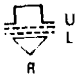
Lube oil No.	Test		Blend Lubricating oil:Fuel, % m/m 9		11		22		23	
L1	TSE	 U L R	0.09 0.08	0.01	0.10 0.09	0.01	0.18 0.12	0.06	0.49 0.21	0.28 (a)
	TSP		0.10 0.09	0.01	0.19 0.09	0.10	2.49 0.18	2.31	NF	
	TSA		0.17 0.08	0.09	0.85 0.13	0.72	5.27 1.14	4.13	NF	
			7		8		11		19	
L2	TSE	 U L R	0.09 0.08	0.01	0.06 0.04	0.02	0.08 0.07	0.01	0.10 0.06	0.04
	TSP		0.08 0.06	0.02	0.06 0.04	0.02	0.30 0.09	0.21	NF	
	TSA		0.16 0.07	0.09	0.5[illegible] 0.15	0.39	NF		NF	

Table No 8

Test Results

F 3

Lube oil No.	Test	Blend Lubricating oil: Fuel, % m/m 5	10	20	30	50	90	95
L1	TSE	< 0.01	0.01	0.62	1.82(a)	2.76(a)	0.35	0.04
	TSP	0.02	0.29	1.70	NF	NF	0.73	0.03
	TSA	0.07	0.57	NF	NF	NF	0.60	0.02
L2	TSE	0.02	0.02	0.33	0.78(a)	1.49(a)	0.07	0.04
	TSP	0.08	0.40	1.21	NF	NF	0.08	0.05
	TSA	0.31	0.86	2.23	NF	NF	0.08	0.05
L3	TSE	0.01	0.01	0.01	0.01	0.03	0.02	0.01
	TSP	0.01	0.01	0.15	0.32	NF	0.02	0.01
	TSA	0.02	0.05	0.39	0.65	NF	0.02	0.01
L4	TSE	0.02	0.01	0.08	0.45(a)	0.86(a)	0.06	0.02
	TSP	0.04	0.19	0.57	NF	NF	0.30	0.11
	TSA	0.22	0.44	0.83	NF	NF	0.25	0.10

a = Sample size 5g NF = Not filterable

Table No. 9

F 4

Lube oil No.	Test	Blend Lubricating oil: Fuel, % m/m 5	10	20	30	50	90	95
L1	TSE	< 0.01	0.01	0.06	0.58 (a)	2.85 (a)	0.90	0.67
	TSP	< 0.01	0.09	1.08	3.41	8.03	1.10	0.26
	TSA	< 0.01	0.28	1.69	4.50	5.46	0.91	0.14
L2	TSE	0.01	0.02	0.30	1.60	2.09	0.38	0.10
	TSP	0.02	0.17	0.71	3.68	5.03	0.52	0.24
	TSA	0.05	0.38	1.22	3.92	4.73	0.36	0.19
L3	TSE	< 0.01	< 0.01	< 0.01	0.01	0.03	0.02	0.02
	TSP	0.02	0.01	0.02	0.28	0.63	0.01	0.01
	TSA	0.03	0.02	0.17	0.42	0.52	0.01	0.01
L4	TSE	0.02	0.01	0.08	0.39	0.68	0.07	0.02
	TSP	0.01	0.05	0.51	0.83	2.44	0.29	0.17
	TSA	0.05	0.25	0.64	1.45	1.83	0.14	0.13

a = Sample size 5g NF = Not filterable

Table No. 11

F 3

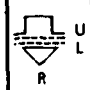
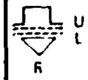
Lube oil No.	Test		Blend Lubricating oil: Fuel, % m/m			
			6	7	14	15
L1	TSE	 U L R	$\frac{0.05}{0.04}$ 0.01	$\frac{0.05}{0.04}$ 0.01	$\frac{0.17}{0.09}$ 0.08	$\frac{0.39}{0.08}$ 0.31
	TSP		$\frac{0.13}{0.04}$ 0.09	$\frac{0.28}{0.06}$ 0.22	$\frac{0.73}{0.08}$ 0.65	$\frac{0.91}{0.10}$ 0.81
	TSA		$\frac{0.35}{0.04}$ 0.31	$\frac{0.48}{0.04}$ 0.44	$\frac{0.96}{0.05}$ 0.91	$\frac{1.77}{0.09}$ 1.68
			11	13	14	15
L3	TSE	 U L R	$\frac{0.04}{0.03}$ 0.01	$\frac{0.03}{0.02}$ 0.01	$\frac{0.04}{0.03}$ 0.01	$\frac{0.03}{0.02}$ 0.01
	TSP		$\frac{0.03}{0.02}$ 0.01	$\frac{0.16}{0.09}$ 0.07	$\frac{0.19}{0.09}$ 0.10	$\frac{0.18}{0.06}$ 0.12
	TSA		$\frac{0.17}{0.03}$ 0.14	$\frac{0.23}{0.03}$ 0.20	$\frac{0.27}{0.03}$ 0.24	$\frac{0.33}{0.07}$ 0.26

Table No. 10

F 4

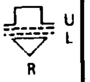
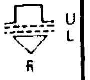
Lube oil No.	Test		Blend Lubricating oil: Fuel, % m/m			
			7	8	15	16
L2	TSE	 U L R	$\frac{0.06}{0.04}$ 0.02	$\frac{0.05}{0.04}$ 0.01	$\frac{0.07}{0.05}$ 0.02	$\frac{0.22}{0.09}$ 0.13
	TSP		$\frac{0.10}{0.06}$ 0.04	$\frac{0.12}{0.04}$ 0.08	$\frac{0.69}{0.12}$ 0.57	$\frac{0.70}{0.10}$ 0.60
	TSA		$\frac{0.17}{0.08}$ 0.09	$\frac{0.23}{0.04}$ 0.19	$\frac{0.85}{0.08}$ 0.77	$\frac{0.90}{0.08}$ 0.82
			6	11	25	26
L4	TSE	 U L R	$\frac{0.06}{0.05}$ 0.01	$\frac{0.05}{0.04}$ 0.01	$\frac{0.13}{0.05}$ 0.08	$\frac{0.24}{0.06}$ 0.18
	TSP		$\frac{0.07}{0.05}$ 0.02	$\frac{0.15}{0.04}$ 0.11	$\frac{0.76}{0.05}$ 0.71	$\frac{0.86}{0.08}$ 0.78
	TSA		$\frac{0.23}{0.04}$ 0.19	$\frac{0.40}{0.06}$ 0.34	$\frac{0.97}{0.11}$ 0.86	$\frac{0.99}{0.09}$ 0.90

Table No. 12

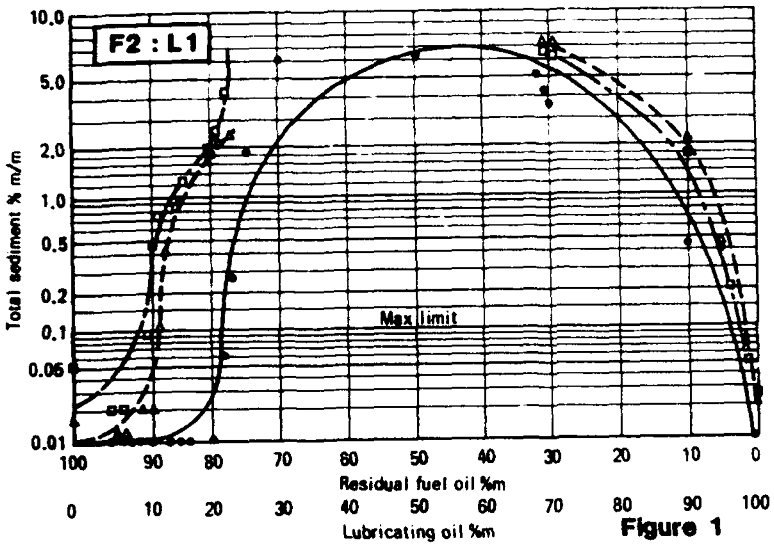


Figure 1

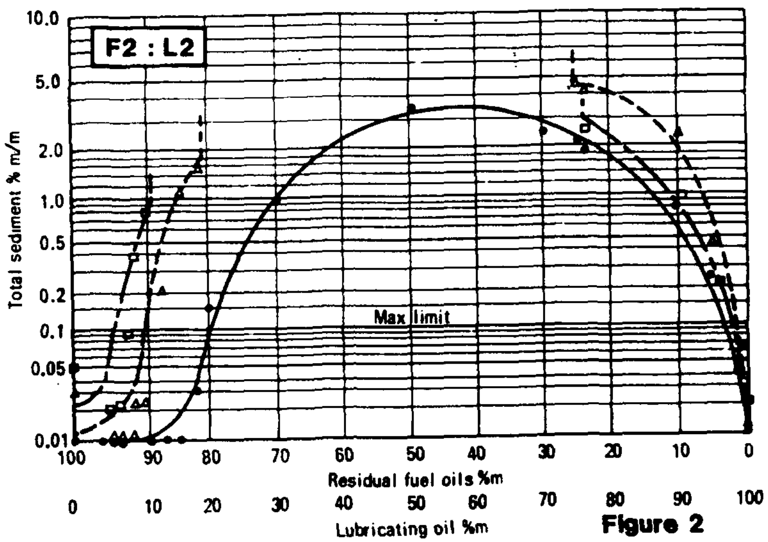


Figure 2

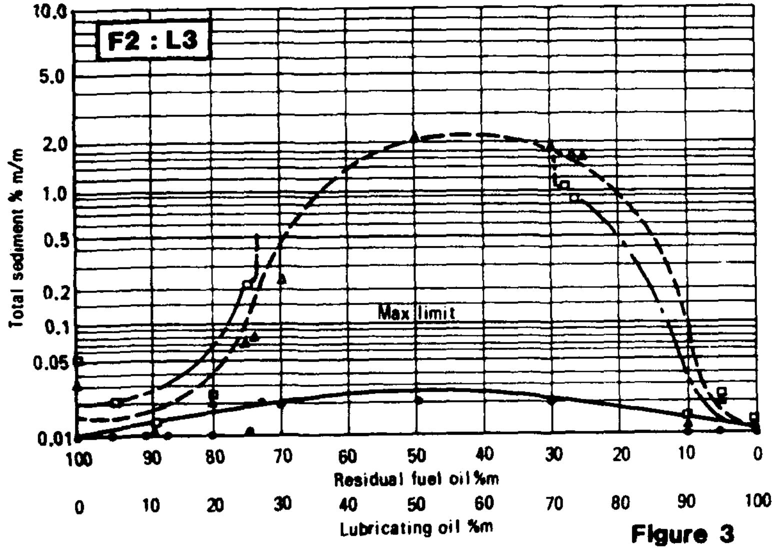


Figure 3

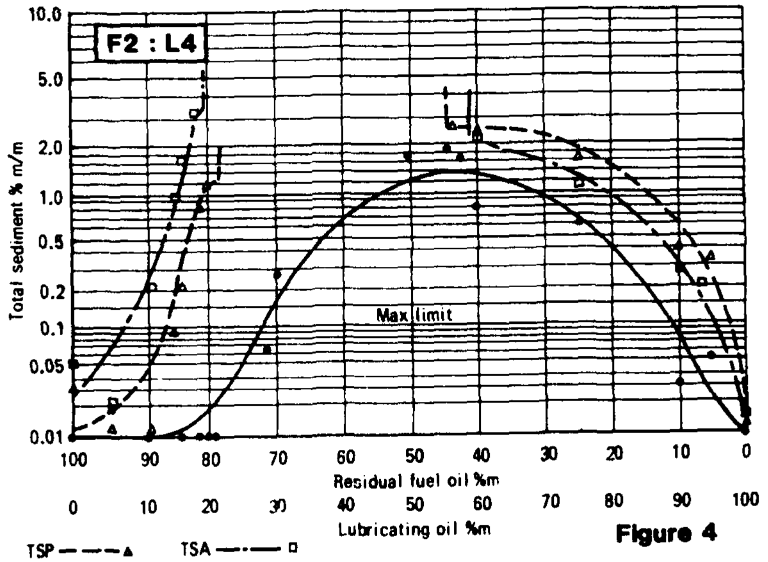


Figure 4

TSE ——● TSP – – –▲ TSA —·—□

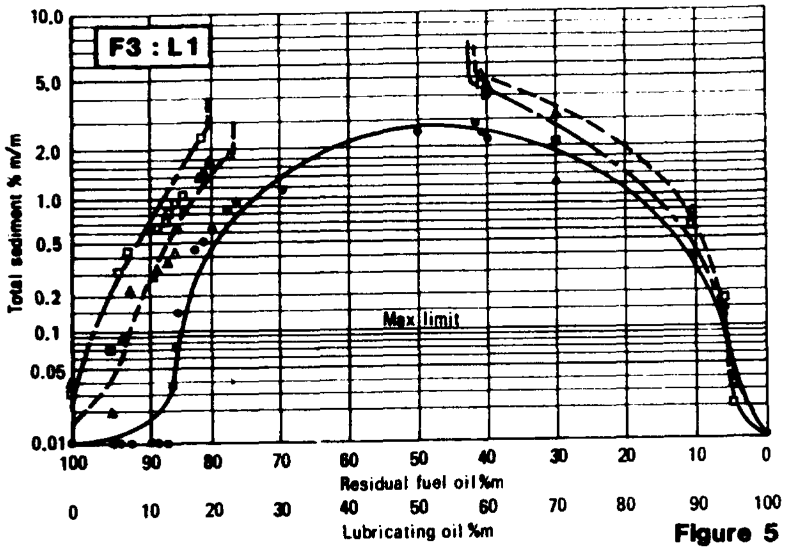
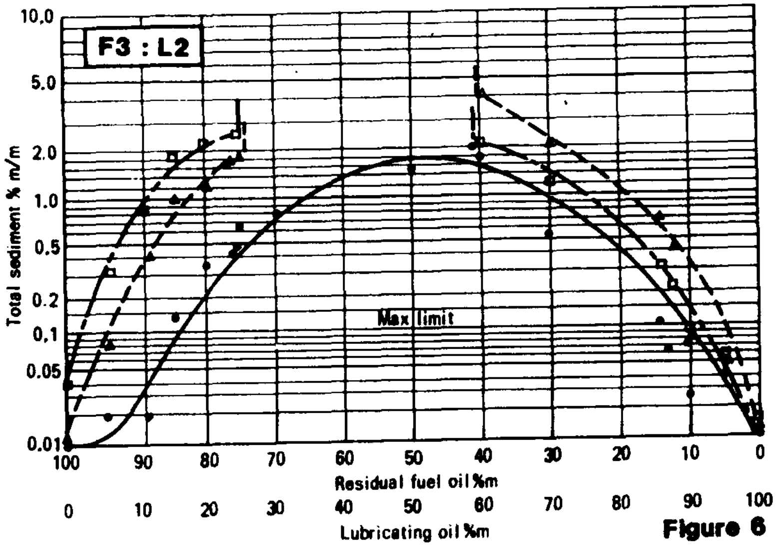


Figure 5



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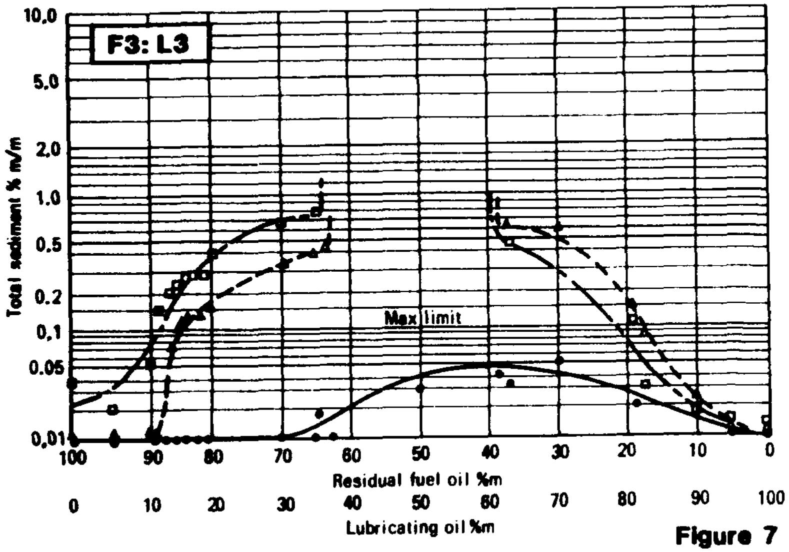

Figure 7

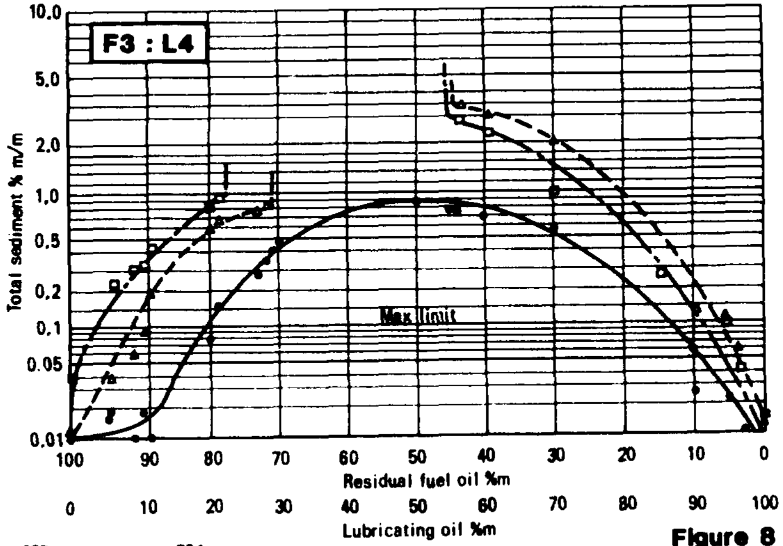

Figure 8

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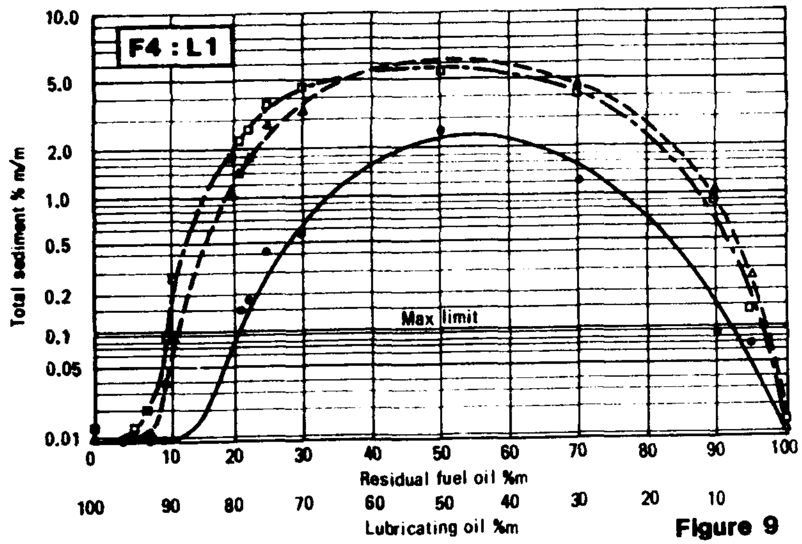

Figure 9

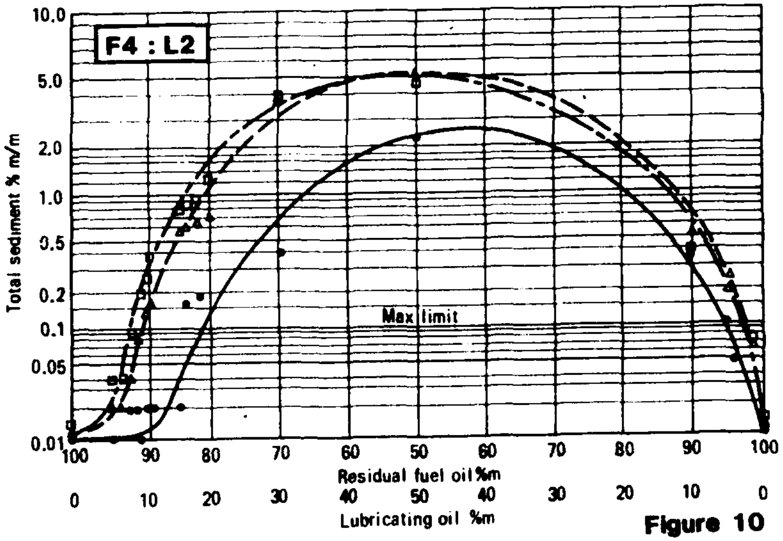

Figure 10

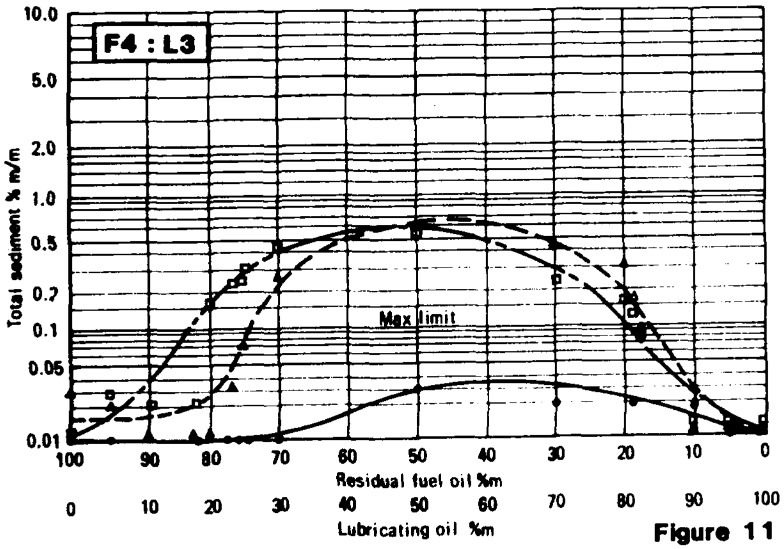

Figure 11

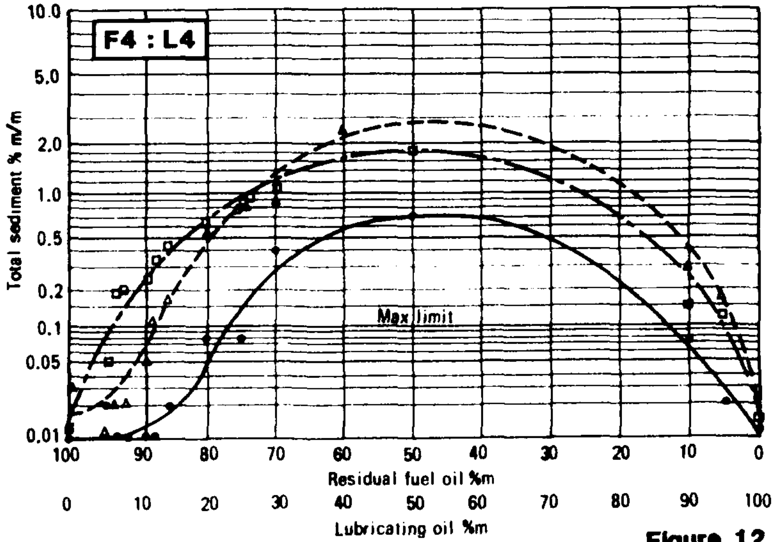

Figure 12

TSE —— ● TSP - - - ▲ TSA —·— □

THE THIRD INTERNATIONAL CONFERENCE ON
STABILITY AND HANDLING OF LIQUID FUELS
13th - 16th SEPTEMBER 1988

QUALITY OF FUELS FORMED BY SEVERE HYDROTREATMENT OF VACUUM RESIDUES

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ABSTRACT

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

Petroleum vacuum residue was severely hydroprocessed in various reaction conditions (395-420°C, LHSV=0.20 h^{-1}, H_2 pressure=130 kg/cm^2, feed rate=150 cc/h) in the presence of a hydrodesulfurization catalyst by a two-stage microreactor. The 538°C+ conversion reached to 57% at the most severe reaction condition. The sludge formed during the hydroprocessing as well as heavy ends (350°C+ and 538°C+) produced by the hydroprocessing were structurally characterized. The storage stability of the products were also discussed.

INTRODUCTION

Acidic nitrogen and oxygen functionalities involved in such heavy molecules as asphaltene in petroleum crude oil are known to show the marked surface-active properties (1,2). The presence of such acidic species was found to enhance the formation of water-oil (W/O) emulsion, which is responsible for the sludge formation during long-term storage of crude oil (3). The solution infra-red spectroscopic technique (4-6) has been developed for the quantitative analysis to characterize the heteroatom functionalities involved in heavy ends derived from various hydrocarbon resources.

In the present study, such polar functionalities as acidic NH group and OH group are quantitatively analyzed for vacuum residues of various petroleum crude oil, compared with those involved in other hydrocarbon resource such as oilsand bitumen, shale oil, coal liquefaction products and coal pyrolysis tar. Structural change of such polar groups caused by various conditions of hydroprocessing has been also discussed. Petroleum vacuum residue was severely hydroprocessed in the presence of a hydrodesulfurization catalyst. The sludge formed during the hydroprocessing as well as heavy ends remainning hydroprocessed product are structurally analyzed. The storage stability of heavy-end (350°C+) is discussed relating to the polar functionalities involved in the products.

EXPERIMENTAL

Infra-red spectra of heavy ends from various resources are analyzed in very dilute solution of carbon disulfide using 2 cm KBr liquid cells and recorded in the region of 2800-4000 cm^{-1} on a JASCO IR-810 infra-red spectrometer. Various OH and NH vibration modes are appeared clealy in the spectrum without broadening due to hydrogen bonding, as shown in Fig. 1, where each absorption is ascribed to a certain specific mode (4-6).

RESULTS AND DISCUSSION

A typical IR spectrum of petroleum vacuum residue is shown in Fig. 2(b). The major functionality involved in Vz-VR (vacuum residue separated from Venezuera crude oil) is found to be acidic nitrogen (pyrrole type), though the spectrum (Fig. 2a) gives no information about heteroatom functionality due to the broadening of the peak by hydrogen bonding. The IR spectra of vacuum residues from other crude oils (KU= Kuwait, AJ=Agha Jari (Iran), and TK=Taching (Chaina)) are summarized in Fig. 3. The existence of phenolic oxygen (3600 cm^{-1}) is also observed in the spectra. The relationship between the contents of total and acidic nitrogen is shown in Fig. 4. The plot for AB-VR (VR separated from Athabasca Bitumen) is also on the line. These VR fractions were hydrotreated in the presence of a hydrodesulfurization catalyst (395°C, LHSV=1.0 h^{-1}). The polar functionalities remainning in vacuum residues separated from the hydrotreated products were analyzed (Table 1). The ratio of acidic nitrogen to total nitrogen is increased after hydrotreatment, which shows acidic nitrogen to be more difficult to remove than other type of nitrogen. Fig. 5 and 6 show the structural change of heteroatom functionalities involved in AB-VR in the different reaction conditions of hydrotreatment. AB-VR is characteristic for having various OH species, which could be removed only in higher reaction temperature of 395°C. Acidic nitrogen containing in AB-VR is much difficult to remove and such species is condensed into heavy ends in the hydrotreated product.

The polar functionalities involved in the corresponding fraction derived from shale oil is also analyzed and the structural change caused by the hydrotratment is also examined (Table 2 and Fig. 7). On the contrary to petroleum VR, nitrogen involved in shale oil is relatively easy to remove. Acidic nitrogen is rather easier to be removed and hydrotreated oil at 380°C has no substantial heteroatom functionality.

Arabian Light VR fraction was severely hydroprocessed in the presence of a hydrodesulfurization catalyst (Fig. 8). Sample 3 is obtained at the most severe reaction temperature of 420°C and the 538°C+ conversion reached to 57%, whereas 42% for Sample 2 and 35% for Sample 1, respectively. At the reaction condition where Sample 3 was formed, the considerable amount of dry sludge is involved in the hydroprocessed oil. Experimental analysis of feed and residual oils (350°C+ and 520°C+) is summerized in Tabla 3. H/C atomic ratio of residual oils is higher than that of feed VR, which indicates hydrocracking reaction occured substantially even in the most severe reaction conditions. Residual oil (350°C+) is separated from the hydroprocessed product and subjected to stand at 100°C in the presence of oxygen. The amount of dry sludge (SHFT) formed during storage was measured at an adequate interval (Fig. 9). The residual oil recovered at more severe hydroprocessing condition shows less stable, judging from the formation of SHFT dry sludge. The result of component analysis for feed VR and residual oils is summerized in Table 4. The decrease of asphaltene fraction as well as resin fraction is clearly shown in the Table. The structural analysis for the sludge isolated from the hydroprocessed oil immediately after the reaction at 420°C as well as the sludge formed during the storage at 100°C shows that both sludges are mainly composed of wax including microcrystal wax (C_{45}+) (7). The insufficient amount of heteroatom functionalities remaining in asphaltene and resin fractions involved in residual oil may responsible for the formation of dry sludge for Sample 3 (8).

ACKNOWLEDGEMENT

This study was partly supported by a grant from The Japan Petroleum Institute and Agency of Natural Resources and Energy, MITI Japan. The authors are indebted to Mr. Tosiaki Hisamitsu, Nippon Mining Co., Ltd. and Mr. Sin-ichi Simizu, Chiyoda Chemical Engineering and Construction Co., Ltd. for stimulating discussions and for preparing of hydroprocessed samples.

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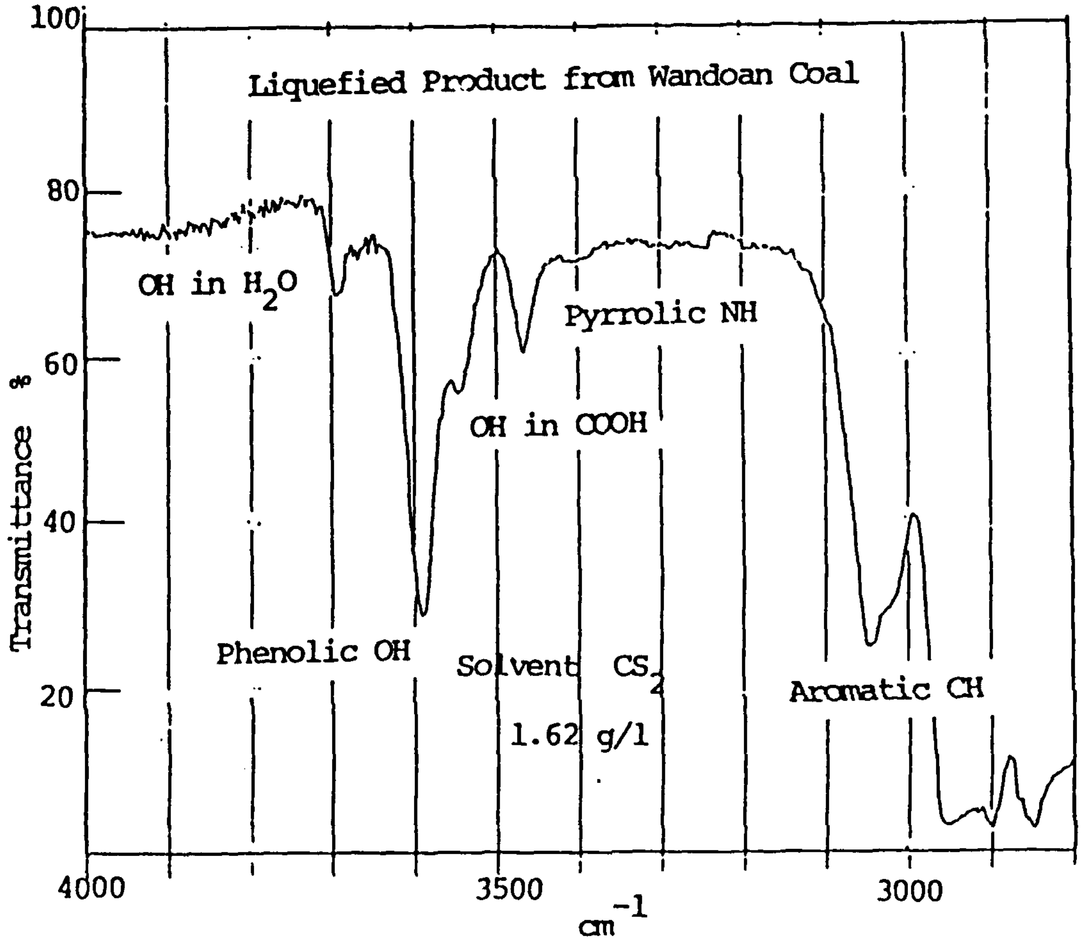


Fig. 1 Solution IR Spectrum of Heavy Distillate
(340 - 450 °C)

Fig. 2(a) IR Spectrum of VZ-VR
(thin film between NaCl plates)

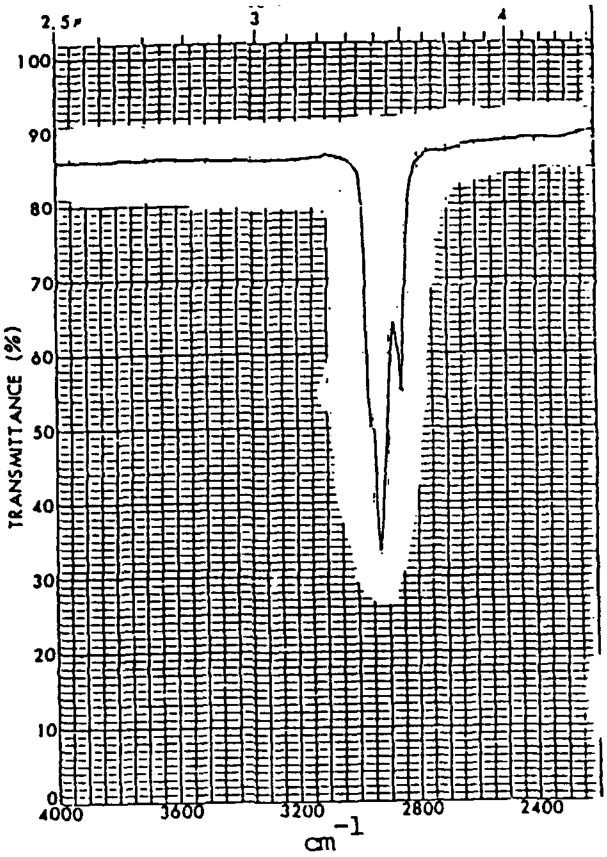
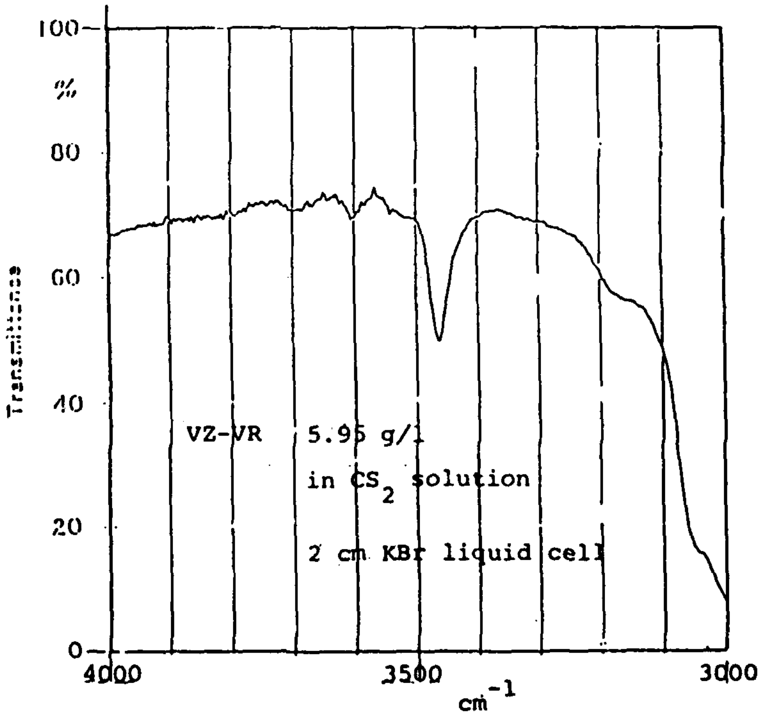


Fig. 2(b) Spectrum of VZ-VR in Dilute CS_2 Solution



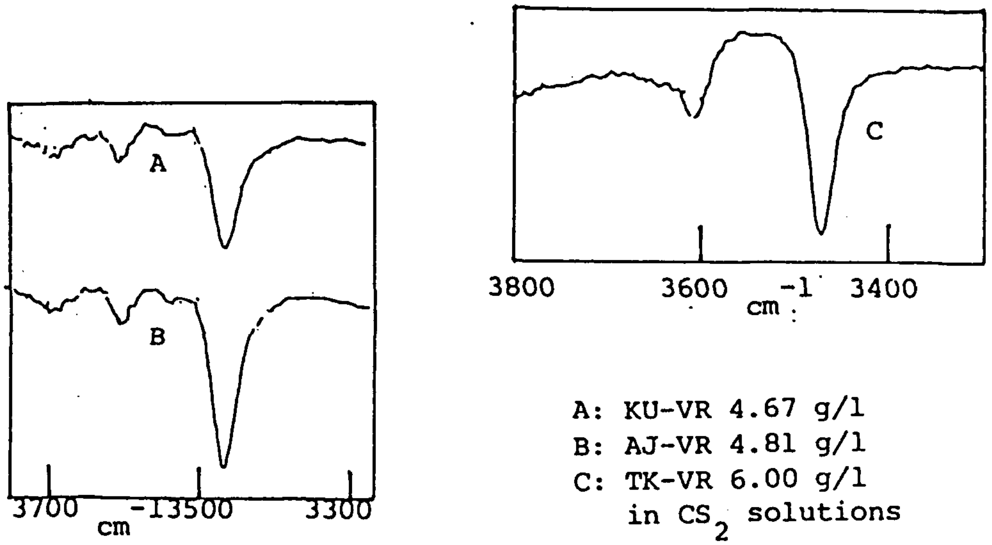


Fig. 3 IR Spectra of Crude Oil-VR in Dilute CS_2 Solutions

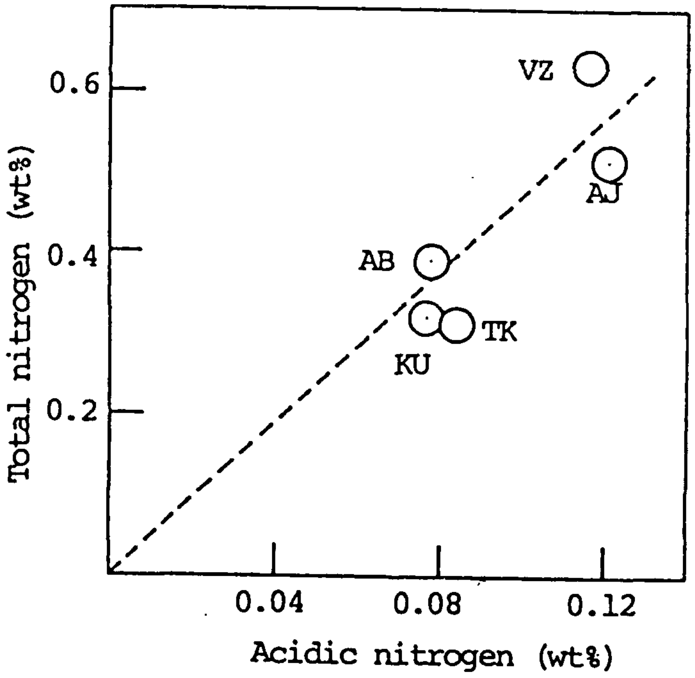
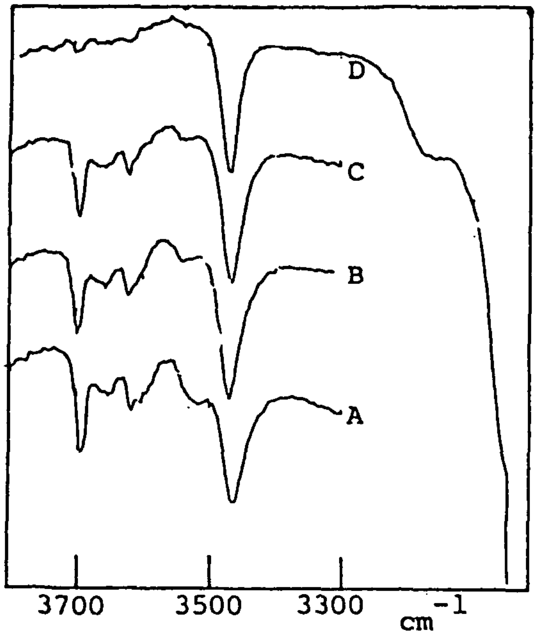


Fig. 4 Contents of Total and Acidic Nitrogen in Crude Oil-VR

Fig. 5 Solution IR Spectra of Athabasca Bitumen and its Hydrotreated Oils



A: AB-VR 7.07 g/l

B: Hydrotreated AB-VR
340.5 °C, 1.00 h^{-1}
6.57 g/l

C: 365.4 °C, 1.01 h^{-1}
5.99 g/l

D: 394.9 °C, 0.99 h^{-1}
5.08 g/l

in CS_2 solution

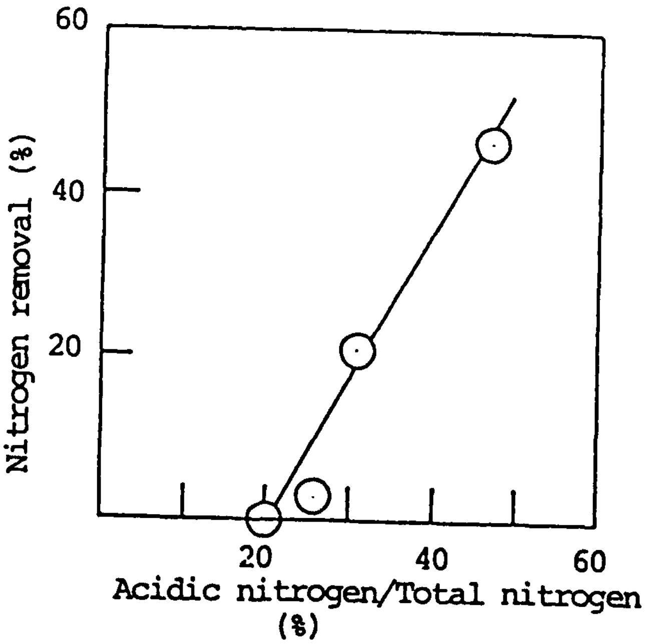


Fig. 6 Removal of Nitrogen by Hydrotreatment of AB-VR

Table 1 Content of Acidic Nitrogen (wt%)

VR	total N (wt%)	A*	M*	acidic N (wt%)	$\frac{\text{acidic N}}{\text{total N}}$
TK-VR	0.31	0.1012	$2.99\text{x}10^{-4}$	0.08_4	27 %
KU-VR	0.32	0.0935	$2.76\text{x}10^{-4}$	0.07_7	24
AB-VR	0.39	0.0938	$2.77\text{x}10^{-4}$	0.07_8	20
AJ-VR	0.51	0.1461	$4.32\text{x}10^{-4}$	0.12_1	24
VZ-VR	0.63	0.1405	$4.15\text{x}10^{-4}$	0.11_6	18

Hydrodesulfurization at 395°C, LHSV=1.0 hr^{-1}

	total N (wt%)	A*	M*	acidic N (wt%)	$\frac{\text{acidic N}}{\text{total N}}$
AB-HDS	0.21	0.1194	$3.53\text{x}10^{-4}$	0.09_8	47 %
TK-HDS	0.27	0.0978	$2.89\text{x}10^{-4}$	0.08_1	30
KU-HDS	0.27	0.1084	$3.20\text{x}10^{-4}$	0.09_0	33
AJ-HDS	0.39	0.1632	$4.82\text{x}10^{-4}$	0.13_4	35
VZ-HDS	0.48	0.1492	$4.41\text{x}10^{-4}$	0.12_3	26

Removal of nitrogen at various temperatures

	total N (wt%)	N removal (%)	acidic N (wt%)	$\frac{\text{acidic N}}{\text{total N}}$
AB-VR	0.39	——	0.07_8	20
AB-HDS 340°C	0.38	2.6	0.09_8	26
AB-HDS 365°C	0.31	20.5	0.09_7	31
AB-HDS 395°C	0.21	46.2	0.09_8	47

	total N (wt%)	N removal (%)	acidic N (wt%)	$\frac{\text{acidic N}}{\text{total N}}$
TK-VR	0.31	——	0.08_4	27
TK-HDS 340°C	0.31	0.0	0.08_4	27
TK-HDS 365°C	0.30	3.2	0.08_4	28
TK-HDS 395°C	0.27	12.9	0.08_1	30

A* : absorbance at 3470 cm^{-1} of 5.00 g/l solution

M* : concentration of acidic N-H group (mol eq./l) of 5.00 g/l solution

Table 2 Total and Acidic Nitrogen in Geokinetics Shale Oil and its Hydrotreated Oils at Various Temperatures

	Total nitrogen wt%	Acidic nitrogen wt%	Acidic/Total %
Feed Shale Oil	1.44	0.23_0	16
HDT Oil 340°C	0.83	0.12_2	15
HDT Oil 360°C	0.46	0.06_8	15
HDT Oil 380°C	0.18	0.02_5	14

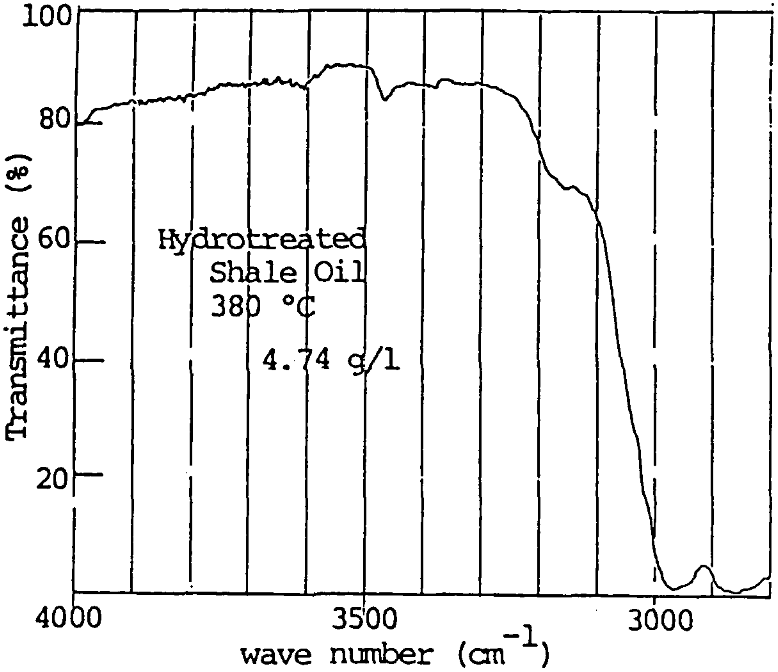
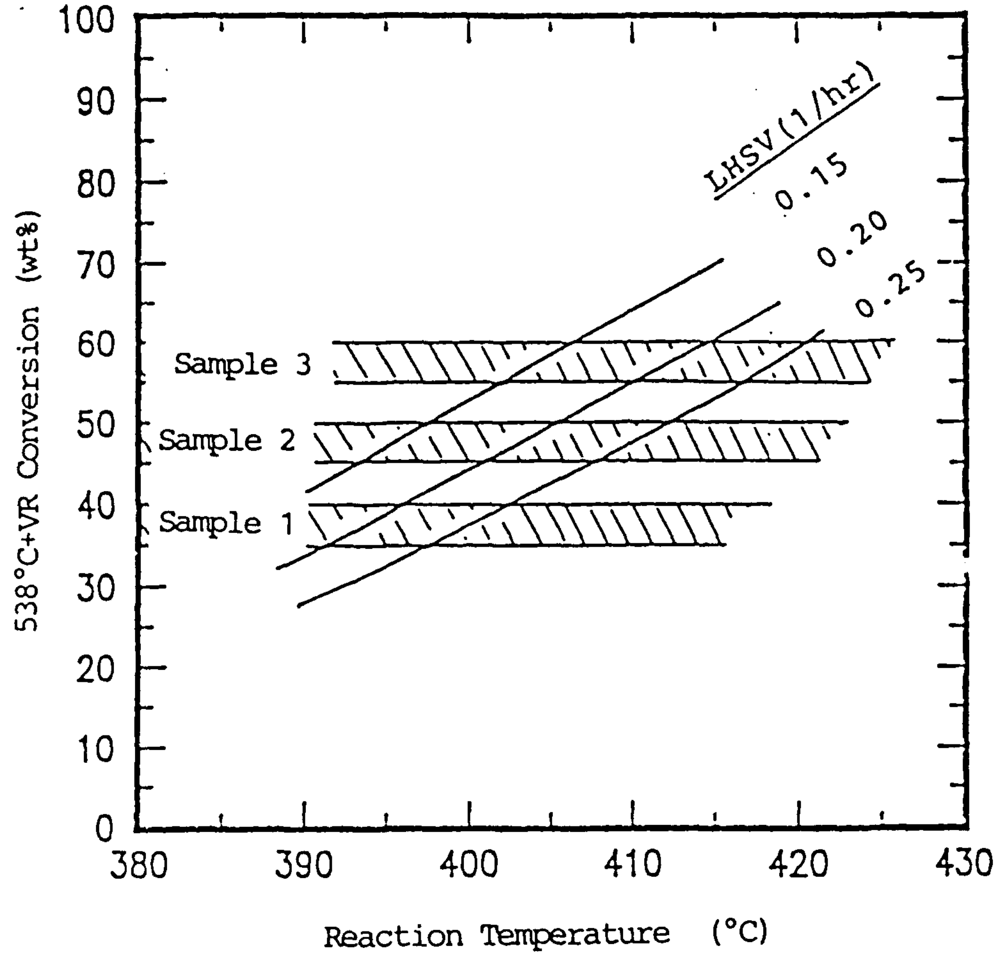


Fig. 7 Solution IR Spectrum of Hydrotreated Shale Oil

Fig. 8 Hydrocracking of Arabian Light VR



Reaction Conditions:

Hydrogen Pressure:	130	kg/cm^2
Hydrogen/Feed Ratio:	1,000	Nm^3/kl
Reaction Temperature:	380-420	°C
LHSV:	0.20	1/hr

Table 3 Experimental Analysis of Feed and Residual Oil in Hydrocracking of Arabian Light VR

	C	H	S	N	O	H/C
Feed VR	85.6	10.5	3.35	0.34	0.2	1.46
350°C+ Sample 1	88.0	11.8	0.35	0.19	0.1	1.59
350°C+ Sample 2	87.8	11.7	0.27	0.18	0.3	1.58
350°C+ Sample 3	88.2	11.7	0.24	0.20	0.1	1.58
520°C+ Sample 1	87.8	11.7	0.42	0.20	0.2	1.59
520°C+ Sample 2	88.0	11.7	0.34	0.19	0.1	1.58
520°C+ Sample 3	87.8	11.6	0.33	0.21	0.1	1.57

C,H,S,N,O: wt%, H/C: Atomic ratio

Fig. 9 Formation of Dry Sludge (SHFT) under Storage at 100°C

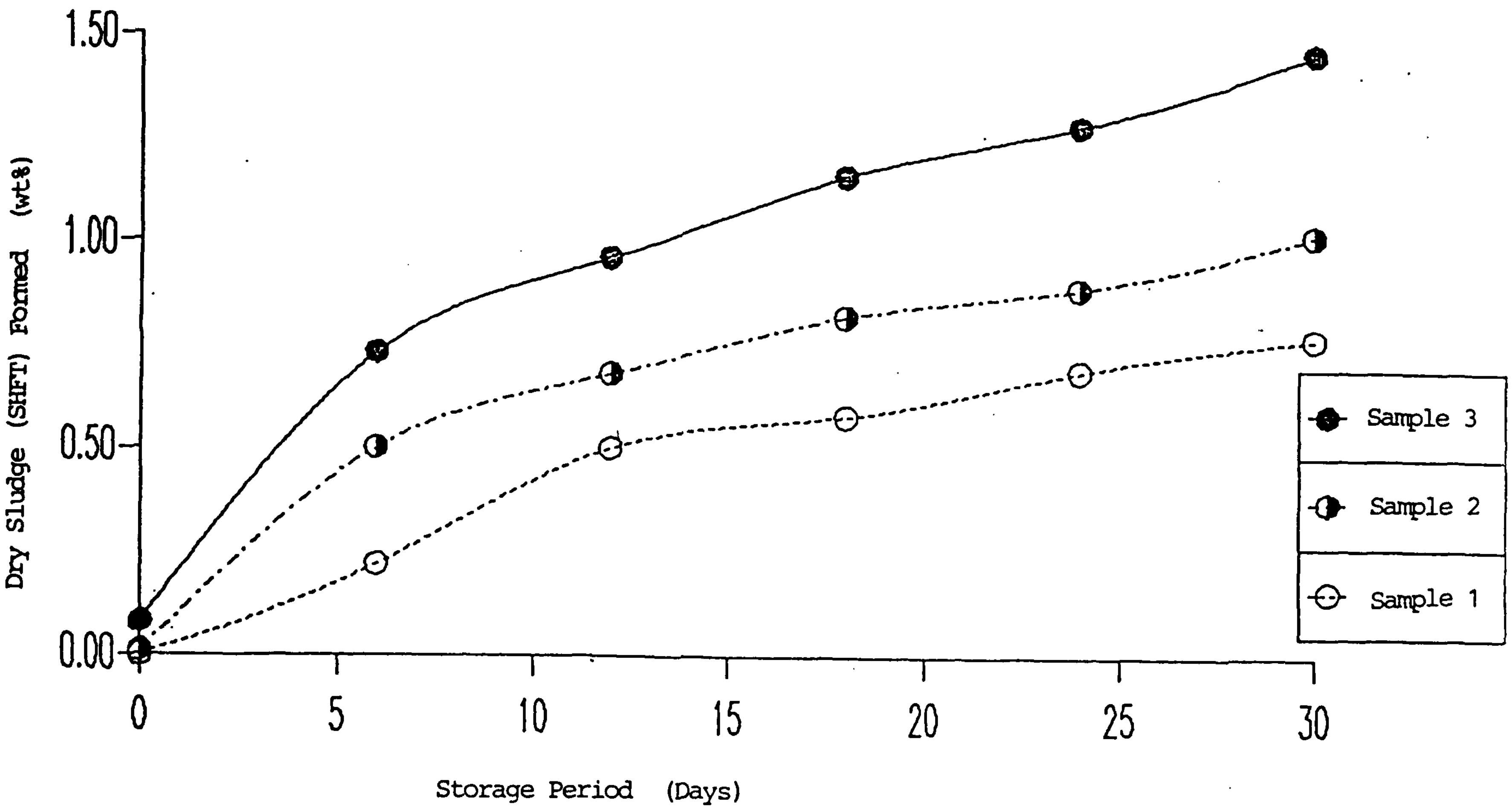


Table 4 Component Analysis of Feed and Residual Oil in Hydrocracking of Arabian Light VR

	Sat wt%	Aro wt%	Res wt%	Asp wt%	Recovery %
Feed VR	16.8	52.6	21.5	8.9	99.8
350°C+ Sample 1	49.3	39.7	8.6	1.9	99.5
350°C+ Sample 2	52.3	37.4	8.4	1.3	99.4
350°C+ Sample 3	54.9	34.9	7.8	1.4	99.0
520°C+ Sample 1	43.3	43.3	10.9	2.6	100.1
520°C+ Sample 2	44.8	41.8	10.6	2.5	99.7
520°C+ Sample 3	45.5	40.0	11.1	2.9	99.5

Sat=Saturates, Aro=Aromatics, Res=Resin
Asp=Asphaltene

3rd International Conference on
Stability and Handling of Liquid Fuels,
The Institute of Petroleum,
London, Great Britain, September 13-16, 1988

BIODEGRADATION OF STORED HEAVY FUEL OIL WITH PRODCUTION OF METHANE IN UNLINED ROCK CAVERNS

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Summary

During storage of heavy fuel oil on a waterbed in unlined rock caverns for long periods of time problems with degradation of oil and production of methane gas have been observed. In order to understand the factors responsible for the microbial methane production and to find methods to inhibit the methanogenic bacteria a study was undertaken.

Chemical and microbiological investigations at two storage plants where problems had occured showed that anaerobic conditions existed in the bedwater and that a complex microbial community was present. The methane production was calculated to be 2-37 g/day, m^3 bedwater. To study methods to inhibit the methanogenic activity laboratory model systems were used. Four methods were evaluated which were increasing the oxygen level in the bedwater, increasing the pH to 9, using a biocide an isothiazolone compound or addition of nitrate. It was found that only nitrate addition gave a satisfactory inhibition at a concentration of 0.5 g/l in the water.

INTRODUCTION

In Sweden a large number of rock caverns have been used for long-term storage of different petroleum products. The principle of storage is that a cavity is created by blasting in the rock below the groundwater table. This cavity, usually in the form of a horizontal tunnel, is pumped free of water and filled with petroleum products. The products are stored on a waterbed and the groundwater pressure prevents the products from leaking out of the caverns.

During the storage of heavy fuel oil for long periods of time in unlined rock caverns on a fixed waterbed problems have in a few cases been observed. The water content of the oil has increased, emulsions have been formed at the water oil interphase, waxy sludges have settled on the bottom of the caverns and methane production has been observed. The methane production has caused special concern because the storage systems are not adequately equipped to be safe in the presence of explosive gases. Increasing the ventilation rate has so far been the way of handling the problem (1).

In order to understand the factors responsible for the microbial methane production and to investigate methods to inhibit the methanogenic bacteria a study was undertaken. This paper presents data on chemical and microbiological analysis at two storage plants where methane production has been noted. It also shows the results from studies to evaluate different methods to inhibit the methanogenic activity in laboratory model systems simulating the conditions in rock caverns.

MATERIALS AND METHODS

Water samples from rock caverns or model systems were collected and analysed within one day in most cases. Chemical parameters in the bed-water were analysed as follows. Sulfide was analysed using the methylene blue method (2). Sulfate was analysed according to Tabatabai (3). Dissolved oxygen was measured using the Winkler method, the biochemical oxygen demand BOD_7, chemical oxygen demand COD and total organic carbon according to standard methods (4). Nitrate was analysed by ion chromatography, and methane was measured with a gaschromatograph (Hewlett-Packard model 5880) equipped with a thermal conductivity detector and a Purapack N column (Alltech Associates). Values for oxygen consumption, sulfate consumption and sulfide production in the rock caverns were calculated by comparing the concentration of each parameter in the incoming water with that in the bedwater. Methane production in rock caverns was calculated from Low Explosion Limit vaslues (100 % LEL represents 5.3 % methane) and the amount of gas that was ventilated away.

For the enumeration of microorganisms the following methods and media were used. Aerobic bacteria, spread plate on Tryptone Glucose Extract Agar with 0.5 g/l cycloheximide; Fungi, spread plate on Malt Extract Agar with 0.5 g/l maleate; Anaerobic bacteria, shake tubes in Thioglycolate medium (Oxoid) with 1.5 % agar; Sulfate-reducing bacteria (SRB), Most Probable Number (MPN) technique with five tubes per dilution in Postgate's medium B (5); Hydrocarbon - utilizing microorganims. MPN teechnique with three tubes per dilution (6) in Bushnell Haas broth (7). Methanogenic bacteria were determined using a MPN technique with three tubes per dilution in a media described by Rönnow and Gunnarsson (8), vials showing methane production significantly above background were scored as positive. To measure some metabolic activities radiorespirometric methods were used. The total aerobic heterotrophic activity was measured by using ^{14}C-glutamate and following the conversion to CO_2 after 8 h incubation (9). The oil degrading activity was measured by using ^{14}C-hexadecane or ^{14}C-naphthalene and following the mineralization to CO_2 after 14 days incubation (6).

To study methods to inhibit the methanogenic activity model systems were constructed to imitate the situation in rock caverns. The model systems consisted of a glass cylinder and two stainless steel end plates with holes for sampling and a size of 2.5 litre. Each fermentor like system was filled with heavy fuel oil, water and sludge from a rock cavern. The amount of fuel was 200 ml and the amount of water was 1800 ml including the sludge. The systems were incubated at 50°C in the dark and before any inhibition method was tested the systems must show methane production. Samples were taken monthly and analysed. The amount of water removed when sampling was replaced by equivalent amounts of autoclaved water to simulate the leakage of water in a cavern. The biodegradable bicide tested was Kathon (10.1 % 5-chloro-2-methyl-4-isothiazolin-3-one and 3.8 % 2-methyl-4-isothiazolin-3-one) which was added at a concentration of 100 ppm active ingredient. The nitrate used was calcium nitrate and in order to increase the pH sodium hydroxide was used.

RESULTS AND DISCUSSION

Investigations in rock caverns

Chemical and microbial investigations were undertaken at two plants with heavy fuel oil. The two plants were situated on the east coast (FO-K) and the west coast of Sweder (FO-S). FO-K has seven caverns and FO-S has nine caverns. Samples of bedwater in the caverns and groundwater surrounding the caverns were analysed. The results for some of the caverns are shown in table 1. The other caverns showed similiar results.

As can be seen the level of dissolved oxygen was very low in the bedwater which showed that close to anaerobic conditions existed in the caverns. The detection of higher levels of both anaerobic sulfate-reducing bacteria and methanogenic bacteria in the bedwater than in the leakage water also confirmed the anaerobic conditions. In the caverns low numbers of aerobic bacteria and hydrocarbon utilizers were detected in contrast to the leakage water where levels of 10^4-10^6 aerobes/ml were found. This is probably due to that the heterotrophic and hydrocarbon degrading activity was limited by the rate of oxygenated groundwater leaking in to the caverns.

Table 1. Physico-chemical and microbiological analysis of bedwater in rock caverns plants with heavy fuel oil.

	Plant		FO-K			FO-S	
Parameter	Cavern	1	2	5	1	3	8
Dissolved oxygen mg/l		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sulfate mg/l		1.7	3.5	4.4	4.2	5.9	1.2
Sulfide mg/l		0.5	1.7	1.2	1.0	0.6	2.0
Methane mmol/l		0.2	0.5	0.6	0.8	1.0	0.9
BOD_7 mg/l		18	17	13	55	25	13
COD mg/l		340	110	280	84	122	63
TOC mg/l		78	22	46	20	33	23
Aerobic bact/ml		0	60	770	80	920	3300
Fungi/ml		0	0	0	0	0	0
SRB/ml		13	13	160	22	49	79
Methanogens/ml		0.9	<0.3	46	0.9	9	0.3
Hydrocarbon utilizers/ml		< 3	3	< 3	<0.3	0.4	<0.3
Heterotrophic activity % CO_2		0.04	0.4	0.2	0.2	15	33

All the data shown in table 1 are from analysis of bedwaters in the caverns. We also analysed the surrounding groundwater (table 2). It was then possible to calculate the proportions of some important microbial processes in the caverns by using leakage rate, bedwater volumes and chemical differences between incoming water and bedwater. The results of these calculations are shown in table 3. Methane production was calculated from Low Explosion Limit values and the ventilation rate.

Table 2. Chemical parameters of groundwater surrounding the plants used for calculations of different microbial processes. G-FO-K: groundwater surrounding the plant FO-K, G-FO-S: groundwater surrounding the plant FO-S.

Parameter groundwater	G-FO-K[1]	G-FO-S
dissolved oxygen mg/l	4.4	6.4
sulfate mg/l	60	492
sulfide mg/	0	0

[1] Mean of four groundwater analysis

Table 3. Values of oxygen consumption, sulfate consumption and sulfide production calculated by comparing the concentration of each parameter in the inflowing water and the bedwater. Methane production was calculated from Low Explosion Limit (LEL) values and the ventilation rate.

Parameter	Plant		FO-K			FO-S	
	Cavern	1	2	5	1	3	8
Leakage rate m^3/day		0.7	5.8	2.5	3.5	2.5	3.5
Bedwater volume m^3		4000	5100	7600	1500	1500	1500
Oxygen consumption mg/m^3 day		0.8	5.0	1.4	14.9	0.7	14.9
Sulfate consumption mg/m^3 day		10	64	18	1140	810	1150
Sulfide production mg/m^3 day		0.1	1.9	0.4	2.3	0.9	4.7
Ventilation rate m^3/h		920	940	760	885	2215	885
LEL %		6	6	3	1	3	4.9
Methane g/m^3 day		11.5	8.9	2.3	4.9	37	4.9

A comparison between the two plants showed that sulfide production and methane production, as calculated per m^3 bedwater, were comparable and that a slightly higher oxygen consumption was noted in FO-S. The heterotrophic activity was also somewhat higher in FO-S. The large difference in the calculated sulfate consumption between the two plants could probably be due to that it was only possible to analyze one groundwater sample at the FO-S plant. This sample showed a very high sulfate content and also a high chloride content (data not shown) indicating a high degree of seawater. The sample might therefore not be representative of the water leaking in to the caverns for this plant.

Studies in model system

In order to evaluate methods to inhibit the methane production laboratory model systems simulating the situation in rock caverns were constructed.

Five systems were set up which contained sediment, water and fuel oil, and four of these were used for inhibition experiments and one was used as a control. Before an inhibition experiment was started the systems had to reach a steady state and show methane production which took about five months.

The methods tested were
- aeration,
- increasing the pH to 9,
- biodegradable biocide, an isothiazolone compound
- addition of nitrate.

Aeration

Aeration was chosen as methanogens are strict anaerobes and an increase in the oxygen level in the water might inhibit their activity and it had previously been shown that this method gave a satisfactory result when minimizing problems with production of hydrogen sulfide by anaerobic bacteria when storing jet fuel (10). Bedwater in one model was circulated and oxygenated by aerating the water. After one month oxygen was detected in the water and a level of 1 mg/l dissolved oxygen could be obtained.

It was found that it was difficult to increase the oxygen level in the water due to the rapid oxygen consumption at 50°C. The number of aerobes including hydrocarbon degraders increased and the number of anaerobes including methanogens in the water decreased but this had little effect on the methane production after 72 days (table 4). Oxygenating the water could not inhibit methane production under these conditions. The reason for this was probably that the main methane producing activity was concentrated in the sediment and then aerating the water had limited effect.

Increasing the pH to 9

Methanogens have a growth optimum between pH 6 to 8, why it was investigated if an increase in pH to 9 could decrease methane production. After 247 days it was found that there was no major change in the number of aerobes or methanogens in water or sediment. There was a decrease in the number of SRB's and a small increase in number of hydrocarbon degraders. It could be concluded that under these conditions an increase in pH to 9 was not sufficient to inhibit the methanogens as hoped.

Table 4. Chemical and microbial analysis in model system with heavy fuel oil. A. Oxygenation of bedwater by circulating water and adding air. B. Increasing the pH of the bedwater to pH 9. Temperature 50°C. SRB = sulfate-reducing bacteria.

	A days		B days	
Parameters	0	72	0	247
pH	7.0	8.4	7.1	8.8
Oxygen mg/l	0	1.3	0	0
Sulfate mg/l	2.9	18.0	3.9	5.0
Aerobic bacteria/ml	$4.0 \cdot 10^3$	$6.9 \cdot 10^5$	$4.6 \cdot 10^3$	$1.1 \cdot 10^4$
Hydrocarbon degr./ml	9.2	$1.1 \cdot 10^3$	$2.1 \cdot 10^1$	$2.1 \cdot 10^3$
SRB water/ml	$1.4 \cdot 10^3$	4.9	$1.6 \cdot 10^3$	9
SRB sediment/ml	-	-	$4.7 \cdot 10^3$	$2.3 \cdot 10^2$
Methanogens water/ml	$4.7 \cdot 10^2$	4.3	$1.2 \cdot 10^2$	$4.3 \cdot 10^1$
Methanogens sediment/ml	$1.8 \cdot 10^4$	$4.3 \cdot 10^2$	$1.4 \cdot 10^4$	$7.5 \cdot 10^2$

Dosing with biodegradable biocide

During studies of microbial problems when storing jet fuel in rock caverns it was found that dosing the bedwater with an isothiazolone compound gave a satisfactory inhibition of SRB activity and H_2S production. The same compound was tested in one of the model systems at a concentration of 100 ppm active ingredient but it was found that the compound was not stable at 50°C. An analysis showed that the half life of the compound at this temperature was only 2.6 days and no inhibitory effect was found in the system why further tests were abandoned.

Addition of nitrate

It is known that electron acceptors like nitrate and other oxidated nitrogen compounds can inhibit methanogenic bacteria in sediments (11,12). The mechanism behind the effect is not quite clear although an increase in redoxpotential in the sediment can be one explanation.

The inhibitory concentration needed was tested by taking out sediment and water from model systems and adding different concentrations of nitrate in serum vials. The amount of methane was monitored at 50°C for 14 days. Based on this a concentration of 50 mg/l was chosen for test in model systems. A test was run up to 243 days with a concentration of 50 mg/l nitrate. It was found that the level of nitrate rapidly decreased in the system and that most was consumed in one months time. When samples were collected, every month, additional amounts of nitrate were supplied to keep up the level of nitrate. A tendency could be seen that the number of methanogens decreased in both the water and sediment but that methane was still produced. No other change in other microbiological parameters were found.

To further investigate the effect of nitrate addition a model system was dosed with 500 mg/l nitrate. An analysis of the water showed that the level in the system stabilized at 330 mg/l. This indicated a consumption rate of 200 mg/month,liter. The test showed a marked effect and after one month no methanogens could be detected and no methane gas production. It was also found that the number of aerobic bacteria including hydrocarbon degraders decreased and one effect of this was that the level of dissolved oxygen in the water increased (table 5).

Table 5. Addition of nitrate 500 mg/l to model system and at each sampling time extra nitrate was added to keep up the concentration. Summary of microbiological and chemical parameters. SRB = sulfate-reducing bacteria.

Parameter	0	28	57	91
pH	7.0	7.5	7.3	7.4
Dissolved oxygen mg/l	0	0	7.5	1.1
Nitrate mg/l	<0.1	119	380	445
Aerobes/ml	$7.4\cdot10^5$	$1.6\cdot10^5$	$5.0\cdot10^3$	$1.1\cdot10^3$
SRB H_2O/ml	$6.1\cdot10^1$	$5.4\cdot10^2$	$3.0\cdot10^2$	$3.5\cdot10^2$
SRB-sediment/ml	$4.4\cdot10^3$	$9.2\cdot10^3$	$5.4\cdot10^3$	$9.2\cdot10^3$
Methanogens H_2O/ml	0.9	<0.3	<0.3	<0.3
Methanogens sediment/ml	9	<0.3	<0.3	<0.3
Hydrocarbon degraders/ml	$2.4\cdot10^3$	$4.6\cdot10^3$	$2.1\cdot10^1$	$2.1\cdot10^1$

To further confirm these results the addition of nitrate was stopped in the system which resulted in that the concentration of nitrate decreased from 445 mg/l to 36 mg/l in 57 days and after 77 days methanogens could again be detected in the sediment and methane in the gasphase.

In the system where nitrate had been added to a concentration of 50 mg/l the level of nitrate addition was increased to 500 mg/l which also resulted in a decrease in the level of methanogens in the bedwater and sediment.

In conclusion it has been shown that the methane production observed in rock caverns where heavy fuel oil had been stored for long periods was caused by microbial activity in the bedwater and bottom sediment. Due to the storage principle oxygen and nutrients were continuously supplied with the groundwater leaking in. In the bedwater hydrocarbon degrading microorganisms degrade the oil which is observed as a rapid oxygen consumption. Due to the oxygen limited conditions the hydrocarbon degradation will not be complete and degradation products like fatty acids can be used by the anaerobic bacteria like methanogens.

It has also been shown that methane production occurs in rock caverns where heavy fuel oil is stored at around 50°C and the amount produced varied from 2 to 37 g/m³ bedwater, day.

In model systems simulating the conditions in rock caverns it could be shown that nitrate addition at a concentration of 0.5 g/l inhibited methane production and decreased significantly the number of methanogens. The number of hydrocarbon degrading bacteria also decreased somewhat. From these results it can be recomended to test nitrate addition in a full scale cavern in order to evaluate the method.

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

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Introduction (1)

MIL-S-53021 is the military specification for stabilizer additive, diesel fuel. This specification is approved for use by all departments and Agencies of the U.S. Department of Defense. The specification covers a stabilizer additive for use in diesel fuels meeting the requirement of the Federal specifications for fuel oil and diesel which are intended for intermediate or long-term storage. The stabilizer additive shall consist of petroleum-soluble compounds which perform the following functions: (a) antioxidant stabilizer, (b) metal deactivator, (c) dispersant, (d) corrosion inhibitor, and (e) biocide. The reference formulation of the stabilizer additive given in the military specification consists of DuPont Fuel Oil Additive FOA-15 and Biobor JF (U.S. Borax), where the FOA-15 covers, as listed above, the functions (a) through (d), and Biobor JF function (e).

ANGUS Chemical Company completed a test program to meet the specifications outlined in MIL-S-53021 for stabilizer additive diesel fuel, as well as tests to show the efficacy of FUELSAVER as a biocide. The combination of DuPont's FOA-15 and FUELSAVER was approved for inclusion in the qualified products list 53021 in October 1986.

General

The studies carried out to comply with MIL-S-53021 revealed FUELSAVER to be equal to or better than the approved biocide in the reference formulation in that it (a) has low water solubility, (b) does not readily decompose in contact with water, (c) has a good particion coefficient, (d) is compatible with most diesel fuel stabilizers, eliminating the need for a two-package stabilizer additive system, and (e) it is soluble in most hydrocarbons.

FUELSAVER has been registered by the U.S. Environmental Protection Agency under number 48301-7AA.

Although the U.S. Military approved stabilizer additives consists of two components, most of this paper will deal with studies on the antimicrobial compound as inclusion of DuPont's FOA-15 is (1) a requirement under MIL-S-53012, and (2) the product has no or neglible antimicrobial activity, and (3) FUELSAVER, as is, is of interest for non-military applications.

Biocide Description

FUELSAVER (2) is formed from the reaction of nitropropane, formaldehyde and tetrahydro-1,4-oxazine by a Mannich condensation reaction. Due to the molar ratios of the raw materials employed the final product does not contain any free formaldehyde, nor does it release formaldehyde in its antimicrobial action.

The active constituents of FUELSAVER are 4-(2-nitrobutyl)morpholine, CAS-Reg.No. 2224-44-4 / EINECS No. 2187483, and 4,4'-(2-ethyl-2-nitrotrimethylene)dimorpholine, CAS-Reg.No. 1854-23-5 / EINECS No. 2174500.

Physical characteristics of FUELSAVER are to be found in Table I, a summary of the toxicological data in Table II.

Table I

Physical Characteristics of FUELSAVER

	ASTM No.	Results
Flash point, Pensky Martens C.C.	D 93	> 100°C
Flash point, Tag closed cup		> 100 °C
Kinematic viscosity @ 0°F	D 445	52.54
@ 40°F	D 445	7.22
Density @ 15°C	D 1298	too heavy
Specific gravity		1.1
Wt. per U.S. Gal @ 68°F		9.15 lb.
Neutralization equivalent as base		170-177
Neutralization No.	D 664	182 mg KOH/gm
Nitrogen by (Dumas)		14.5-15.5 wt. %
Colour max.		5 Gardner
Freezing point		~ -2°C
Boiling point @ 1 Atmos.		> 200 °C
Vapour pressure @ 90°C		< 100 mmg Hg
Refractive index, r_D @ 20°C		1.472
Solubility in H_2O @ 20°C		1.1 gm/100 ml
@ 50°C		1.4 gm/100 ml
pH of saturated aqueous solution		7.5 ± 0.5
Ash	D 482	< 0.05
Metals by X-ray Fluorescense		none detected
Solubility test		Meet specification 1-H Diesel Fuel
Corrosion	NACE TM-01-76	No effect - iso-octane & 1-H-Diesel Fuel -
Storage in clear glass with U.V., >1 yr		No visual, ppt., separation, or visual discolouration
Compatible with DuPont FOA-15		Passes test
Partition coefficient in I-H Ref. Diesel Fuel	$P=\frac{(B)_w}{(B)_f}$	0.595
Stability, I-H Ref. Diesel	D 2274	Passes test
Stability - 100°F, dark storage, I-H Ref. diesel		Passes test

Table II

FUELSAVER - Summary Toxicological Information

1. **Acute Toxicity**	
Oral, rat, LD_{50}	310-455 mg/kg
Dermal, rabbit, LD_{50}	1100 mg/kg
Inhalation, rat, LC_{50}	746 mg/l
Skin irritation, rabbit	non sensitizing
Skin sensitization, Guinea pig, Magnusson & Kligman	non sensitizing
Skin sensitization, human, 100 volunteers:	
- 0.666% in cutting fluid, diluted 1:20	non sensitizing
- 0.1% and 0.3% aq. solution	allergic reaction in 3 subjects
2. **Subacute Toxicity**	
Dermal, rabbit, 21-day (0.1%)	no significant changes
3. **Ecotoxicity**	
(a) **Fresh water organisms**	
Acute, *Daphnia magna*, 48 hrs.	1.9 mg/l
Acute, rainbow trout, 96 hrs.	1.1 mg/l
Acute, bluegill sunfish, 96 hrs	1.3 mg/l
(b) **Marine organisms**	
Acute, pink shrimp, 96 hrs	2.2 mg/l
(c) **Wildlife**	
Mallard duck, LD_{50}, oral single dose	2695 mg/kg
Mallard duck, LC_{50}, 8-day dietary	> 5620 ppm
Bobwhite quail, LC_{50}, 8-day dietary	> 5620 ppm

Rogers and Kaplan (3) formulated the requirements for an ideal biocide, viz.

- toxic to both fungal and bacterial organisms at low concentrations;
- nontoxic to mammals at use concentrations;
- fuel- and/or water-soluble;
- stable over a range of in-use temperatures (18-57°C);
- non-corrosive to metals and compatible with other fuel additives and fuel tank coatings
- not form soaps or emulsions with fuel;
- low ash content;
- be easily handled and capable of being readily mixed with fuel or water bottom;
- stable in storage;
- easily detected by a simple quantitative method to monitor concentration;
- have no deleterious effect on engine performance and engine parts;
- reasonably priced.

Throughout this paper the points mentioned above will be evaluated, leading to the conclusion that FUELSAVER meets most of these requirements.

Typical MIL-S-53021 Studies

- **Stabilizer Compatibility**

  The compatibility of FUELSAVER with many of the commercially available diesel fuel stabilizers was tested and was found to be compatible with most. Since DuPont's FOA-15 is the military approved additive several blend ratios were run ranging from 1/1 to 10/1 FUELSAVER /FOA-15.

- **Stability**

  Stability tests were run in accordance with ASTM D-2274 and the 110°F dark storage ASTM test. The ASTM D-2274 stability test, using the I-H Reference Diesel Fuel, showed that FUELSAVER did not negatively influence fuel stability. The 110°F dark storage, also with I-H Diesel Fuel,test showed identical results. These data demonstrate that FUELSAVER does not cause stability problems in conjunction with DuPont's FOA-15.

- **Corrosion**

  Corrosion tests run in accordance with NACE TM-01-76, using the I-H-Diesel Fuel, showed the non-corrosive character of FUELSAVER at use-level. In conjunction with duPont FOA-15 corrosion was entirely eliminated. Identical results were obtained in the same test using depolarized isooctane.

- **Biocidal activity**

  Activity against three test organisms has to be determined, i.e. *Cladosporium resinae* (ATCC 20495), *Pseudomonas aeruginosa* (ATCC 33988) and *Candida tropicalis* (ATCC 48138), using a minimum of three concentrations of stabilizer in a hydrocarbon fuel known to be susceptible to microbial degradation. A concentration of 250 ppm FUELSAVER showed to be effective against all three types of microorganisms.

- **Engine tests**

  Tests run at UCLA with a Mercedes truck engine using a # 2 Diesel Fuel stabilized with 500 and 1,000 ppm FUELSAVER showed no deleterious effect on engine performance or emissions, nor adverse effect on fuel economy.

Recommended Use under MIL-S-53021 (4)

The stabilizer additive package is most effective when added to clean, fresh fuel as a preventive measure. After the fuel has started to deteriorate the additive can only slow down or (at best) stop the process but cannot restore the deteriorated fuel to its original condition. The additive package should be used primarily in situations in which fuel or equipment is subject to storage or infrequent use, or when fuel stability is required, as e.g. in strategic reserves or with marginally stable fuel stored under hot weather conditions.

Additional Studies

The priciple of the additional studies was, and is, to evaluate FUELSAVER in a laboratory model simulating as closely as possible actual Industrial conditions. In addition studies were carried out with FUELSAVER modifications to improve certain properties.

- **Thermal Stability**

  Thermal stability tests, using Differential Scanning Calorimetry (DSC) indicate FUELSAVER to be stable at temperatures below 300°C. Samples heated in either stagnant or flowing air displayed similar thermograms.

- **Partition Coefficient**

  The partition coefficient P is a measure of biocide presence in both fuel and water layer, it is calculated by means of the equation:

$$P = \frac{[B]_w}{[B]_f}$$

where P = partition coefficient
$[B]_w$ = concentration of biocide in the water layer
$[B]_f$ = concentration of biocide in the fuel layer

MIL S-53021 requires equal volumes of distilled water and test formulation, after through mixing, to equilibrate for at least 24 hrs at 25 ± 1°C. Under these conditions the calculated partition coefficient for FUELSAVER is 0.595, representing 37.3% of the biocide to be in the water phase. Changing the fuel/water ratio to 100/1, which is closer to most industrial conditions, showed a reduction of the partition coefficient to 0.197, representing only 16.5% of the biocide to be in the water phase. Modification of FUELSAVER to obtain a higher degree of water solubility, thus increasing the partition coefficient, without sacrificing any of its antimicrobial properties seemed to be the answer. Initial microbiological studies have confirmed this hypothesis, although actual P-values cannot yet be made available.

- **Hydrolysis**

  Decomposition of FUELSAVER by hydrolysis is entirely pH and temperature dependent. No significant influence on the antimicrobial properties against 8 different strains of bacteria and 8 different strains of moulds and yeasts over a pH range of 5.5 to 10.0 was observed. However, at pH levels below 5.5 in aqueous media gradual decomposition takes place, accelerated by either lower pH or higher temperatures.

- **Antimicrobial efficacy**

  As a general rule it can be stated that the level of biocide required for adequate protection of the fuel stored is dependent on storage temperature, and frequency, degree and type contamination. The laboratory model utilized excluded the temperature factor by running all studies at ambient temperature, the contamination factors were standardized whenever possible.

  - In order to meet California registration requirements on FUELSAVER an 8-week study was conducted under simulated actual in-use conditions. The fresh fuel was stabilized with 250 ppm FUELSAVER, no apparent water bottom was present, the fuel was circulated once per week. None of the samples, taken weekly, exhibited siginificant levels of bacterial or fungal growth.

  - **Fuel Preservation (5):**

    Method

    The test was performed using glass bottles containing 500 ml of diesel fuel and 1 ml of Bushnell and Haas solution - inoculated with the test organisms as the water bottom. Treated oil was challenged with *Cladosporium resinae* in one test series, and with a mixture of the yeast *Candida lipolytica* and three oil degrading bacteria *Alkaligenes sp.*, *Pseudomonas sp.* and *Serratia odorifera* in a second series. Fungal Bushnell and

Haas medium was used for *C.resinae* and bacterial Bushnell and Haas for the mixture of bacteria and yeast. Samples of diesel oil containing FUELSAVER at 250, 125, 62.5 and 31.25 ppm over 1 ml inoculated water bottoms were examined. All treatments were in-cubated for 10 weeks at 25°C. At the end of the 10-week incubation period all water bottoms were examined for surviving microorganisms by spread and spiral plating using malt extract agar (MEA) for *C.resinae*, MEA + streptomycin (30 μg/ml) + chlortetracycline (40 μg/ml) for *C.lipolytica* and tryptone soya agar (TSA) for bacteria.

Results

The minimum inhibitory (biostatic) concentration for interface deposit due to growth or membrane formation was found to be between 125 and 250 ppm. The minimum lethal concentration was found to be 125-250 ppm against *C.resinae* and oil degrading bacteria, and 250 ppm to a value greater than 250 ppm against *C.lipolytica*. FUELSAVER at 250 ppm in diesel fuel prevented the growth of all fuel deteriogens and effected a total kill after 10 weeks with the exception of *C.lipolytica* which survived 250 ppm FUELSAVER after 10 weeks.

Conclusion

These results show that FUELSAVER performed well as a fuel preservative. It should be noted that the deteriogenic bacteria which have been shown to generate a membrane deposit at the oil/water interface were inhibited by 250 ppm FUELSAVER.

* Growth Prevention of Bacterial Polymeric Material (6):

Introduction

One of the most serious consequences of bacterial growth in fuel is the formation by fuel deteriogens of a solid polymeric material. This material is both hydrophylic and lipophylic, and would seem to be the necessary precursor for the bacterial attack on the oil. There is evidence that this material is initially secreted as a thin film at the oil/water interface where it probably facilitates the assimilation of the oil. Bacterial exploitation of the oil leads to an accumulation of the polymer as multi-layered sheets at the oil/water interface, to form a slimy mass of polymer, oil and water which can be 10 mm or more thick. Some of the membrane material is also taken up into the overlaying oil causing turbidity and filter blockage. If the oil has been subject to violent agitation, droplets of oil encased in the polymer film become suspended in the main body of the oil and accumulate above the oil/water interface. There is evidence that, when present in oil in sufficient amounts, this polymer also enhances the propensity of diesel fuel to gel at low temperatures. It is not unusual to find some bacteria surviving under oil that has been treated with a biocide, but these organisms necessarily damage the fuel.

Method

FUELSAVER was added to diesel fuel to give test concentrations of 31.25, 62.5, 125 and 250 ppm in the fuel. In the first experiment 250 ml conical flasks were prepared containing 56 ml of oil treated with FUELSAVER and 14 ml of Bushnell and Haas solution, giving an oil/water ratio of 4:1. In the second experiment 35 ml of oil was added to 35 ml of bacterial Bushnell and Haas solution in 250 ml flasks to give an oil/water ratio of 1:1.

The water bottoms were then inoculated with three polymer forming bacteria, a *Pseudomonas* sp. and two *Alkaligenes* spp., which had been isolated from spoilt fuel. These isolated bacteria were cultured in nutrient broth, washed by centrifugation and added to the water bottoms to give a final concentration of each organism of 10^5/ml. The flasks then were shaken at 250 rpm for three weeks at 25°C. Each treatment was executed in triplicate and the bacterial population in the water bottoms sampled weekly. After three weeks the flasks were examined visually for polymer formation and the presence/absence of polymer material in each flask was recorded. The contents of the three flasks for each treatment were then pooled and transferred to 250-ml measuring cylinders for further examination. Transferring the contents of the three flasks to a measuring cylinder reduced the area of the oil/water interface by 20, thereby increasing the density of any interface deposit by a similar amount and making any polymer formation more readily detectable. The amount of polymer in each measuring cylinder was assessed on an arbitrary scale from 0 to 5.

Results

The results for viable counts of polymer forming bacteria are presented in table III. These data showed that after three weeks under diesel fuel containing 250 ppm FUELSAVER all bacteria had been eliminated from the water bottoms. The results for the presence of polymer in individual flasks and the assessment of the amount of polymer produced in each treatment are summarized in table IV. These data show that diesel fuel was susceptible to microbiological attack, and polymer formation was clearly visible in oil containing FUELSAVER upto 125 ppm, but polymer formation had been severely inhibited in diesel fuel containing 250 ppm FUELSAVER. The interface of one of the three flasks containing fuel with 250 ppm FUELSAVER was free from any polymer and the presence in the pooled sample had come from the other two flasks and could only be detected by the increased reflectance at the oil/water interface. There is evidence that in the control treatment the bacteria were attached to the films of polymer and not free in the water bottoms. Thus bacterial counts on the water bottoms can be a poor guide to the level of the microbiological hazard and examination for polymer formation might be a much more reliable indicator. It was observed that only 5 ml of the original 14 ml of water remained on the bottom of the 250 ml flasks at the end of the first experiment. When the control diesel fuel and fuel containing 31.25 and 62.5 ppm FUELSAVER were left to stand for 24 hours, this small puddle became attached to the flask bottom by the polymer material and the water bottom could not be readily drained from the flask.

Table III

The survival of polymer forming bacteria in water bottoms under diesel fuels with oil/water ratios of 4:1 and 1:1

Oil/Water Ratio	4:1			1:1		
Week No.	1	2	3	1	2	3
FUELSAVER,ppm						
Control	>4×10^4	3×10^3	1.2×10^2	1.5×10^5	10^4	1.7×10^6
31.25	50	3×10^3	1.4×10^3	10^5	2×10^5	2.2×10^5
62.50	10^5	8×10^2	5.4×10^2	10^3	3×10^5	1.4×10^5
125	3×10^4	3×10^3	2.3×10^3	5×10^2	0	0
250	10	8×10^3	0	6×10^2	0	0

Table IV

Polymer formation with oil/water ratios of 4:1 and 1:1

Oil/water ratio	**4:1**		**1:1**	
	F	P	F	P
FUELSAVER,ppm				
Control	3/3	5	3/3	4
31.25	3/3	5	2/3	3
62.50	3/3	5	3/3	2
125	3/3	5	3/3	2
250	3/3	1	2/3	1

Key:

F No. of flasks containing polymers
P Polymer rating

Polymer rating scale:

5 Copious polymer in oil phase forming interface. Wide interface band.
4 Thick layer of polymer at interface. Not moving up into the oil, may move down into the water.
3 Interface layer-developing polymer modules or bubbles.
2 Polymer visible as distinct skin.
1 Skin just visible at interface - no thickness.
0 No polymer.

Conclusion

Examination for polymer formation as a criterion for assessing biocidal activity against fuel tank deteriogens has been shown to give more consistant results than counts of surviving bacteria. The results show that FUELSAVER was able to prevent all but a trace of polymer formation in diesel fuel containing 250 ppm FUELSAVER.

Since these experiments were performed under optimal conditions of temperature and mineral nutrition for bacterial growth it is probable that the rate of growth and polymer formation will be much slower in the normal fuel environment. Thus the protection conferred on fuels by FUELSAVER over the three week period of these experiments probably represents long term protection in the normal fuel tank environment.

* Fuel Preservation:

Studies were conducted to evaluate the comparative efficacy as preservative of FUELSAVER and a modified FUELSAVER against two competitive products, i.e. a bis-oxazolidine and a chloro/ methylisothiazolinone. With exception of the isothiazolinone the products could be easily incorporated into the test fuel to make stock solutions for preparation of different biocide levels. Clean fuel was inoculated with a water bottom containing viable spoilage bacteria and added moulds and yeasts which were isolated from previously spoiled fuels and fuel water bottoms. The original contaminated water bottom was obtained from actual fuel storage, the moulds and yeasts were added to give approx. 10^2 cfu/ml.

Visual assessment of the water bottom after 4 weeks storage at ambient temperature showed the control with a thick layer of growth at the fuel/water interface, the fuel near the interface was discoloured (dark purple), and the water remained opaque after standing for one day with little sediment settling out.

The bis-oxazolidine at a level of 50 ppm showed much growth at the interface, fuel at the interface was slightly discoloured and opaque, and the water was clear after standing and slightly discoloured with much fine sediment settled out.

FUELSAVER at a level of 50 ppm showed growth at the interface to be light in colour but readily apparent, the fuel was opaque but not discoloured, and the water was clear but discoloured after standing with a dark sediment. The modified FUELSAVER at a level of 50 ppm showed growth at the interface to be light and only present in thin layer, the fuel was slightly opaque but not discoloured, the water was clear and yellowish on standing. The above assessments demonstrate the improvement obtained with the modification of FUELSAVER. As this study is still ongoing further results will be reported at a later date.

* **Fuel disinfection:**

The significance of killing microbes (disinfection) in the fuel phase is that this prevents the onward transmission of infection as fuel is distributed. Disinfection of the water bottom prevents further microbial spoilage/corrosion in the storage tank.

FUELSAVER, the modified FUELSAVER and the bis-oxazolidine were used at 250, 500 and 1000 ppm, and the isothiazolinones at 100 and 200 ppm, to disinfect a heavily contaminated fuel and associated water bottoms. These water bottoms were visually assessed after 5 and 24 hours.

Before dosing the biocides the water bottoms were turbid and a relatively thick (1-2 mm) microbial pellicle was visible at the fuel/water interface. Fungal/microbial flocs were visible in the water phase. The fuel was opaque and slightly discoloured (darker). The control did not change in appearance over the 24 hour period. The treated water bottoms did no vary much between different biocides after 5 hours, and were not significantly different from the control. After 24 hours all water bottoms, except the control, showed some degree of clearing which was most noticeable in all of the 1000 ppm dosed flasks and the 500 ppm bis-oxazolidine water bottom. Only the two isothiazolinones-dosed fuels showed clearing of the fuel phase. Both bis-oxazolidine dosed fuels were less opaque than fuel dosed with other biocides.

Conclusions:

Due to the change in the chemical character of the middle distillate fuels the products have become more water soluble thereby becoming considerably more susceptible to microbiological attack. Microbial contamination of fuels has been reported in literature as the cause of numerous problems in fuel storage and distribution systems. The utilisation of preservatives in distillate fuels assists satisfactory performance in engines, and retains product quality until used by the customer. Choice of the preservative will not only depend on its microbial efficacy but also on its toxicity profile vis-à-vis people and the environment, its ease of diposal, and last, but not least, its cost/efficiency rating.

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A SURVEY OF THE MICROBIAL CONTAMINATION LEVEL OF SOME FINNISH FUEL STORAGE SYSTEMS (24)

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ABSTRACT

The aim of the project was to estimate the degree of microbial contamination of jet fuel and light heating oil in both long and short term storage in Finland. The nine storage systems studied included both rock caverns and above-ground and subsurface steel tanks. Samples were taken biannually. Sampling methods were developed. Certain physical and chemical factors relevant to the appearance of microbiological problems were analyzed, too.

No corrosiveness was found in the fuel samples studied in the standard silver and copper corrossiveness tests, nor when a more sensitive Swedish method was applied, utilizing piezoelectric crystals. No water bottoms were found in the jet fuel storage systems and few microbes were found in the fuel itself. In the light heating oil water bottoms the microbial counts were higher.

Cladosporium resinae, a common fuel contaminant, was absent from the two rock caverns studied. The constantly low temperature in these tends to select an aerobic flora consisting chiefly of cold tolerant gram-negative rods, including some psychrophilic forms. Many of the bacteria are pseudomonads, which are especially difficult to eradicate with biocides, because resistant mutants are likely to develop quickly.

The water bottoms of the fuel tanks and the bed waters of the caverns, as well as the fuels, were analyzed for C_2-C_{19} saturated aliphatic straight chain carboxylic acids. These compounds are likely to accumulate in fuel-water systems, where microbial growth has taken place. They were found in low concentrations usually not exceeding those of fresh products and, with a few exceptions, are not thought to be of microbiological origin.

INTRODUCTION

In Northern Europe rock caverns are used for long-term storage of petroleum products. Fuels are stored on a waterbed and the caverns are located below the groundwater table. It is the water pressure that keeps the products in the caverns (1).

In Sweden problems of microbiological origin have been encountered in these caverns. Jet fuel has become corrosive due to hydrogen sulphide produced by sulphate-reducing bacteria living in the bottom sediments of rock caverns (1). No such practical problems have arisen in Finland, because no jet fuel is stored on a waterbed here. But light heating oil is stored on fixed waterbeds, where the groundwater level is kept constant by pumping out excess groundwater leaking into the cavern.

The aerobic microflora of rock cavern waterbeds had never been characterized microbiologically in detail before, so some progress was made in this respect. Because the temperature in the caverns is low, a microflora well adapted to cold temperatures could probably thrive there. There is a shortage of dissolved oxygen in the waterbed, which prevents complete microbial oxidation of hydrocarbons, possibly resulting in accumulation of intermediate products, like fatty acids (2). Rock cavern waters have not been analyzed for these compounds before. In this study a sensitive method has been developed with a detection limit of 0.01 ppm. There have been considerable difficulties in the past to obtain proper samples from the bottom sediments, where the sulphate-reducing activity is highest. A promising application of pre-existing water sampler for obtaining sediment samples is presented below.

MATERIALS AND METHODS

Descriptions of the sampled systems are found in the tables of results. Each system was sampled both in February-March and in June-July. Small tanks were sampled using a regular hand-operated pump. Bottom samples from rock caverns were drawn with a special 250 ml metal syringe equipped with a trigger mechanism (3). The device was originally constructed for microbiological lake water sampling purposes. The waterbed samples were taken with a glass bottle device published by Väätäinen (4). The interface between oil and water, as well as the oil itself, was sampled with a commercial oil sampler (Oceco type 40/S071-1193NP). It is a metal cylinder with two flaps in both ends. The flaps were open, when the sampler was lowered to the desired depth and they were closed, when the device was pulled up. This permitted sampling the interface with minimum turbulence.

Fuels were analyzed for copper (5) and silver (6) corrosion applying standard methods and also a more sensitive Swedish method utilizing piezoelectric crystals (7). Water content was determined with a Metrohm KF -coulometer. Elemental sulphur and H_2S in fuel and water were analyzed according to Olofsson and Roffey (8). The samples to be analyzed for H_2S were immediately mixed 1:1 with SAOB II buffer to prevent evaporative losses (9).

C_2-C_{19} saturated aliphatic straight chain carboxylic acids in fuel and water samples were analyzed as follows: The hydrocarbon sample was extracted with aqueous sodium bicarbonate. The bicarbonate solution was acidified to pH 3 and the acids were backextracted twice with diethyl ether. The combined ether extracts were dried with anhydrous sodium sulphate and concentrated to a small volume. The water sample was acidified to pH 3 and the acids extracted with two aliquots of diethyl ether.. (as above). The acids were determined by gas chromatography-mass spectrometry using the selected ion monitoring technique. Typical fatty acid ions (m/e 45, 60, 73, 87 and 101) were monitored and the quantification based on m/e 45 data for C_2-C_4 acids and m/e 60 data for all the other acids. The measured recoveries for the individual acids were used to correct the results. The limit of determination was in the order of 0,01 ppm.

Water samples were analyzed for nitrogen by a chemiluminescence method (10), phosphate (11) and sulphate (12). The BOD_7 (Biochemical Oxygen Demand) and dissolved oxygen analyses were performed according to Finnish standards (SFS). The pH and temperature were recorded, too.

The microbiological analyses were performed immediately after the samples had arrived to the laboratory. The quantitation of microbes in water samples was performed using the standard serial dilution - plate count method with duplicates. Total aerobic bacteria were enumerated on Industrial Plate Agar (13) and total anaerobes on Thioglycollate Agar (Difco) plates in GasPak (BBL) jars. Sulphate-reducing bacteria (SRB) were counted in Postgate E medium with five tubes for each dilution step (14). Moulds and yeasts were cultured on Potato Dextrose Agar (Difco), with 0.01 % chloramphenicol and tetracycline hydrochloride added to prevent bacterial growth. Cladosporum resinae was selectively isolated on Potato Dextrose Agar with 0.1 % creosote. Morphologically different colonies of aerobic organisms were isolated and their ability to use jet fuel as a sole source of carbon and energy was tested in a Bushnell-Haas - jet fuel biphasic system (15). The fatty acid determinations using pure strains were performed with this medium, too. Growth curves of some bacteria were prepared in Industrial Broth in a temperature corresponding to the winter temperature of the storage system in question. The generation times were calculated. Fuel samples were filtered through Gelman 0.45 μm membranes, which were washed with sterile 0.1 % Triton X-100 solution and saline and placed on the appropriate media. All incubations were at +28 °C, unless otherwise stated. The sulphate reducing activity was determined by a radioisotope method (16) in two rock bottom sediment samples.

The bacterial isolates were characterized using the following methods: pigment production, growth at +0 °C in two weeks to differentiate psychrophilic organisms (17), nitrate reduction, cellular morphology, gram-reaction, acid fast and spore stains, oxidase reaction, catalase reaction, Hugh-Leifson O/F test with glucose and lactose, motility (hanging drop method) and transmission electron microscopy to determine the mode of flagellation of motile bacteria. All tests were performed as described by Lennette et al. (18). Selected gram-negative rods were tested with API 20 NE (API system S.A.) From samples collected in summer, obligate psychrophiles were searched for, too, with primary incubation at +0 °C.

RESULTS AND DISCUSSION

The results of chemical and physical analyses are presented in tables 1 - 2 and microbiological data in tables 3 - 9 and figure 1. The systems studied were: 1 - 3 small subsurface tanks containing light heating oil, 4 - 7 steel tanks with jet fuel and 8 - 9 rock caverns with light heating oil. Because corrosive sulphur compounds were known to diffuse to the oil bulk from the bottom of a system, only the fuel layer nearest to the bottom was analyzed for corrosiveness, H_2S and elementary sulphur. Fatty acids were analyzed from both bottom and surface layers to detect any differences. If these acids were of microbiological origin, their concentration should be higher in the bottom layers near the water interface, where microbial activity takes place.

The corrosiveness of all fuels, according to the standard copper and silver methods were 1a or 0, respectively (results not included in tables 1 - 2). The piezoelectric frequencies were low, not indicating any corrosiveness (2). No water bottoms were found in the jet fuel storage systems. No H_2S was detected in the fuels, while some elementary sulphur was present in the samples taken in winter, but no more in summer. No phosphate was found in any water samples (analytical lower limit 0.02 ppm; results not included in tables 1 - 2). Nitrogen was mainly present in the bottom sediments of the rock caverns and in the water bottoms of the "badly kept" light heating oil tanks (nr 1 and 2).

According to the Swedish workers, there are a few environmental parameters, that are important in determining, if fuel will become corrosive in a rock cavern. Groundwater with a high leakage rate together with a high sulphate concentration and a low oxygen concentration in the bedwater are unfavourable. If the oxygen content in the bedwater of a plant falls below 3 ppm, the risk of corrosive fuel increases, as H_2S can then enter the fuel phase before being oxidized to elementary sulphur (2). The two rock caverns studied are different in these respects. Number 8 is located on the coastline, and groundwater is brackish water with a high sulphate concentration, favouring the activity of sulphate-reducing bacteria. The leakage rate of groundwater into this cavern is low, 1 m^3 per day. Number 9 is surrounded by fresh water, but with a high leakage rate of 100 m^3 per day. The sulphate concentration difference between surrounding groundwater and outpumped water is high in system 8, indicating an effective sulphate reduction process. Especially in winter, the H_2S concentrations in the bottom sediments and bedwater are high in this system.

In contrast with all other bedwater samples, the oxygen concentration fell below 3 ppm in winter in this system, allowing some elemental sulphur to be formed in the fuel phase (1.3 ppm). This did not result in the fuel becoming corrosive, however, and in the summer sample the oxygen content was 4.2 ppm and H_2S went down substantially, too. Because so few samples were taken, it was not possible to say, if this was seasonal or other variation. The sulphate reducing activities of the bottom sediments of the two caverns, measured at +4 °C, were similar, $1x10^{-11}$mol SO_4^{2-}/ml, day for system 8 and $8x10^{-12}$ for system 9.

The BOD_7 in outpumped water in both caverns was similar to that of the surrounding groundwater, although it was far higher in the bedwaters. This means that although biodegradable soluble organic matter was dissolved in the bedwater, it was almost completely used up before it was pumped out.

The fatty acid contents of freshly made products were analyzed for reference and were 2.54 - 5.05 ppm in jet fuel and 0.16 ppm in light heating oil. The maximal concentrations were at chain lengths C_8 - C_{10}. Because the concentrations in stored products were smaller and there were no consistent differences between bottom and surface samples, the acids are probably not of microbiological origin. Some of the isolated microbes were tested for fatty acid production in vitro (table 9). It could clearly be seen, that short chain (C_2 - C_5) acids predominated. In one system (nr 8, summer), however, higher fatty acid concentrations could be detected in interface fuel (9.3 ppm, mainly butyric acid) and in interface water (7.1 ppm, mainly acetic acid). These could have been of microbial origin. It can be summarized, however, that saturated aliphatic carboxylic acids are present in the systems studied, and available as nutrients to organisms not capable of hydrocarbon degradation themselves (eg SRB). The concentrations are extremely low.

The total counts of aerobic bacteria were quite high (10^4 - 10^6) in the water bottoms of the light heating oil tanks studied (nr 1 - 3). "Badly kept" tanks had intentionally been chosen for the study. Cladosporium resinae was isolated too, from all but one of these storage systems. Sulphate-reducing bacteria were not present in these tanks in significant numbers. Because no water bottoms were found in the jet fuel systems (4 - 7), only fuel was cultured. With one exception (nr 4, winter) the microbial counts of jet fuel were low, in the order of several tens of colony forming units per litre. Cladosporium resinae was present as a rule and no sulphate-reducers were found. In the rock cavern waters, aerobic bacteria were isolated in counts of 10^3 - 10^5, sulphate-reducing bacteria being present in quite low numbers, from nil to some thousands of colony forming units per millilitre.

As a whole, some 40 % of the 297 aerobic microbial strains isolated were found to be able to utilize jet fuel as a sole source of carbon and energy. Bacteria were grouped to the genus level (tables 6 and 8). With a single exception, all aerobic bacteria were oxidase positive and either oxidative or inert in the Hugh-Leifson O/F-test.

In this study, Cladosporium resinae was isolated for the first time in Finland (19). Although Cladosporium resinae was a dominating contaminating microbe in this and numerous other fuel microbiological surveys, it was absent from the two rock caverns studied, both from the water and fuel phases. Possibly the low temperature in the caverns all year round tends to select out a cold-tolerant bacterial flora, consisting mainly of gram-negative rods (tables 3-8). Psychrophilic bacteria, organisms capable of profuse growth at +0 °C in two weeks, were isolated from systems 1 and 9. Of the five strains, four belong to the Pseudomonas fluorescens species, which is a common contaminant of various refrigerated foodstuffs. There seems to be some variation in their capability of growing in cold among the isolated bacterial strains, as the generation times in figure 1 show.[1] Bacteria that can grow at +0 °C, but cannot grow at +28 °C, for example, are called for obligate psychrophiles. These organisms are found in oceans. No such bacteria were isolated in this study, although they were cultured from the summer samples.

The dominance of gram-negative rods in rock cavern waters poses special demands on biocides intended to be used in these systems. Many of the bacteria belong to the genus Pseudomonas, which are known to be naturally very resistant to various antimicrobial substances. Besides, these bacteria often quickly develop resistant mutant strains, the resistance being readily transmissible by several genetic material exchange mechanisms known to operate among these bacteria. Many of the biocides used in the oil storage systems have originally been directed mainly against Cladosporium resinae, and not against gram-negative rods.

CONCLUSIONS

In conclusion we find that microbial growth in the jet fuel systems studied was sparse. In some of the other systems higher microbial counts were found. No product deterioration caused by micro-organisms could be detected in any of the samples.

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1) The generation time of a bacterial strain is a measure of the rate of binary fission - the shorter the time, the faster the rate of multiplication.

TABLE 1. The results of physicochemical analyses, winter

System nr	H_2O (%)	$S_{elem.}$ (ppm)	H_2S (ppm)	Total N (ppm)	O_2 (ppm)	SO_4^{2-} (ppm)	Piezoel. freq. (kHz)	Fatty acids (ppm)	BOD_7 (mg/l)	pH	Temp. (°C)
1. fuel, bottom	0,1	<0,1	<0,1				0,68	0,05			
fuel, surface								<0,01			
waterbottom			<0,1	15	-	39		0,07	71	6,8	+4,5
2. fuel, bottom	0,2	<0,1	<0,1				0,85	0,11			
fuel, surface								0,10			
waterbottom			<0,1	60	3,5	110		0,40	498	5,9	+4,3
4. fuel, bottom	0,003	0,14	<0,1				0,75	1,21			
fuel, surface								0,21			+10,0
5. fuel, bottom	0,004	0,55	<0,1					<0,01			
fuel, surface								0,34			+15,3
6. fuel, bottom	0,004	0,25	<0,1				0,55	0,10			
fuel, surface								<0,01			+1,0
8. fuel, interface	0,02	1,3	<0,1				0,40	0,20			
fuel, surface								0,17			
water, interface			4,2	<1	0,5	7,4		0,02		7,2	+7,1
waterbed			4,8	<1	1,1	9,0		0,32	94,2	7,1	+7,3
bottom sediment			12,2	4,1	<0,3	11		0,04		7,5	+8,2
groundwater			<0,1	<1	9,6	440		0,02	18,8	7,3	+5,8
outpumped water			3,8	<1	<0,3	14		0,00	27,2	7,4	+7,2
9. fuel, interface	0,01	<0,1	<0,1				0,42	0,51			
fuel, surface								-			
water, interface			1,1	1,7	3,0	26		<0,01		6,7	+5,8
waterbed			1,7	<1	6,4	27		0,18	171,2	6,5	+5,9
bottom sediment			1,3	2,9	2,7	59		0,20		9,0	+5,8
groundwater			<0,1	<1	11,4	25		0,01	7,2	6,6	
outpumped water			1,5	<1	<0,3	22		0,04	6,6	6,5	+6,5

1 - 3: small subsurface tanks containing light heating oil, 4 - 7: steel tanks with jet fuel and 8 - 9: rock caverns with light heating oil. Systems 3 and 7 were not sampled in winter.

TABLE 2. The results of physicochemical analyses, summer

System nr	H_2O (%)	$S_{elem.}$ (ppm)	H_2S (ppm)	Total N (ppm)	O_2 (ppm)	SO_4^{2-} (ppm)	Piezoel. freq. (kHz)	Fatty acids (ppm)	BOD_7 (mg/l)	pH	Temp. (°C)
1. fuel, bottom	0,12	<0,1	<0,05				0,52	0,01			
fuel, surface								<0,01			
waterbottom			0,7	19	<0,3	43		0,64	100,9	6,5	+11,1
3. fuel, bottom	0,073	<0,1	<0,05				1,51	0,18			
fuel, surface								0,05			+12,5
4. fuel, bottom	0,005	0,1	<0,05				0,73	0,58			
fuel, surface								0,67			+9,7
5. fuel, bottom	0,007	<0,1	<0,05					0,30			
fuel, surface								0,46			+16,4
7. fuel, bottom	0,012	<0,1	<0,05				0,47	0,23			
fuel, surface								1,0			+14,2
8. fuel, interface	0,02	0,1	<0,05				0,62	9,3			
fuel, surface								0,17			
water, interface			0,3	<1	1,6	1,6		7,1		6,8	+8,2
waterbed			0,4	<1	4,2	4,7		0,08	177,6	6,5	+7,5
bottom sediment			4,5	<1	<0,3	23		<0,01		6,1	+7,6
groundwater			<0,1	<1	11,8	410		<0,01	19,4	6,7	+13,1
outpumped water			0,5	<1	1,9	8,0		0,20	19,8	6,5	+7,7
9. fuel, interface	0,012	<0,1	<0,05				0,54	0,12			
fuel, surface								<0,01			
water, interface			0,4	<1	2,4	25		<0,01		6,0	+6,2
waterbed			0,5	1,5	3,2	24		0,09	336	6,3	+6,1
bottom sediment			0,4	<1	2,4	50		<0,01		7,8	+6,2
groundwater			<0,1	<1	12,8	20		<0,01	27,8	6,2	+6,5
outpumped water			<0,1	<1	4,8	24		0,12	7,0	6,3	+6,2

Systems 2 and 6 were not sampled in summer.

TABLE 3. The results of microbiologigal analyses, winter

System nr	Total aerobic bacteria	SRB	Total anaerobic bacteria	Total moulds	Cladosporium resinae	Total yeasts
1. waterbottom	$4,5 \times 10^6$	0	$1,9 \times 10^2$	0	0	25
2. waterbottom	$1,2 \times 10^5$	5	10	30	$3,0 \times 10^2$	$1,5 \times 10^3$
4. fuel, bottom	$1,5 \times 10^3$	0	10	40	40	0
5. fuel, bottom	18	0	2	28	4	0
6. fuel, bottom	4	0	2	40	40	0
8. water, interface	$9,7 \times 10^2$	53	$3,5 \times 10^2$	0	0	0
waterbed	$6,7 \times 10^3$	$4,3 \times 10^3$	68	0	0	15
bottom sediment	$1,3 \times 10^5$	$2,3 \times 10^2$	$1,1 \times 10^4$	0	0	35
groundwater	$1,7 \times 10^4$	$1,5 \times 10^2$	$2,6 \times 10^2$	10	0	0
outpumped water	$4,7 \times 10^3$	30	$6,9 \times 10^2$	0	0	0
9. water, interface	$5,5 \times 10^5$	$7,3 \times 10^2$	$4,5 \times 10^3$	$3,2 \times 10^3$	0	0
waterbed	$1,3 \times 10^5$	$5,0 \times 10^2$	$6,7 \times 10^2$	0	0	0
bottom sediment	$5,2 \times 10^3$	0	$3,5 \times 10^2$	20	0	5
groundwater	$1,2 \times 10^2$	0	$4,0 \times 10^2$	0	0	0
outpumped water	$4,8 \times 10^4$	$1,0 \times 10^2$	$3,5 \times 10^2$	0	0	0

Microbial counts are in CFU (colyny forming units) per millilitre for water samples and CFU/litre for fuel samples
SRB = sulphate reducing bacteria

TABLE 4. The results of microbiological analyses, summer

System nr	Total aerobic bacteria	SRB	Total anaerobic bacteria	Total moulds	Cladosporium resinae	Total yeasts	Psychrophilic bacteria 1)
1. waterbottom	$2,2 \times 10^6$	0	$1,1 \times 10^3$	$2,2 \times 10^2$	0	45	$2,5 \times 10^4$
3. fuel mixed with water	$3,5 \times 10^4$	0	0	$7,3 \times 10^4$	$7,3 \times 10^4$	0	0
4. fuel, bottom	8	0	0	56	44	0	0
5. fuel, bottom	30	0	0	2	0	0	0
7. fuel, bottom	14	0	0	90	90	0	0
8. fuel, interface					0		
water, interface	$1,2 \times 10^3$	0	40	0	0	0	0
waterbed	$1,2 \times 10^3$	20	40	0	0	0	0
bottom sediment	$2,1 \times 10^3$	$5,0 \times 10^2$	$2,5 \times 10^3$	0	0	0	0
groundwater	$1,3 \times 10^3$	35	$5,8 \times 10^2$	0	0	0	0
outpumped water	$1,7 \times 10^3$	$1,7 \times 10^2$	30	0	0	0	0
9. fuel, interface					0		
water, interface	$2,7 \times 10^4$	$2,7 \times 10^2$	$5,0 \times 10^2$	0	0	0	$7,5 \times 10^2$
waterbed	$3,1 \times 10^4$	$3,3 \times 10^2$	$4,5 \times 10^2$	0	0	0	$2,2 \times 10^2$
bottom sediment	$3,0 \times 10^4$	$1,2 \times 10^3$	$4,9 \times 10^2$	$2,0 \times 10^2$	0	0	$1,5 \times 10^2$
groundwater	$2,8 \times 10^3$	0	35	10	0	0	0
outpumped water	$2,8 \times 10^4$	$4,5 \times 10^2$	$3,0 \times 10^2$	0	0	0	90

For legend, see table 3

1) Facultative forms capable of growing at + 28 °C.

TABLE 5. Types of isolated aerobic microbes, winter

Organism	nr of strains	hydrocarbon utilizing	
		number	%
Bacteria	100	40	40
Yeasts	9	9	100
Moulds (incl. 4 Cladosporium resinae)	14	7	50
Total	123	56	46

TABLE 6. Groups of hydrocarbon utilizing bacteria, winter

Organism	nr of strains
Flavobacterium	9
Pseudomonas	8
Other gram-negative rod	12
Total gram-negative rods	29
Staphylococcus	1
Micrococcus	2
Total gram-positive cocci	3
Gram-positive rods (non-sporeforming)	8

TABLE 7. Types of isolated aerobic microbes, summer

Organism	nr of strains	hydrocarbon utilizing	
		number	%
Bacteria	155	50	32
Yeasts	5	4	80
Moulds (incl. 3 Cladosporium resinae)	14	10	71
Total	174	64	37

TABLE 8. Groups of hydrocarbon utilizing bacteria, summer

Organism	nr of strains
Flavobacterium	10
Pseudomonas	23
Other gram-negative rod	16
Total gram-negative rods	49
Micrococcus	1

TABLE 9. The production of fatty acids by some isolates from jet fuel in oxygen-deprived conditions[1)]

	Strain nr						
Acid	1	2	3	4[2)]	5	6	7
C_2	11	0,45		0,24	6,0		
C_3		1,7	0,21	0,1	1,0	0,4	
C_4	1,2	3,1	0,16	0,1	0,2	0,4	
C_5				0,1	11,3	7,4	0,6
C_6		1,9			0,4		
C_7							
C_8							
C_9			0,25				
Final pH	6,3	6,0	6,5	6,5	6,2	6,6	6,3
Final O_2, ppm	1,1	0,06	4,9	0,78	....	1,3	1,9

The concentrations of acids are given in ppm. The chain length is given by numbers, C_2 being acetic, C_3 propionic acid etc. The incubation time was four weeks. A sterile bottle was included for control.

Isolates: 1 = Flabobacterium/system 9
2 = Pseudomonas fluorescens/system 1
3 = Yeast/system 2
4 = Flavobacterium/system 8
5 = Pseudomonas/system 9
6 = Pseudomonas/system 9
7 = Pseudomonas/system 9

1) Screw-capped bottles, static cultures with no aeration
2) C_{16} was produced at a concentration of 0,4 ppm

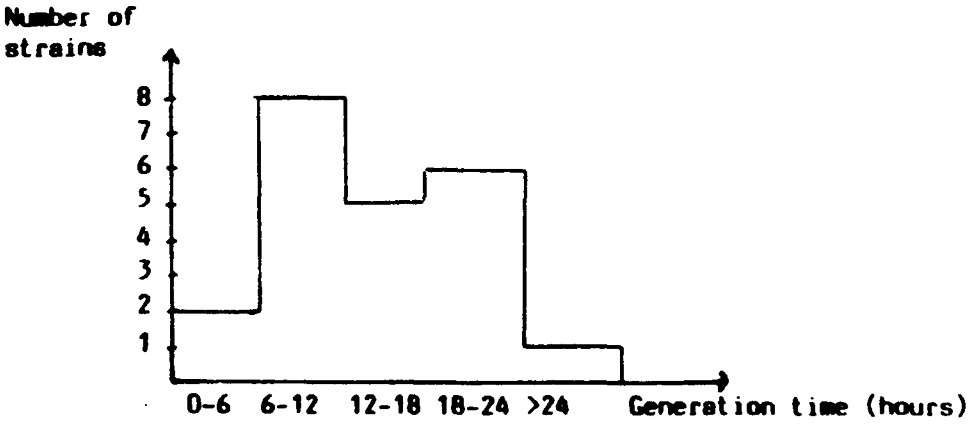

FIGURE 1. Generation times of some isolated hydrocarbon utilizing bacteria at cold temperatures (4/7 °C)

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

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1. INTRODUCTION

Microbial deterioration of hydrocarbon based products has been known for many years (1) and the field of biodeterioration of petroleum products has been reviewed by several workers (2,3).

In the case of distillate fuels, microbial problems such as biocorrosion, filter blockage, coalescer malfunction and water entrapment have been of great concern, principally in the aviation industry.

In more recent years, however, microbiological problems have been associated with other fuel systems such as tractor vapourizing oil, diesel, paraffin and gas oils (4). Particular note has been paid to the increase in microbiological problems in marine applications (5). The reasons for the apparent increase in microbiological problems may be due to changes in crude source (6), refining and blending techniques (6), storage and handling facilities (7) and the increased use of fuel additives (8). In addition there has been a change in the type of organism causing microbiological problems away from *Hormoconis resinae (Cladosporism resinae)* to bacteria and yeasts (5).

To minimise microbiological problems in fuel systems several methods have been suggested, including good housekeeping, production of microbiologically harder fuels, physical control, e.g. heat treatment (9) and chemical control, e.g. the use of chemical biocides.

Bronopol (2-bromo-2-nitropropane-1,3-diol, BNPD) is a versatile antimicrobial agent traditionally used as a preservative to control bacterial growth in pharmaceuticals, cosmetics and toiletries. In recent years its use in controlling industrial biofouling problems, either alone (10,11) or in combination with other biocides (12), has grown significantly. This paper reports studies to evaluate its potential as a biocide for microbial contamination in fuel systems.

2. PHYSICO-CHEMICAL PARAMETERS

2.1 Solubility

BNPD shows excellent solubility in water and polar organic solvents but has a low affinity for non polar or paraffinic solvents (see Table 1). By using a suitable carrier solvent, however, it is possible to improve the solubility of BNPD in paraffinic solvents. Solutions in methoxyethanol, propyleneglycol methyl ether and dipropyleneglycol methyl ether enable BNPD to be incorporated into fuel systems such as diesel and kerosene.

TABLE 1

Approximate solubility of BNPD at room temperature (22-25°C in some common solvents

SOLVENTS	% w/v
Water	28
Methanol	89
Ethanol	56
Isopropanol	41
Ethylene Glycol	61
Propylene Glycol	52
Dipropylene Glycol	48
Propylene Glycol Methyl Ether	61
Dipropylene Glycol Methyl Ether	54
Propylene Carbonate	42
Methyl Carbitol	54
N-methylpyrrolidone	102
Isopropyl Myristate	<0.5
Diethyl Sebacate	10
Arachis Oil	<0.5
Castor Oil	<0.5
Cottonseed Oil	<0.5
Olive Oil	<0.5
Liquid Paraffin	<0.5

2.2 Partition Coefficient

2.2.1 Radiolabelled Study

The partition coefficient values of BNPD between three two-phase systems were determined by the use of carbon-14 labelled BNPD. Three fuels were used in the experiment - Aviation turbine fuel (AVTUR), Diesel and Kerosene.

Two methods were used for the determination:

A. by incorporating BNPD at about 100 ppm into pH4 buffer solution (aqueous phase) and determining the partitioning effect into each fuel (Aviation turbine fuel, AVTUR, Diesel and Kerosene).

B. by incorporating BNPD at about 100 ppm into each fuel using methyl cellosolve (methoxy ethanol - "antifreeze"), as carrier-solvent, and determining the partitioning effect into the aqueous phase (pH4 buffer).

The radioactive moiety was incorporated at a level so as to obtain total counts of, when assayed, about 23.00 x 10^3/min.

METHOD A

BNPD (10.6 mg) and [^{14}C] BNPD (0.99 mg at specific activity of 13.0 mCi/gm) were combined and dissolved in pH4 buffer solution in a 100 ml standard flask.

10.0 ml aliquots of the aqu. soln. were pipetted into 3 x 25 ml "pear-shaped" flasks, each containing 10.0 ml aliquots of AVTUR, Diesel and Kerosene oils respectively.

The flasks were securely stoppered and shaken in a "Vortex Genie" shaker for 18 hours.

The phases were separated, coded and 0.1 ml aliquots of each phase taken, diluted with "Ria-Lipo-Luma" scintillator (20.0 ml) and each sample counted using a Beckman Scintillation Counter. The results were tabulated.

METHOD B

BNPD (9.96 mg) and [^{14}C] BNPD (1.10 mg) were combined and dissolved in methyl cellosolve (0.1 ml). 10.0 µl aliquots of the solution were delivered into 3 x 25 ml "pear-shaped" flasks each containing 10.0 ml aliquots of AVTUR, Diesel and Kerosene respectively.

10.0 ml aliquots of buffer pH4 aqu. soln. were then pipetted into each of the three flasks. The flasks were securely stoppered and shaken in a "Vortex Genie" shaker for 18 hours.

The phases were separated, assayed as previously and the results tabulated.

RESULTS AND CONCLUSION

Results from METHOD A

Phases	Counts/min (80% effic.)	*Corrected counts c/min	% Distribution aqu./oil	K, aqu./oil	K, oil/water
Aqu. Ex. AVTUR Avtur	24296 348	23996 0.00	100	∞	-
Aqu. Ex. Diesel Diesel	23690 385	23390 71	99.69	329	0.003
Aqu. Ex. Kerosene Kerosene	23737 325	23437 44	99.81	532	0.0018

* Counts have been corrected for background.

Results from METHOD B

Phases	Counts/min (80% effic.)	*Corrected counts c/min	% Distribution aqu./oil	K, aqu./oil	K, oil/water
Aqu. Ex. AVTUR Avtur	22151 369	21851 0.00	100	∞	-
Aqu. Ex. Diesel Diesel	23133 457	22833 143	99.37	159	0.0062
Aqu. Ex. Kerosene Kerosene	23802 331	23502 50	99.78	470	0.0021

* Counts have been corrected for background.

The Distribution Law was applied to the dilute solutions used, and the radio-active counts were used as a measure of concentration levels:

$$\frac{\text{Concentration in aqu. phase (pH4 buffer) c/min}}{\text{Concentration in oil-phase, c/min}} = \text{K-Partition coefficient}$$

The results from Method A indicated that there was >99.5% retention of BNPD in the aqu. buffer soln., and from Method B >99.3% of BNPD dissolved in the oil-phase had partitioned into the aqueous buffer phase.

2.2.2 Laboratory Flask Test

For ease of handling a fuel:water ratio of 1000:1 was chosen although in many cases the ratio may well be in excess of this figure.

Two litres of diesel fuel and 2 mls of water were placed in each of 2 glass separating funnels. One flask was treated with 2 mls and the other 4 mls of a 1% solution of BNPD in EGME (2-methyoxyethanol). These doses corresponded to 10 ppm and 20 ppm respectively of BNPD in the fuel phase. The treated separators were inverted once through 180° and allowed to settle and stand for 7 days. After this time the aqueous phase was removed and assayed for BNPD content using an HPLC technique.

The results showed a residual of 3000 ppm BNPD in contact with the fuel dosed with 10 ppm and 5760 ppm from the 20 ppm dosed fuel.

The partition co-efficient K (oil/water) is defined as :-

$$K = \frac{Cf}{Cw} \qquad . \quad . \quad . \quad . \quad . \qquad (1)$$

where Cf = concentration in the fuel phase
Cw = concentration in the water phase

The dose is defined as :-

$$\text{Dose} = \frac{CfVf + CwVw}{Vf + Vw} \qquad . \quad . \quad . \quad . \quad . \qquad (2)$$

where Vf = vol. of fuel phase
Vw = vol. of water phase

Rearranging Eqn. (2) and substituting for Cf from Eqn. (1).

$$Cw = \frac{\text{Dose }(Vf + Vw)}{KVf + Vw} \qquad . \quad . \quad . \quad . \quad . \qquad (3)$$

Applying equation (3) to the results determined in this experiment the partition coefficient, K, was calculated as 0.0033 from the 10 ppm dose results and 0.0035 from the 20 ppm results. These figures are in good agreement with the figure of 0.003 for diesel/water partition determined using ^{14}C labelled BNPD and a scintillation counting technique.

2.3 Fuel Compatibility Studies

Samples of marine gas oil were subjected to a series of standard tests to establish whether the addition of BNPD at 10 ppm to the fuel had any detrimental effect. The BNPD was added to the gas oil as a 1% solution in EGME. The results are reported in Table 2 below.

TABLE 2

Test	Method	Gas Oil	Gas Oil + 10 ppm BNPD
Sulphur Content % wt.	IP 336	0.23	0.23
Ramsbottom Carbon Residue on 10% Bottoms	IP 14	0.19	0.11
Viscosity @ 40°C cst	ASTM D445	3.19	3.18
Density @ 15°C g/cm^3	ASTM D4052	0.8532	0.8532
Flash Point °C	IP 34	78	76
Water Content % Vol.	ASTM D95	<0.0[illegible]	<0.05
Sediment % wt.	IP 53	<0.01	<0.01
Ash Content % wt.	IP 4	<0.001	<0.001
Copper Corrosion 3 hours @ 100°C	IP 154	1A	1A
Cold filter Plugging Point °C	IP 309	-7	-8
Centane Index	IP 364	48	47
Distillation Data	ASTM D86		
Initial Boiling Point °C		172	173
90% Recovery °C		339	340
Final Boiling Point °C		354	355

NOTE

All results comply with BS 2869 Class A2 specification for fuel oils. The additive has no significant effect on the fuel.
Note; The cold filter plugging point is above the maximum level permissible for winter quality fuels.

3. MICROBIOLOGICAL STUDIES

3.1 Activity of BNPD against fuel storage tank water bottom micro-organisms

A pooled sample of fuel tank water bottoms containing slime was dispersed in 20 ml volumes and stored at ambient temperature. Samples of the water/slime were treated with 50, 250, 500 and 1000 ppm BNPD and were examined for total viable counts initially and at 1, 2 and 5 days. Total viable counts were carried out by making serial dilutions of the sample in ¼ strength Ringers solution. 1 ml volumes of this dilution series were plated in Tryptone Soya Agar (TSA) to enumerate aerobic bacteria and Sabouraud Dextrose Agar (SAB) to enumerate yeasts and moulds. The TSA plates were incubated at 32°C for 3 days and the SAB plates at 25°C for 5 days. The numbers of sulphate reducing bacteria (SRB) in the samples were estimated using a modified iron sulphite agar tube technique, the tubes being incubated at 32°C for up to 21 days.

Any predominant bacterial types from the TSA plates were identified using biochemical tests based on the API 20NE test system (API Laboratory Products Ltd.) and microscopic examination.

Fungi were identified on their colony morphology and microscopic structure.

The water bottom sample comprised a mixed microbial population containing *Pseudomonas stutzeri, Achromobacter* sp., *Pseudomonas vesicularis* and several other Pseudomonas species. The principal sulphate reducing bacteria were *Desulfovibrio desulfuricans.* The main fungal contaminants were mycelial yeasts and *Phytophthora* spp.

The effect of BNPD against the aerobic bacteria, sulphate reducing bacteria and filamentous yeasts in the pooled water sample can be seen in Figures 1, 2 and 3. The results show that BNPD, even at 50 ppm, caused a significant reduction in the number of aerobic bacteria, anaerobic sulphate reducing bacteria and filamentous yeasts found in the water phase samples.

3.2 Activity of BNPD against micro-organisms in fuel/water systems

Two litre separating funnels were filled with diesel fuel. Each flask was then inoculated with 2 ml of a concentrated mixed microbial inoculum. The mixed inoculum was composed of both aerobic bacteria and fungi. The bacterial inoculum was prepared by washing off Tryptone Soya Agar plates of bacteria isolated from contaminated diesel fuel/water samples. This inoculum was diluted with sterile distilled water to give approximately 10^6 colony forming units per ml. The fungal inoculum was prepared from washed off slopes of two strains of *Hormoconis resinae (Cladosporium resinae)* isolated from contaminated aviation fuels, two strains of *Penicillium* sp. and a *Hormoconis (Cladosporium)* sp. isolated from infected diesel fuels. The mould inoculum was diluted in sterile distilled water to give approximately 10^4 colony forming units per ml. 2 ml of the bacterial and fungal inoculum were added to 16 ml of sterile distilled water to give the final mixed inoculum.

Following addition of the 2 ml of mixed inoculum to each flask, the flasks were inverted once to mix. The flasks were then treated with two formulations of BNPD - a 1% w/v solution in EGME (Product A) and a 10% w/v solution in dipropyleneglycol methyl ether (Product B). An untreated control flask was also used. The flasks were stored at room temperature for up to 7 days and samples were removed initially and at 7 days following mixing by swirling. The number of viable micro-organisms present in the water phase was examined using a viable plate count technique (see Table 3).

TABLE 3

	Number of viable colony forming units per ml			
	Initial		7 days	
Treatment	Bacteria	Fungi	Bacteria	Fungi
Control	5.0×10^4	1.4×10^6	4.4×10^6	5.9×10^4
1000ppm Product A (=10ppm BNPD)	5.0×10^4	1.4×10^6	<10	<10
2000ppm Product A (=20ppm BNPD)	5.0×10^4	1.4×10^6	<10	<10
100ppm Product B (=10ppm BNPD)	5.0×10^4	1.4×10^6	<10	3.2×10^4
200ppm Product B (=20ppm BNPD)	5.0×10^4	1.4×10^6	<10	8.0×10^3

The results show that in the untreated control system the numbers of aerobic bacteria increased from approximately 50,000 colony forming units per ml to 4,400,000 colony forming units per ml during the one week trial period. During the same period the number of fungi recovered showed a slight drop in numbers. In both the Product A treated systems no viable aerobic bacteria or fungi were recovered at 7 days. In the case of the Product B treated system no viable bacteria were isolated and there was some reduction in fungal numbers.

3.3 Activity of BNPD against micro-organisms in a marine gas oil tank

A marine vessel known to suffer from microbial contamination in one of its gas oil tanks was treated with Product A at 1000 ppm (=10 ppm BNPD). Samples were removed from the fuel and water phase before and after treatment. Viable counts on the water phase were carried out as in Section 3.1. Fuel phase samples were tested using the IP test method 385/88 (13).

The results of the study are shown below in Table 4.

TABLE 4

Use of Product A in marine gas oil tank

		Number of viable colony forming units per ml		
Sample	Phase	Aerobic bacteria	Fungi	Sulphate reducing bacteria
Port main bunker tank Day 0	Water Fuel	3.7×10^4 G-veR <10	1.8×10^4 MY <10	<10 <10
Port main bunker tank Day 1	Water Fuel	<10 <10	2.0×10^1 MY <10	<10 <10

G-veR = Gram negative rod shaped bacterium
MY = Mycelial yeast

The results show the gas oil water bottom sample taken on Day 0 contained high numbers of Gram negative bacteria and lower numbers of mycelial yeasts. These organisms appeared to be restricted to the water phase as no viable organisms were recovered from the hydrocarbon phase. Following treatment with Product A no viable bacteria were isolated from the water phase and the numbers of mycelial yeast were greatly reduced. Again the hydrocarbon phase was found to be free from contamination.

3.4 Activity of BNPD against micro-organisms in fuel storage tank studies

Several land-based fuel storage tanks known to have contaminated water bottoms were treated with Product B at 100 ppm (≈10 ppm BNPD). Samples were removed for viable counts as above from both the water and hydrocarbon phases. The concentration of BNPD in the water phase was determined by a HPLC technique (14).

All the hydrocarbon phase samples tested contained a very low microbial content with no viable micro-organisms being recovered in most cases. The microbial content and BNPD concentrations in the water phase are shown below.

TABLE 5

Microbial numbers and BNPD concentration in a motor spirit water bottom from a storage tank

	Day 0 before treatment	Day 0 after treatment	Day 10	Day 47
Aerobic bacteria	4.0×10^4 G-veR	-	-	1.9×10^2 G+veR
Fungi	1.0×10^1 Y 3.0×10^1 M	-	-	<10
SRB	1.5×10^5	-	-	5.0×10^1
[BNPD] ppm	0	3000	1808	548

TABLE 6

Microbial numbers and BNPD concentration in a Kerosene water bottom from a storage tank

	Day 0 before treatment	Day 0 after treatment	Day 13	Day 23	Day 60
Aerobic bacteria	1.9×10^6 G-veR	-	1.0×10^2 G+veR	-	9.6×10^3 G+veR
Fungi	<10	-	<10	-	2.5×10^4 M
SRB	1.0×10^4	-	<10	-	1.0×10^1
[BNPD] ppm	0	885	79	61	21

TABLE 7

Microbial numbers and BNPD concentration in a Derv water bottom from a storage tank

	Day 0 before treatment	Day 6	Day 17	Day 30	Day 38	Day 77
Aerobic bacteria	1.6×10^6 G-veR	<10	-	-	-	<10
Fungi	1.7×10^3 MY 8.0×10^1 M	5.0×10^3 MY 1.0×10^2 M	-	-	-	9.0×10^3 Y 2.0×10^1 M
SRB	2.0×10^3	<10	-	-	-	2.0×10^1
[BNPD] ppm	-	-	91	22	3	3

G-veR = Gram negative rod shaped bacteria
G+veR = Gram positive rod shaped bacteria
M = Mould
Y = Yeast
MY = Mycelial yeast

Table 5 reports the results obtained from the water bottom samples of a motor spirit tank. Initially before treatment the water bottom contained high levels of SRB and Gram negative aerobic bacteria with lower numbers of fungi. Following treatment with Product B the numbers of these organisms were drastically reduced. The bacterial population had changed from high numbers of a predomonantly Gram negative spoilage population to low numbers of Gram positive spore forming bacteria. The level of BNPD assayed fell from 3000 ppm on Day 0 to 548 by the 47 day sample.

The results obtained in a Kerosene storage tank can be seen in Table 6. The water bottom contained a high aerobic Gram negative bacterial population and a high SRB count. Following treatment these numbers were reduced by the 13 day sample with aerobic bacteria dropping from 1,900,000 colony forming units (cfu) per ml to 100 cfu per ml (principally Gram positive spore forming bacteria) and SRB dropping from 1,000,000 cfu per ml to none detectable. By Day 60 some regrowth of moulds and bacteria was evident. Again a gradual reduction in BNPD concentration was seen.

In the Derv samples (Table 7) the water bottom contained a high aerobic bacterial population with moderate numbers of fungi and SRB. Following treatment the numbers of aerobic bacteria were reduced to below levels of detection and remained at this level during the 77 day study. Fungal numbers remained at a relatively constant level and SRB numbers were significantly reduced.

4. CONCLUSIONS

Solubility and partition coefficient measurements suggest that BNPD could offer the required physico-chemical properties for a fuel treatment biocide. Fuel compatibility studies confirm also that BNPD does not adversely affect the normal fuel performance parameters.

The laboratory and field studies on microbiological efficacy demonstrate that BNPD, added to a fuel system, achieves excellent control of aerobic and anaerobic bacteria in water bottoms associated with the stored fuel.

Good control of fungi was shown under laboratory conditions (Figure 3). In field trials, however, BNPD was less effective when formulated in dipropyleneglycol methyl ether. When formulated in EGME, the known antifungal activity of this solvent provided a good broad spectrum product.

RE/WGG/YED
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Figure1. Activity of BNPD against aerobic bacteria

in a water bottom sample

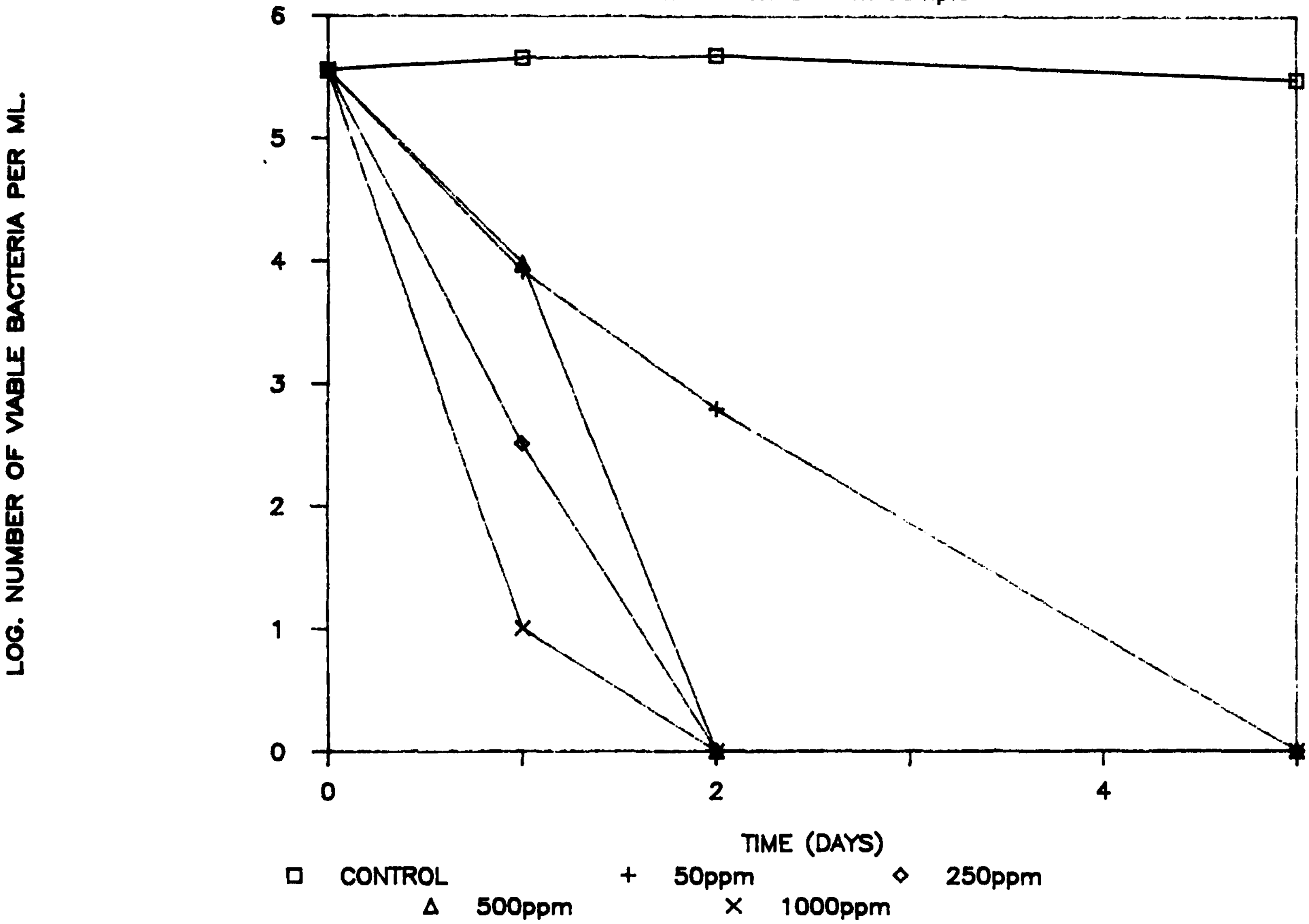


Figure 2. Activity of BNPD against anaerobic bacteria

in a water bottom sample

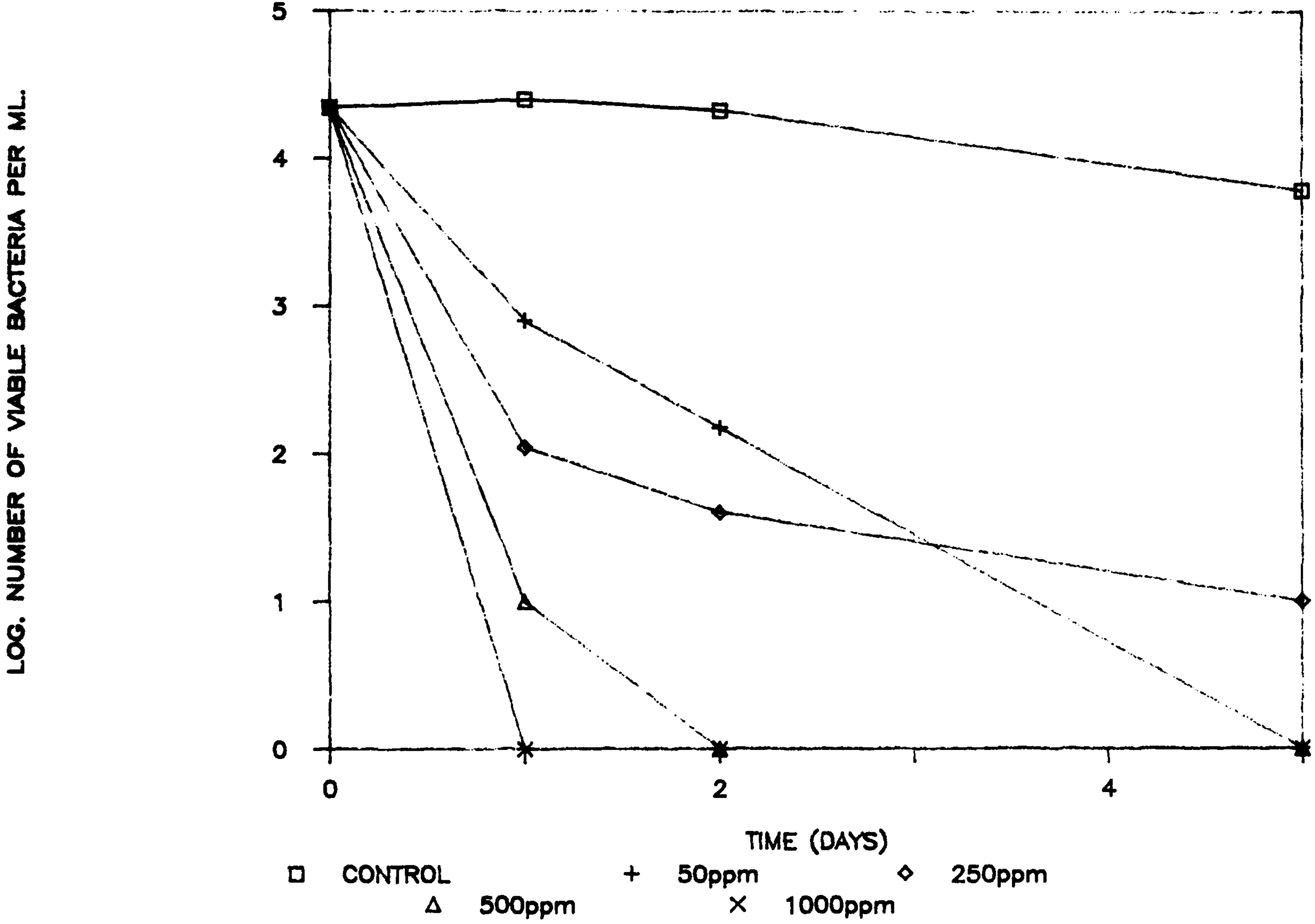
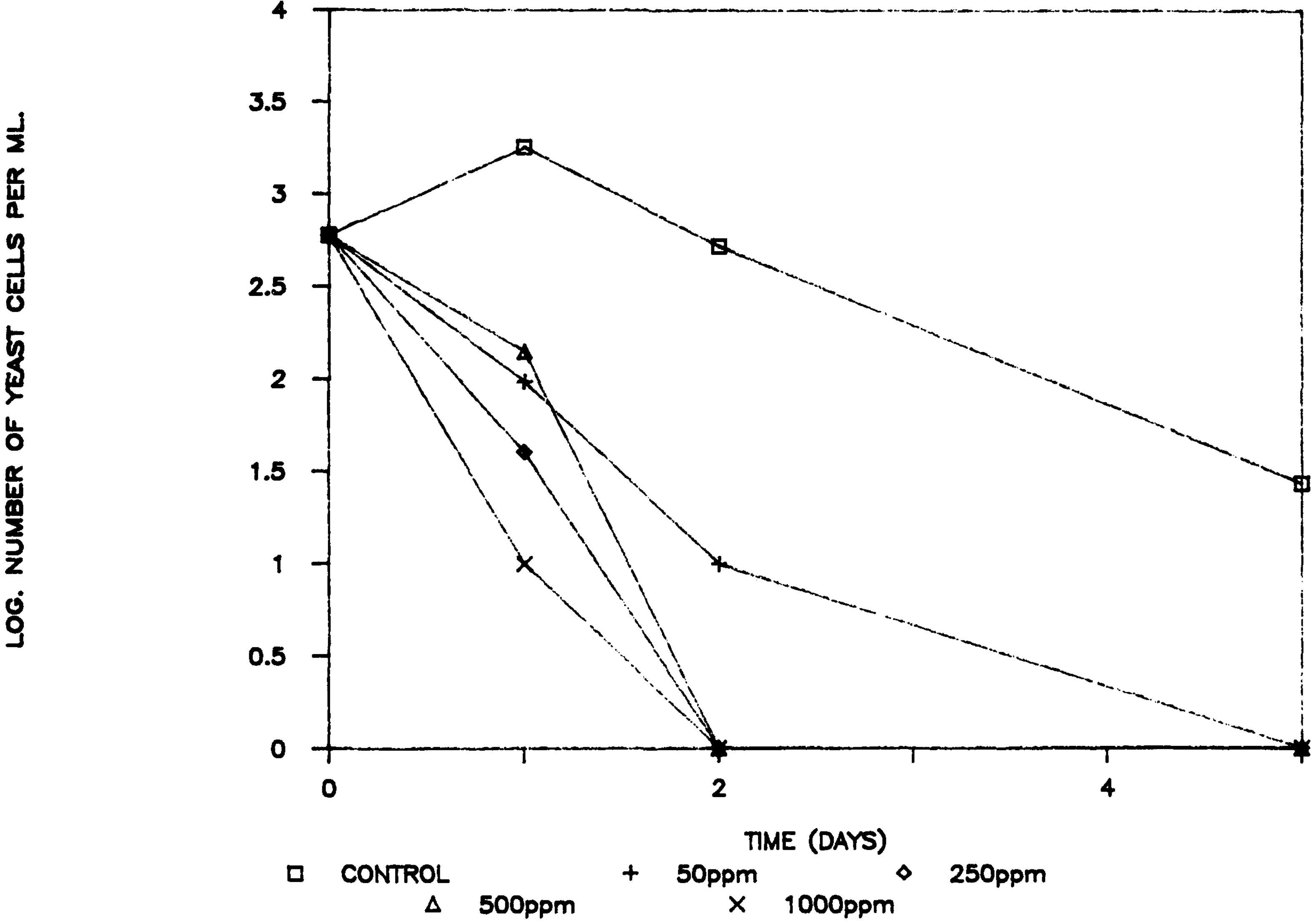


Figure 3. Activity of BNPD against yeast cells

in a water bottom sample



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

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ABSTRACT

Large diesel fuel storage containers are subject to microbiological related problems, ie biofouling biocorrosion and degradation of the fuel. Micro-organisms are able to use diesel fuel as carbon and energy source. Four fungi and nineteen bacteria species were isolated from contaminated diesel fuel and blocked filters, all proved to be primary users of diesel fuel. Two bacteria species specifically were found to be the most common cause of microbial induced filter blockages due to their ability to form spores and to inhibit the growth of other hydrocarbon utilising micro-organisms. It was shown that one of these was capable of excreting a gummy substance which was able to rapidly block fuel filters.

Factors which contribute to the development of a biological treatment strategy are the presence of water with readily available nutrients and carbon source within the tank, cost of treatment and operational considerations. The use of a water soluble biocide treatment programme in these storage facilities has proved successful and has prevented the establishment of a food chain which can cause the blockage of fuel filters, the corrosion of containers, pipelines and meters and the degradation of the fuel.

The first report of hydrocarbon utilization by micro-organisms (mos) is usually ascribed to a Japanese botanist Miyoshi in 1895 who reported paraffin being attacked by a fungus (Miyoshi 1895)(1). Today this aspect of microbial contamination of hydrocarbon products is well known. Extensive work had been done on the preservation of jet fuel (Scott 1971)(2) and was thus considered as a reference point in looking for solutions for similar problems experienced in diesel fuel.

Scheduled inspections of diesel fuel storage facilities taken off line helped to answer the initial question if problems experienced can be related to micro-organisms. Three aspects were identified:

1) chemical corrosion of the tank wall and floor,
2) biocorrosion of the tankfloor and tankwall below the waterline and
3) a waterbottom (ca 15 cm) being present.

This confirmed the existence of the regenerative cycle causing the deterioration of distillate fuels through oxidation, microbiological activity and corrosion. (Fig 1) as described by O'Conner (1984)(3).

Waste byproducts from microbial growth on diesel fuel lead indirectly to the corrosion of tank surfaces while certain groups of organisms like sulphate reducing bacteria can cause biocorrosion. Metals released to the fuel speed oxidation through catalytic action which in turn yields more water to form a better environment for microbial growth.

Isolates from the tankbottoms and blocked in-line fuel filters had shown a microbial population consisting of various bacteria and fungi species. Work done by Darby et al (1968)(4) on fungi and Cooney and Kula (1970)(5) on bacteria isolates from hydrocarbons suggested that not all isolates are primary hydrocarbon utilizers. Taking into consideration that micro-organisms can only grow where all nutrient requirements are met all isolates were screened to identify primary hydrocarbon users. A test medium meeting the requirements for growth : inorganic salts nutrient medium with diesel fuel as only carbon source was used. Pure cultures of each isolate was inoculated into separate test flasks. After a test period of 30 days at 30°C primary hydrocarbon utilizers were identified using an increase in biomass as criterium for hydrocarbon utilization.

From all the isolates nineteen bacteria species and four fungi species were identified as primary hydrocarbon utilizers. A catch phrase HUM BUGS was developed for these hydrocarbon utilizing micro-organisms. The fungi included the specie well known in jet fuel, *Cladosporium resinae*. Two micro-organisms were prevalent in most problem areas examined and are able to survive microbiocide treatments. The micro-organisms were provisionally identified as a specie related to *Bacillus cereus* and a strain of *Bacillus coagulans* (Cowley 1985)(6). The *B coagulans* related specie is a sporeforming micro-organisms which grows rapidly on diesel fuel, inhibits the growth of other micro-organisms (specifically fungi) and produces a gummy substance which is able to block fuel filters completely within a relatively short time. The degradation of diesel fuel in storage facilities by HUM BUGS gives rise to another regenerative cycle (Fig 2).

With the primary diesel fuel utilizers identified in the microbial population the establishment of a foodchain in the tankbottoms was easily explained. Two possible alternatives were considered to control the micro-organisms population. The first alternative is limiting nutrients to the micro-organisms population using Liebig's Law of Minimum (Liebig's law states that the total yield or biomass of any organism will be determined by the nutrient that is present in the lowest concentration in relation to the requirements of the given organism.) Limiting nutrients proved not to be acceptable; the carbon source (diesel fuel) is constantly present while water with inorganic nutrients is always present in diesel fuel. In floating roof storage tanks rain can substantially contribute to the waterbottom. The second alternative to target the biological control procedures at the HUM BUGS and thus prevent a microbial population from establishing itself was therefore a more viable consideration.

Experience gained from jet fuel preservation had shown excellent results with biocides preventing microbial contamination. Faced with a bewildering array of commercial biocides in a list which seems to increase at a rate not unlike that of the bacteria themselves, adding to this that each product is the ultimate answer to the problem, the choice of a biocide is truly baffling.

The various biocides proposed for application in diesel fuel storage facilities were evaluated for biocidial effectiveness against the HUM BUG isolates. A short term evaluation test lasting 96 hours was used to select or screen biocides for a longer term evaluation. The evaluation test consisted of test flasks with test medium which is diesel fuel : inorganic nutrient salt solution in a ratio of 5:1 inoculated with the HUM BUG isolates. Biocides were evaluated at the dosage level proposed by the suppliers, half the recommended dosage level and double the proposed dosage level. Surviving micro-organisms were determined every 24 h for the test period using plate count procedures. Results obtained are given in Fig 3(a) (b) (c). Four biocides proved to be superior against the HUM BUG population. However none of the biocides had achieved the expected limit set for an excellent kill. This limit was determined by the number of spores present in the inoculum. Biocides are per definition only required to kill vegetative micro-organisms and thus a requirement for an excellent biocide can be set.

Taking into consideration that a biocide treatment programme will have an economic implication two biocides were selected for the longer term evaluation. Biocide treatment of the total volume diesel fuel produced will contribute largely to the consumer price. An effective water soluble biocide, dosage calculated on the waterbottom present, will minimise the economic implications and will be active against the initial micro-organism population present at the diesel fuel : water interphase while the operational "problem" of water bottoms always present in diesel fuel storage tanks will serve as medium to combat microbial problems in the tanks. The two biocides selected were therefore water soluble with effectiveness against the primary hydrocarbon utilizing micro-organisms.

The longer term evaluation test included the determination of the period of biocidial effectiveness with rechallenge at seven day intervals and the possible contribution of the biocides to the chemical corrosion rate. Test flasks with similar conditions as the short term test were used. A mild steel corrosion coupon was also suspended in the test medium for corrosion rate determination. The biocides were evaluated at the proposed dosages only.

After every seven day period the surviving micro-organisms population numbers were first determined before reinoculation with a fresh HUM BUG inoculum to evaluate the biocides for effectiveness over the 30 day test period. Biocide B lost control over the micro-organisms population after 16 days while Biocide C showed biocidial effectiveness up to day 28 (Fig 4).

The final requirement Biocide C had to meet before recommendation for use in diesel fuel storage facilities is that it had to be proven not to cause adverse effects on the diesel fuel properties. A simulated larger scale test using 200 l mild steel containers with a waterbottom containing inorganic nutrients were used. Mild steel corrosion coupons were suspended over the diesel fuel : water interphase for corrosion rate determinations every 30 days for the 90 day test period. Biocide additions, calculated on the waterbottom, were done at the end of each period of biocidial effectiveness while the micro-organisms population were monitored twice a week. At the end of the test period the diesel fuel was tested to meet all requirements for diesel fuel (eg fuel injector and plunger tests and diesel fuel specifications). Showing no adverse effects on the diesel fuel over a longer period the biocide was recommended for use in diesel fuel storage facilities.

The biological control strategy was introduced and maintained in the large diesel fuel storage facilities. Factors which contributed to the development of a biological treatment programme are the presence of water, cost of treatment and operational considerations. The water soluble biocide, dosage calculated on the waterbottom (dead volume) is dosed on the incoming line (Fig 5). The effectiveness of the biocide is monitored using a bottom sampler consisting of a sterile glass container under vacuum to obtain a sample at the bottom of the storage tank for microbiological counts (Fig 6a & b). After the effective treatment period of the biocide, the waterbottom is drained and the tank redosed. Biological control can thus be achieved by an effective biocide treatment programme with a regular monitoring programme.

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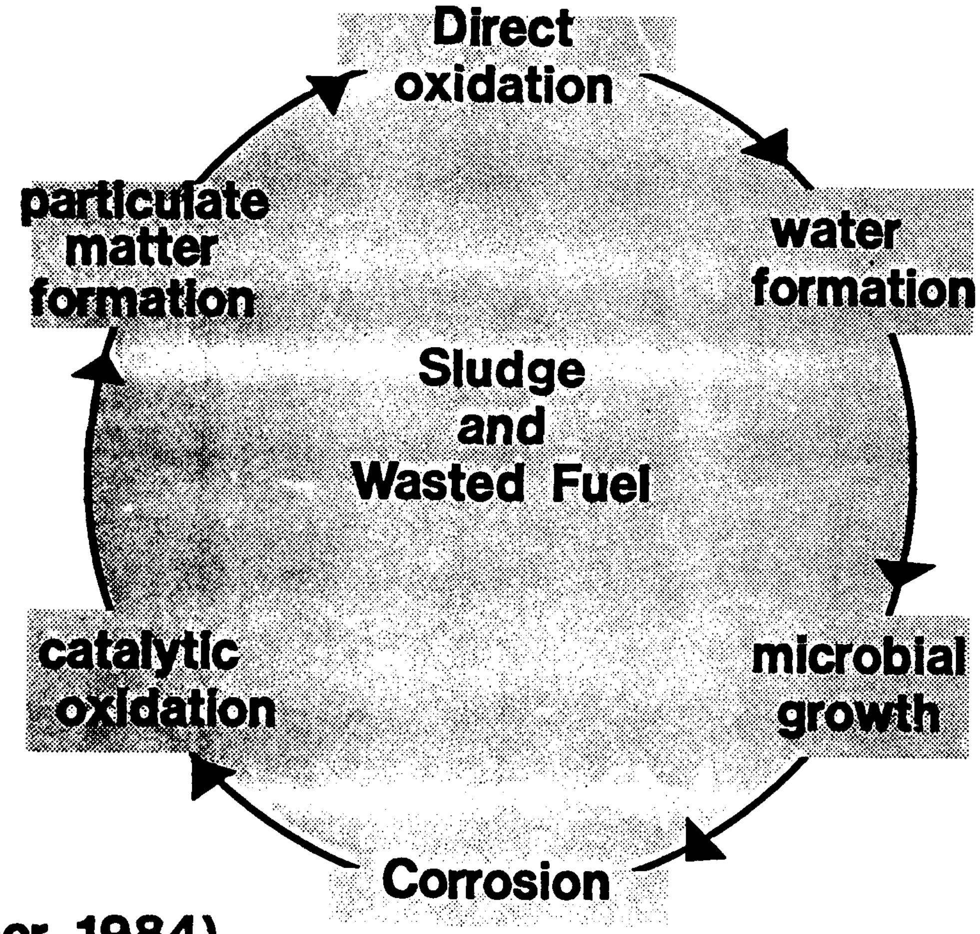
FIG 1 : OXIDATION, CORROSION AND MICROBIAL GROWTH COMBINE TO CREATE A REGENERATIVE CYCLE (O'CONNER 1984)

REGENERATIVE CYCLE



Direct oxidation

water formation

microbial growth

Corrosion

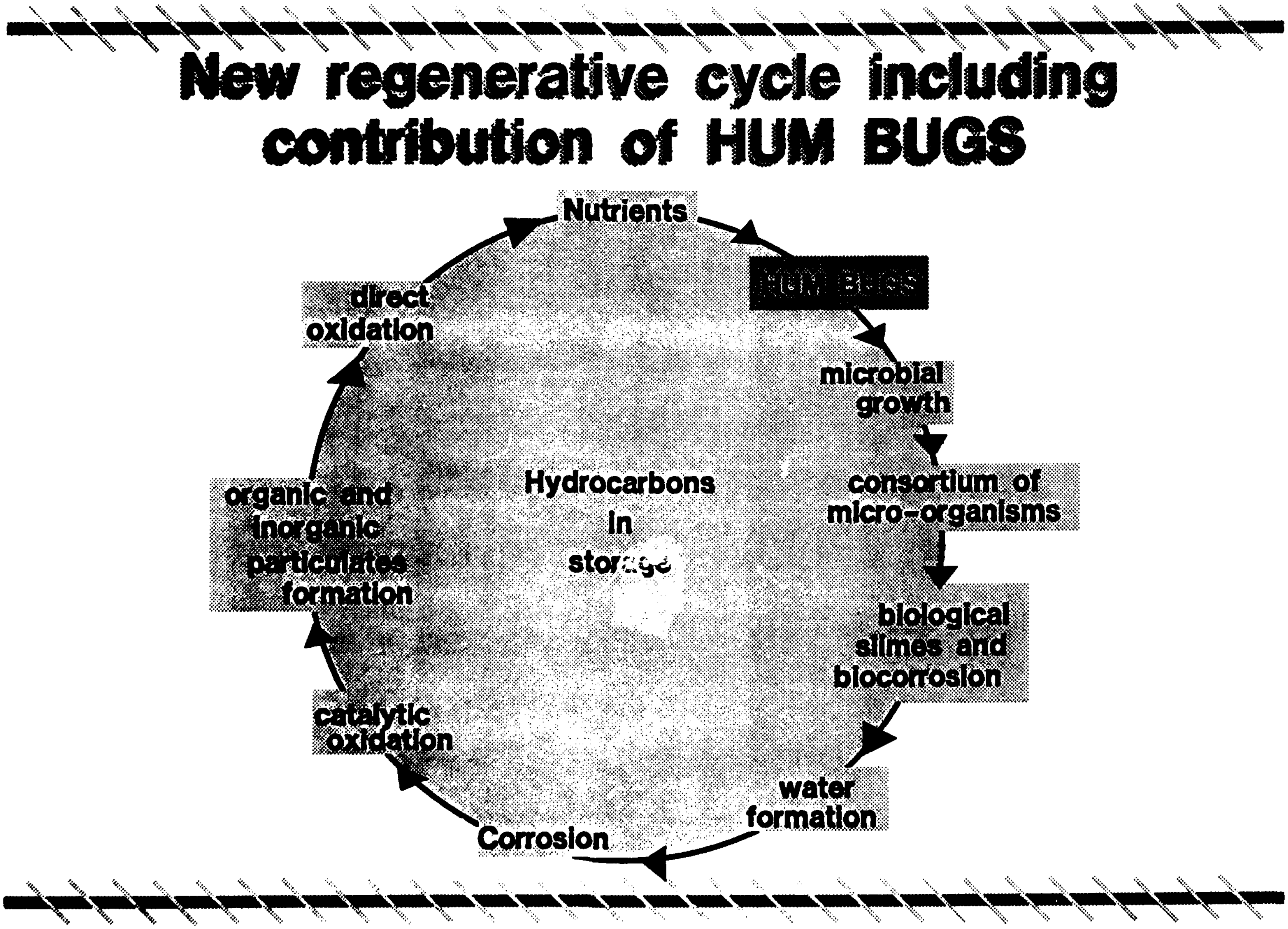
catalytic oxidation

particulate matter formation

Sludge and Wasted Fuel

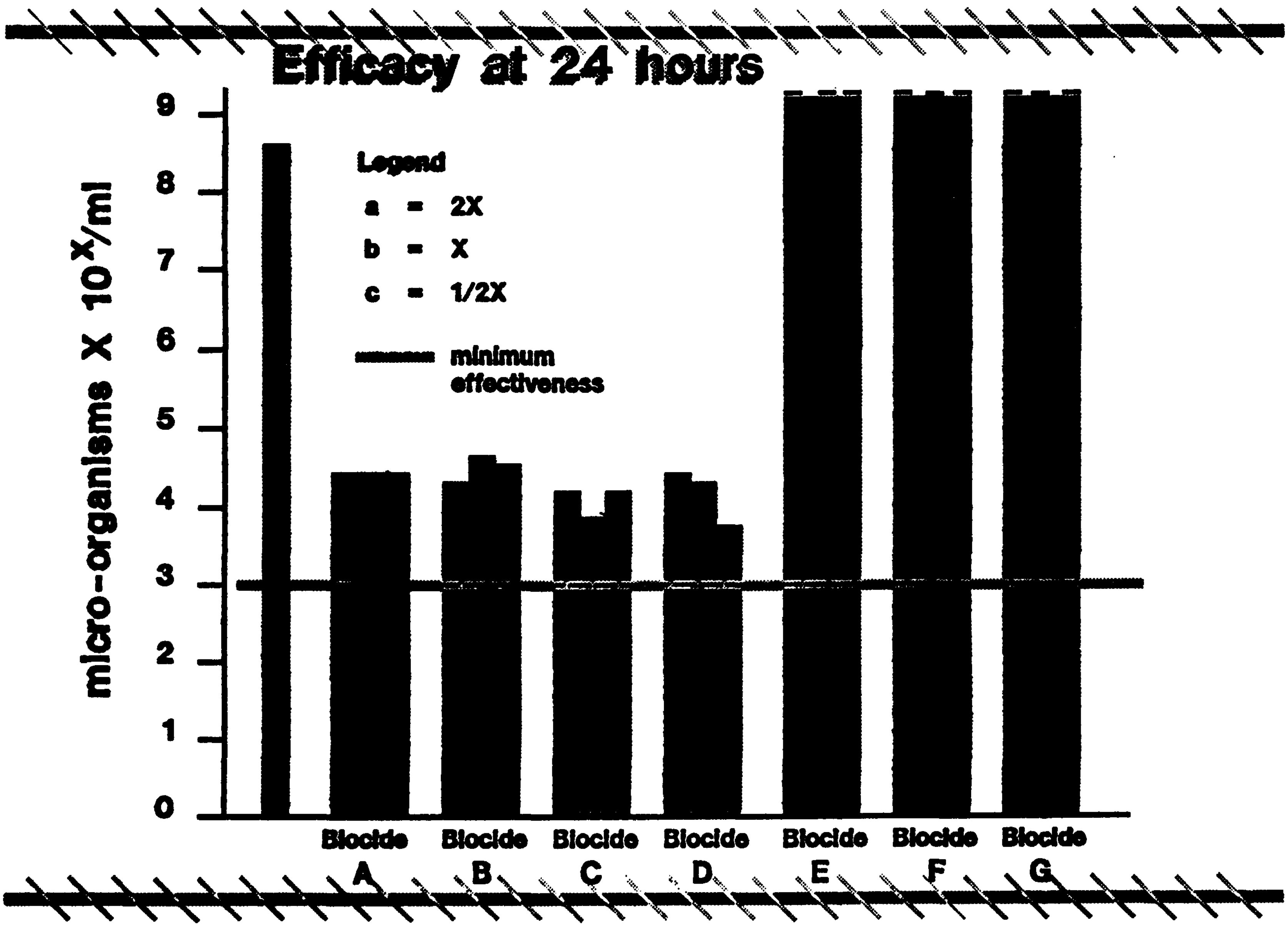
(et al O'Connor 1984)

FIG 2 : THE REGENERATIVE CYCLE IN HYDROCARBON STORAGE FACILITIES INCLUDING THE CONTRIBUTION OF HUM BUGS
(HYDROCARBON UTILISING MICRO-ORGANISMS)



New regenerative cycle including contribution of HUM BUGS

FIG 3a



Efficacy at 24 hours
micro-organisms X 10^x/ml
9
8
7
6
5
4
3
2
1
0
Legend
a = 2X
b = X
c = 1/2X
minimum effectiveness
Biocide A
Biocide B
Biocide C
Biocide D
Biocide E
Biocide F
Biocide G

FIG 3b

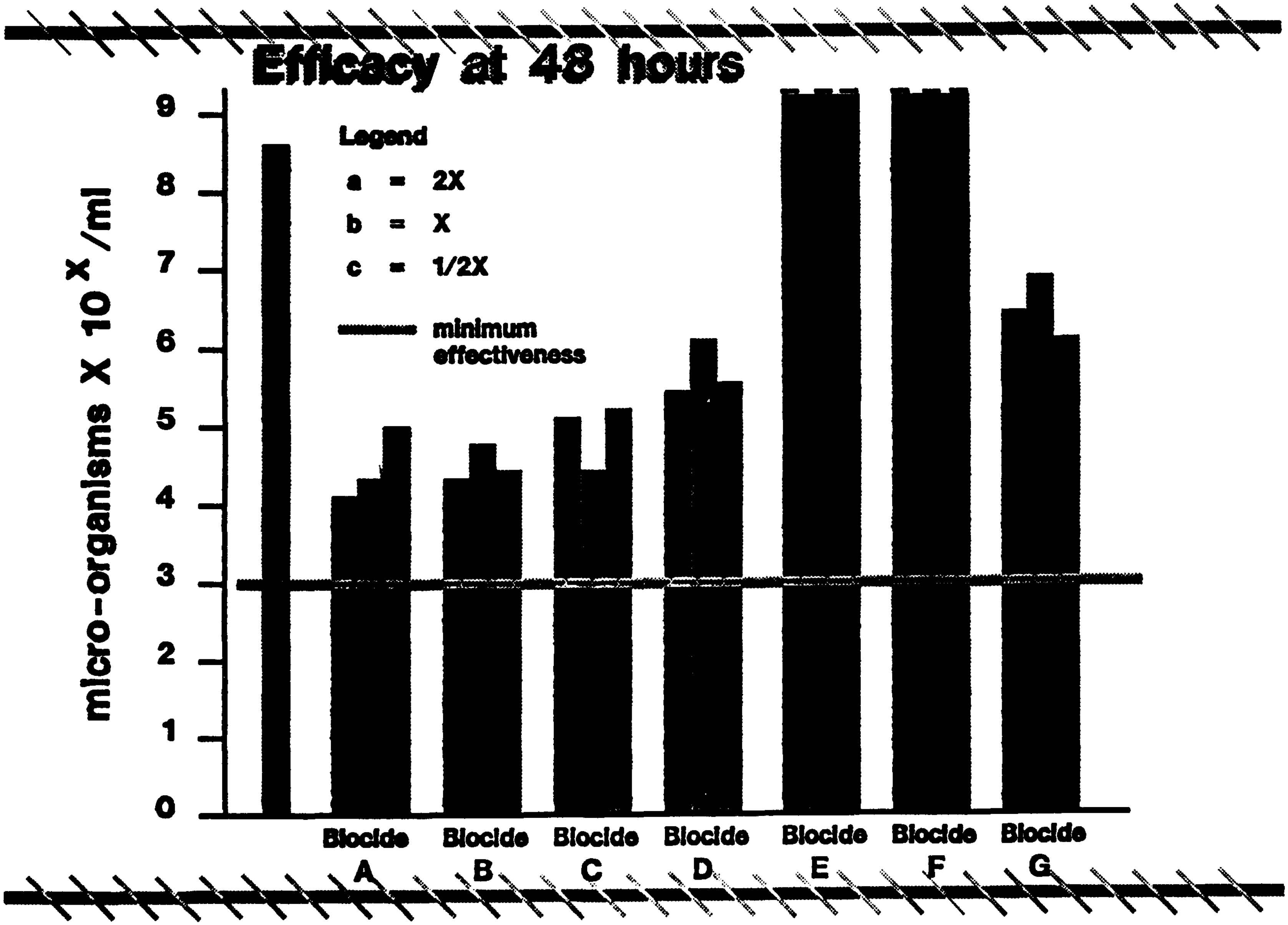

Efficacy at 48 hours
micro-organisms X 10^X/ml
0
1
2
3
4
5
6
7
8
9
Legend
a = 2X
b = X
c = 1/2X
minimum effectiveness
Biocide A
Biocide B
Biocide C
Biocide D
Biocide E
Biocide F
Biocide G

FIG 3c

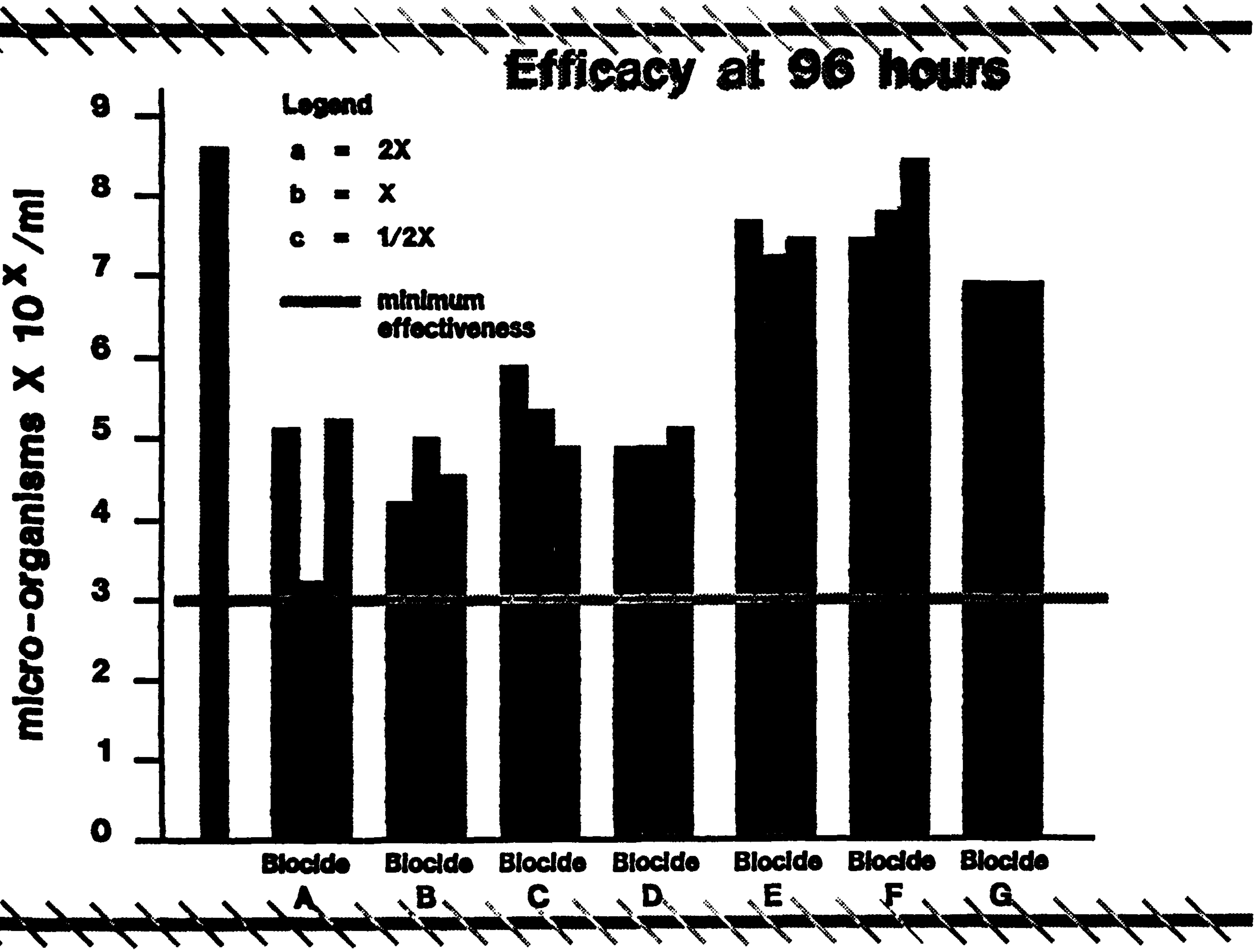

Efficacy at 96 hours
micro-organisms X 10^x /ml
9
8
7
6
5
4
3
2
1
0
Legend
a = 2X
b = X
c = 1/2X
minimum effectiveness
Biocide A
Biocide B
Biocide C
Biocide D
Biocide E
Biocide F
Biocide G

FIG 4

Efficacy of biocides in 30 day evaluation

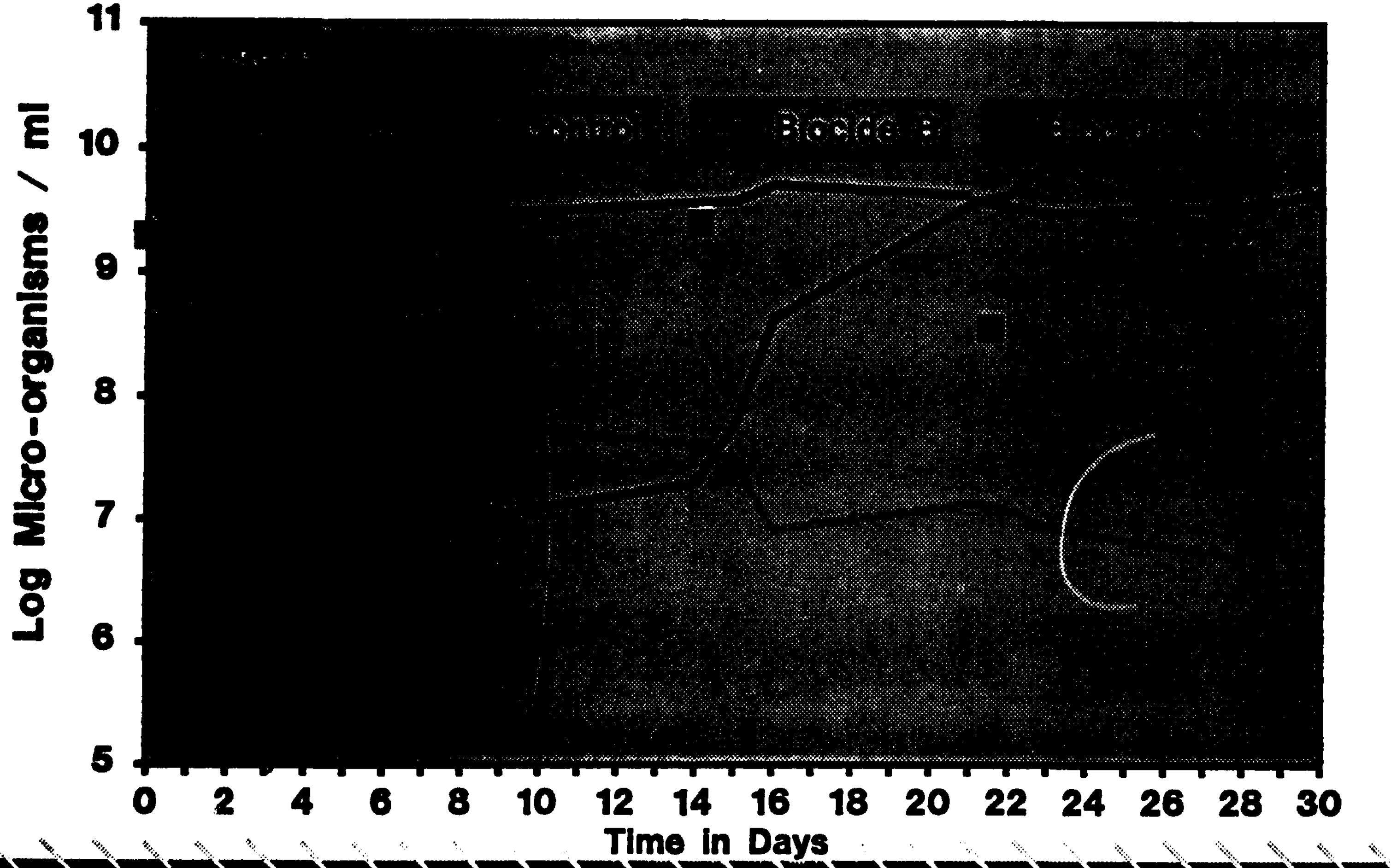


FIG 5

Schematic Diagram of a Diesel Fuel Storage Tank

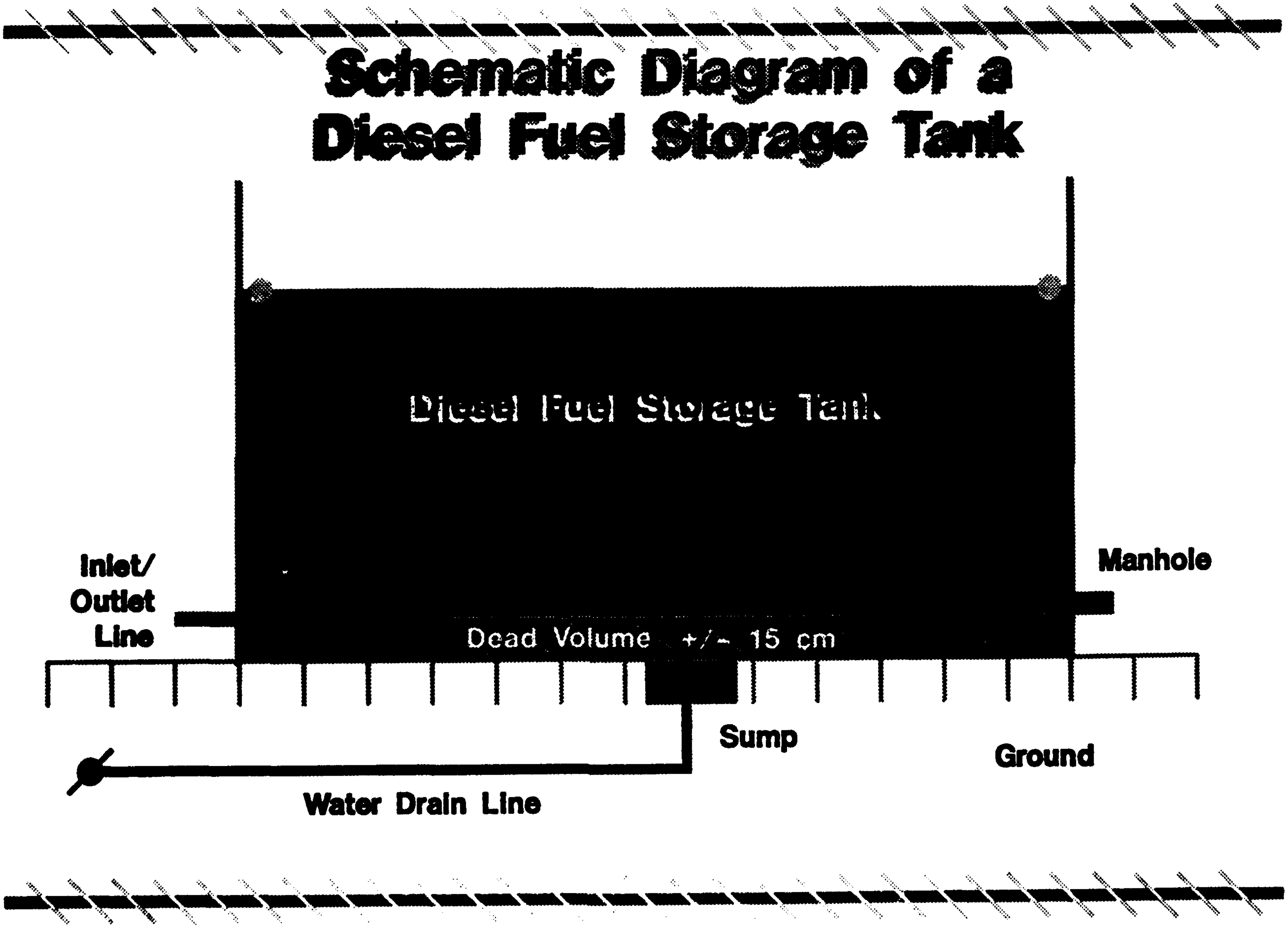


FIG 6a

Bottom sampler with sterile glass container under vacuum

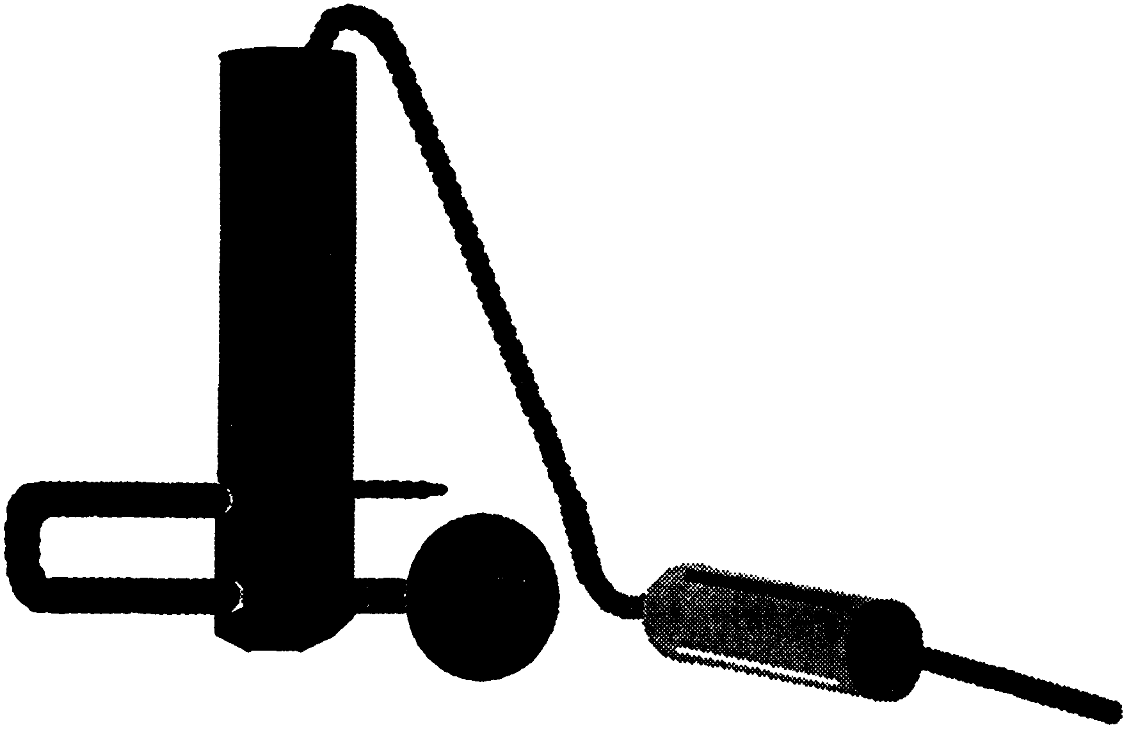
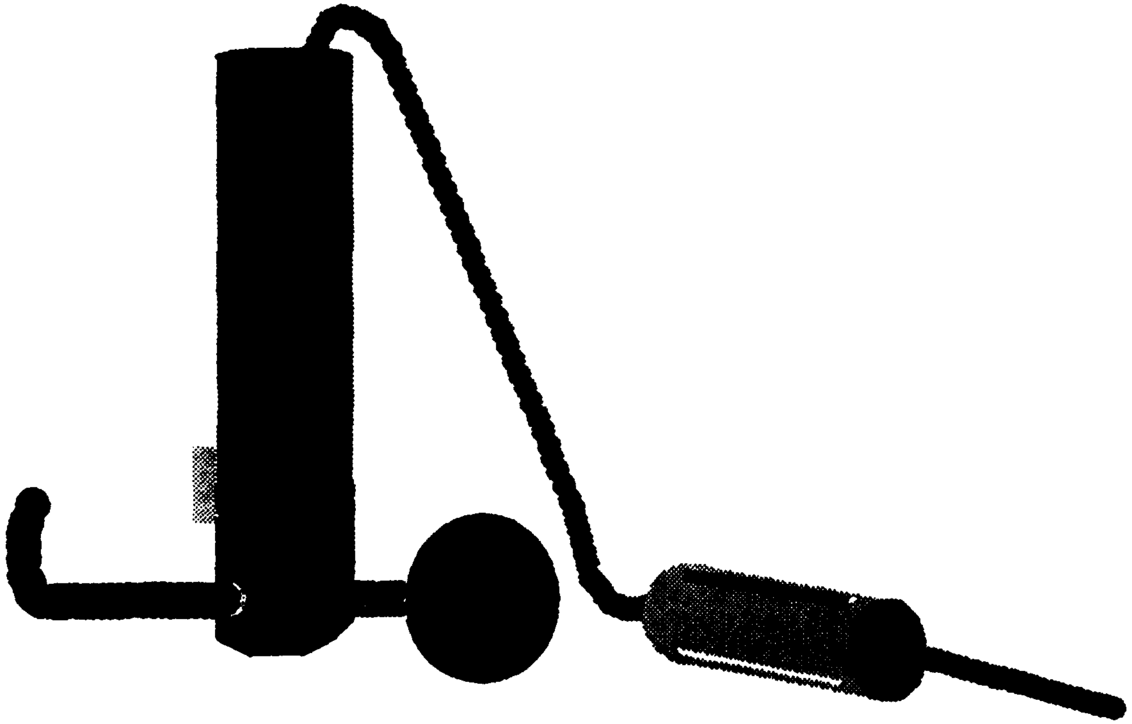


FIG 6b

Bottom sampler with water sample



MICROBIOLOGICAL TEST METHODS FOR FUELS IN THE LABORATORY AND ON SITE

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1. Introduction.

Microorganisms can proliferate in free water associated with distillate fuels and subsequently may become dispersed in the fuel phase. Both aqueous and fuel phase samples may be presented for microbiological examination. In general the typical Gram negative spoilage bacteria rapidly lose viability in the fuel phase (1) whilst moulds, particularly spores, tend to pass readily into the fuel phase and survive there; yeasts may exhibit better fuel tolerance than Gram negative bacteria. Thus the result of any test for viable microbes in the fuel phase is influenced by the age of the sample as well as the extent of aqueous phase growth and the intensity of agitation.

We have noticed an increased incidence of Gram positive sporing bacilli in fuel systems. These organisms seem to be more common in long established infections, presumably stimulated by the metabolic products of primary spoilage organisms, and they may be found in large numbers (in excess of 10^4 ml^{-1}) after sub-optimal applications of biocides. Spores of bacilli can be found in the fuel phase but we have not yet systematically investigated their survival or significance.

The testing for microorganisms in the fuel phase is itself a challenge to microbial technologists but the subsequent interpretation requires knowledge of the system, the exact location of the sampling point and the history of the sample. Unfortunately, very frequently the only sample available is the fuel phase.

Table 1 gives results of actual tests (using a membrane filtration technique) which illustrates this dilemma.

2. Tests on Aqueous Phase Samples.

The basic methodology for microbiological tests on aqueous samples is available in every practical microbiological handbook. Quantitative tests normally involve culturing measured aliquots of a range of dilutions of the sample. Although media such as Tryptone Soya Agar (eg.Oxoid CM131) can support a wide range of bacteria, yeasts and fungi it is preferable to additionally use a media which favours yeasts and filamentous fungi and allows them to develop without being overgrown by the more rapidly replicating bacteria. Malt Extract Agar (eg.Oxoid CM59) and Sabouraud's Agar (eg. Difco 0109.05.5) are traditional favourites for this but acid-tolerant bacteria can still overgrow fungi and in these cases Rose Bengal Agar supplemented with chloramphenicol (eg. LabM 36) is more selective.

However it is light sensitive and can change and suppress those organisms which it was designed to select. There is still no method of quantifying fungal infections satisfactorily by counting colony forming units (cfu) as each colony can arise from a single spore or a large fragment of mycelium. Visual and microscopic examination must supplement cfu counts.

A specific growth medium for sulphate reducing bacteria (SRB), Sulfate API Broth, is recommended by the American Petroleum Institute (Recommended Practice 38, 1959). We find it is not supportive of many SRB's and we routinely supplement with 0.25% sodium acetate. We also make it up in artificial sea-water if we are examining tank bottoms containing sea-water. Other workers have devised other modifications. For example, in ASTM E686-80 it is supplemented with 0.1 g of ferrous ammonium sulphate and 0.6 g of sodium sulphite per litre. SRB live in close association with steel surfaces and/or biofilm and hence may only be present in small numbers in a typical aqueous sample. Any numbers detected should give cause for concern.

The temperature of incubation should, of course, be related to the temperature of the system from which the sample was drawn. Incubation times are arbitary but 3 days for bacteria and 5 days for yeasts/fungi are usually adequate.

A variety of sterile fluids have been used as diluents when conducting viable counts e.g. distilled water, physiological saline, buffered saline, 1/4 strength Ringer's solution. We have not found significant differences between them.

Although the microbiological tests are relatively conventional it should not be assumed that the organisms are homogenously distributed in the water phase. Fig 1 illustrates how aerobic, facultive and anaerobic (SRB) bacteria tend to be heterogenously distributed and how this distribution is related to nutrients, oxygen, Eh and sulphide. Microbiologists often prefer to examine interface samples as the worst case sample but this is not always possible. The microbiological results of tests on aqueous phase samples can in fact be misleading as the exact location of the sampling probe in the water bottom may not be known. Table 2 shows microbiological results of water bottom samples drawn via the tank top in a laboratory simulation. The depth of fuel was 32 cm and the depth of water bottom 3 mm.

The entire water bottom was then recovered and assessed visually. The visual assessment was not in line with the microbiological results; a fuel user would probably have found the appearance of Tanks 4 and 5 acceptable despite the microbiological results.

It has become very apparent to us that, when preservatives or biocides are present, sufficient may be carried over into the growth media to inhibit subsequent microbial growth. Unfortunately many published papers ignore this. When testing such samples we routinely make a first dilution into a neutralising solution. For some preservatives there are specific neutralisers listed in the supplier's data sheet. If none are designated our first dilution is into a sterile solution of 4%

Tween 80 plus 0.5% lecithin or 0.5 % histidine solution. It will be apparent if carry-over of biocide is affecting results as a cfu count from greater dilutions of the sample will be disproportionally high when compared to cfu counts from lesser dilutions. In some cases there may be no easy neutralising method, particularly when only low numbers of survivors are present after a challenge test. One possible procedure is to membrane filter the sample and wash through thoroughly with sterile water or saline before transferring the membrane to a growth medium. However, field samples may not be readily filterable in practice. An alternative or additional strategy is to culture on a proprietary neutralising agar such as D/E Neutralising Agar (Difco 0686-17-2) but we find its opacity and colour are not helpful.

3. Microbiological Tests on Fuel Phase Samples.

Simple direct techniques such as spreading the sample onto agar or using a Dip-slide, yield inconsistent results because of the immiscibility of the oil sample and the aqueous growth medium. However if the fuel sample has a high emulsified water content it is possible to recover and culture some of the microbes dispersed in this by direct inoculation onto agar.

A number of strategies are available for recovering microbes from fuel into an aqueous phase so that they can be manipulated and tested by conventional microbiological techniques. In brief these strategies are

a) Shaking with water - simple but not very quantitative
b) Centrifuging over water (2). This can be made quantitative if deposits are resuspended.
c) Membrane filtration.
d) Emulsification with a non-toxic emulsifier and water.
e) Using a flocculant to entrain organisms in the fuel.

Strategy c), membrane filtration is probably the most widely used and is now an Institute of Petroleum Method (3). The procedure is intended more as a guide line than a rigid procedure as the volume of fuel to be filtered depends on the anticipated population density and on the filterability of the fuel. After filtering fuel, the membrane is washed through with an aqueous non-toxic surfactant before transferring it to a growth agar. The chemical structure of the membrane is not specified as there is not yet a concensus on this point. The membrane can alternatively be examined microscopically and biological particles counted.

Fuels which are not readily filterable can be emulsified and then tested as an aqueous phase sample. Our procedure uses 9 ml of 0.1% emulsifier plus 1 ml of fuel. Results obtained by this technique and by membrane filtration of the same fuel show good correlation.

We have developed strategy e) as the first stage of an on-site method and it will be dealt with in the next section.

All of these tests (except direct microscopy) detect viable microorganisms and will not reveal dead or moribund microbes in the fuel phase although these will still contribute to fouling, filter plugging etc.

4. On-site Test Procedures for Detecting Microorganisms.

A. Aqueous Samples.

A major step-forward in on-site detection occured when Dip-Slides were introduced in 1975 (4). Since then there have been many permutations of growth media and design details in Dip-Slides from a variety of suppliers. Dip-Slides are often used uncritically - calibration charts from the suppliers are based on tests on aqueous fluids and cannot be applied to non-aqueous fluids such as fuels. It has been our experience that when preservatives are present in the sample these may absorb so strongly to the agar that little or no growth can occur and a false low or negative result is obtained, yet no supplier advises on a neutralisation procedure. The quality of the product is not always acceptable; agar frequently falls from its carrier or rapidly desiccates. Selective media, particularly Rose Bengal Agar, often perform poorly and allow unwanted organisms to grow.

A variation of the Dip-Slide concept is the Microstrip (Biomet Laboratories Ltd., UK, Biosan Laboratories, USA, and others). A porous pad, impregnated with nutrients and tetrazolium, absorbs the sample and yields varying intensities of red after incubation. It is claimed that if it is pre-wetted it can be used on a non-aqueous sample; it is also available with a neutraliser to add to the pad if preservatives are present. A different concept was described by Hill (5). In essence small bottles of semi-solid gels were so formulated that they would detect a significant microbiological characteristic of a fluid sample added to them. The most useful for fuel water bottoms has been the "Sig-Sulphide" gel which rapidly detects sulphide generating microbes. The large size of the sample tested creates its own anaerobic conditions. Other gel devices are available and are inoculated with pipe cleaners (Biosan Laboratories) or capillary tubes (Orion Diagnostica). These methods are all suitable for on-site use.

Dip-Slides are in general no more rapid than conventional microbiological methods as they still rely on the development of individual colonies. Because of the large sample applied and detection of a metabolic process rather than colony development "gel tests" tend to be speedier than Dip-Slides.

To achieve greater reaction speed some direct measurement of microbial metabolic activity can be made. In 1970 (6) Hill proposed a one hour method for detecting fuel tank water bottom contamination; it was based on a colorimetric assay of the microbial enzyme phosphatase. Other tests for detecting metabolic activity have been proposed for metal working fluids and should be applicable to water bottoms. In 1972 (7) Rossmore proposed a dye reduction test and in 1981 (8) Gannon and Bennett described a device for assaying the microbial enzyme catalase. A microbial biosensor has been described at Symposia by Turner of the Cranfield Institute of Technology, UK, but publications in the scientific literature are awaited.

Many attempts have been made to quantify microbes in aqueous phase samples using instruments which detect microbial ATP, microbial heat, microbially induced impedance changes or fluorescent microbial cells. There are many problems, apart from expense, which have not been satisfactorily resolved. It may be surprising that these rapid techniques have made so little impact in the petroleum industry but in many cases complex sample pre-processing, inadequate sensitivity, lack of calibration data for comparison with older methods and lack of knowledge of interfering substances (particularly preservatives) have inhibited progress.

A new generation of ATP detecting instruments (e.g. Speed Tech 2000 Clear Ltd, Cardiff, UK) have greatly enhanced sensitivity and better sample pre-treatment, and may offer a way forward.

Indirect methods such as protein assay (2) or elemental analysis, particularly for phosphorus and/or potassium are feasible but are not widely practiced. They have the merit of detecting total contamination, dead or alive.

B. Fuel Phase Samples.

Despite the fact that in very many cases the only sample available is of the fuel phase there has been little interest in devising on-site test procedures. There are various configurations of membrane filtration which can be used on-site but the membrane still has to be processed by a technician with microbiological skills and equipment.

We have explored a range of strategies which had potential as simple, rapid, on-site, semi-quantitative microbiological tests for fuels. The key to success was the use of a flocculant which could be shaken with a fuel sample and which then, on standing, settled into an aqueous phase carrying with it entrained microorganisms (9).

The test procedure (see Fig 2 and 3) is as follows:

20 ml of fuel is shaken with 5 ml of sterile water containing a flocculating agent. This agent entraps microbes in the fuel and carries them into the water phase on settling. Conventional microbiological tests could be carried out on this water phase but, as the objective of the research was to develop a rapid on-site test, we prefer to transfer circa 2 ml to a nutrient semi-solid gel containing a highly reactive tetrazolium salt. After incubation at 25°C - 30°C a colour change occurs in the gel and its intensity and rate of development is semi-quantitatively related to the degree of microbial contamination in the original fuel sample. We refer to this test as the SIG-Fuel Test.

An advantage of using a porous nutritive gel as an indicator system is that microorganisms can permeate the gel and reproduce there. In the case of bacteria this is frequently accompanied not only by tetrazolium reduction but also by gas production which is manifest by obvious cavities blown in the gel.

To confirm that the use of the flocculating agent transferred a significant proportion of the viable microbial population from the fuel to the aqueous phase, known infected fuels were processed by the standard SIG-Fuel Test procedure then pipetted off from the aqueous phase as completely as possible and re-extracted. In each case 1 ml of aqueous phase was removed for conventional shake plate counts using Tryptone Blood Agar Base (Oxoid Ltd) at 30°C for 2 days; 2 ml was transferred to the Tetrazolium gel and incubated for 24 h at 30°C. The results are shown in Table 3.

Any microbiological test which measures some aspect of metabolic activity may continue to remain positive for some time after viability has been lost. Preliminary experiments suggest that the ability of fuel microbes to reduce the tetrazolium salt used is lost within a few hours of adding a potent biocide (500 ppm Bioban FP).

5. Anti-microbial Chemicals.

A. Preservation.

To avoid microbial spoilage it is possible to add an anti-microbial chemical to the fuel in the expectation that it will migrate to any associated water. Provided it establishes an equilibrium concentration above the minimum required to inhibit microbial proliferation any contaminating microbes arriving will be controlled. The concentration of such an agent in the water phase will be influenced not only by its solubility in both phases but also by the volume ratio of the phases. If the preserved fuel is subsequently transferred and is then in contact with another water bottom another equilibrium will be established. These various aqueous equilibrium concentrations are difficult to predict and historically have been difficult to assay.

B. Disinfection.

As an alternative to preservation a disinfecting dose of anti-microbial chemical can be applied when fuel contamination is detected. Rapid action is then required and this depends on a high aqueous phase concentration for a specified time.

C. Assay of Anti-microbial Chemicals.

For both preservation and disinfection there has been a need for an on-site test to detect the aqueous phase concentration of chemicals which have been added to the fuel phase.

A technique has been described by Hill (10) for on-site assay of anti-microbial chemicals. A device, a "Biocide Monitor" (ECHA Products, Cardiff), is utilised. It consists of a small plastic strip which carries a porous pad impregnated with nutrients, the growth-indicating dye tetrazolium and dried spores of a harmless assay microorganism. The strip is dipped into the water to be assayed and incubated overnight. The nutrients rehydrate and the spores are activated. In the absence of inhibitory chemicals, the assay organism grows rapidly and reduces the tetrazolium to a visible red pigment. An anti-microbial chemical, present at or above its inhibitory concentration, prevents growth and the pad remains white. The device can be calibrated for anti-microbial chemicals of interest to establish their MIC's (the minimum inhibitory concentration in ppm).

The sample can be diluted over an appropriate range and each dilution tested to determine which contains the MIC. The concentration of anti-microbial chemical present can then be calculated. A simple strategy is to decide the minimum concentration of biocide needed to preserve or disinfect a water bottom and then dilute a field sample appropriately and test so that the result will indicate whether a top-up of biocide is necessary to bring the concentration up to the target concentration.

Example:

Biocide GB has an MIC to the Biocide Monitor of 150 ppm.
Concentration in water bottom should not fall below 450 ppm.
Strategy: Dilute field sample three-fold and test with monitor.
Result: White - no action; Red or pink - top-up with Biocide GB.

The device has some limitations. It is not suitable for detecting Biobor JF or glycol ethers. It is very suitable for the new generation of anti-microbial fuel additive agents.

6. Conclusions.

A wide range of laboratory and on-site microbiological tests are available for fuel and water bottom samples. Unfortunately they may not all give the same answer and they may not correlate quantitatively with visual assessments or operator experience. There is still a long way to go to achieve agreement on test procedures. There is even further to go to achieve international agreement on standards; this may never be realised as test results can only be interpreted with the local knowledge of exact sample point, sample handling and history and risk factors.

TABLE 1.

MICROBES IN FUEL SAMPLES

FUEL SAMPLE	NUMBER OF MICROORGANISMS PER ml					
	WATER PHASE			FUEL PHASE		
	BACTERIA	YEASTS	FUNGI	BACTERIA	YEASTS	FUNGI
M1	42,000	1,200	100	2	51	10
M2	1,740	2,750	50	0	26	0
M3	17,000*	7,900	2,350	1	122	1
L1 (CO)	290,000	150	0	0	66	1
A8	40,000*	6,400	0	0	7	0
A9	1,600	300	50	1	3	1

* PLUS SRB

Tests on c. 500 ml of Gas Oil Samples, each containing free water. Samples were several days old when tested.

Table 2.

VISUAL AND MICROBIOLOGICAL ASSESSMENT OF FIVE FUEL TANK WATER BOTTOMS.

VISUAL ASSESSMENT	COLONY FORMING UNITS ml^{-1}		
	BACTERIA	MOULDS	YEASTS
1. Dark brown/black, thick layer at interface, opaque with large flocs suspended and on surfaces.	13,060,000	<20	40
2. Dark brown, thick layer at interface, but water clear, large number of flocs.	35,300,000	180	1720
3. Yellow/brown layer at interface, clear with deposit and suspended flocs.	17,500,000	120	200
4. Yellow, clear, slight layer at interface, few large flocs.	38,300,000	200	520
5. Yellow/brown, clear, slight layer at interface, slight deposit.	3,060,000	280	120

Fuel depth, 32 cm; water bottom depth, 3 mm.

Sample 5 would probably have been rated visually as acceptable.
Sample 4 would possibly have been rated visually acceptable.

Table 3.

EFFICACY OF EXTRACTION OF MICROBES FROM FUEL PHASE BY FLOCCULATING AGENT. (SIG-FUEL TEST).

Fuel Sample	*cfu ml^{-1} of aqueous phase 1st Extraction	2nd Extraction	#Colour in gel 1st	2nd	Colour in supernatant 1st	2nd
1	27,760	145	+++	±	+++	-
2	1,520	74	+	-	+	-
3	1,400	17	+	-	+	-
4	45,920	416	+++	+	+++	-
5	36,000	268	+++	±	+++	-

* The viable count was in Tryptone Blood Agar Base at 30°C for 2 days.
# Tetrazolium reduction was assessed after 24 hours at 30°C and recorded from strong red (+++) to negative (-).

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FIGURE 1. DISTRIBUTION OF MICROORGANISMS IN A FUEL WATER BOTTOM IN RELATION TO PHYSICAL PARAMETERS.

The results were obtained by gelling the water bottom with a little agar thus stabilising the microbial, physical and chemical gradients.

FIGURE 2. ON-SITE TEST FOR DISTILLATE FUELS - EXTRACTION STEP.

a) Bottle containing 5 ml of water plus flocculant before use.
b) After shaking with 20 ml of fuel and settling.

Key: (1) Clear glass screw-capped bottle.
(2) 5 ml sterile water plus flocculant, (3).
(4) 20 ml fuel.

FIGURE 3. ON-SITE TEST FOR DISTILLATE FUELS - INCUBATION STEP.

a) Nutritive semi-solid gel before use.
b) Gel after transfer of 2 ml of aqueous phase from 2b(See Fig.2) and incubation. Light infection detected.
c) Gel after transfer of 2 ml from 2b(See Fig.2) and incubation. Heavy infection detected.

Key: (1) Clear glass screw-capped bottle.
(2) Nutritive semi-solid gel incorporating tetrazolium indicator.
(3) Gas bubbles in gel.
(4) Red/purple colour development.
(5) 2 ml aqueous phase transferred from 2b(Fig.2).

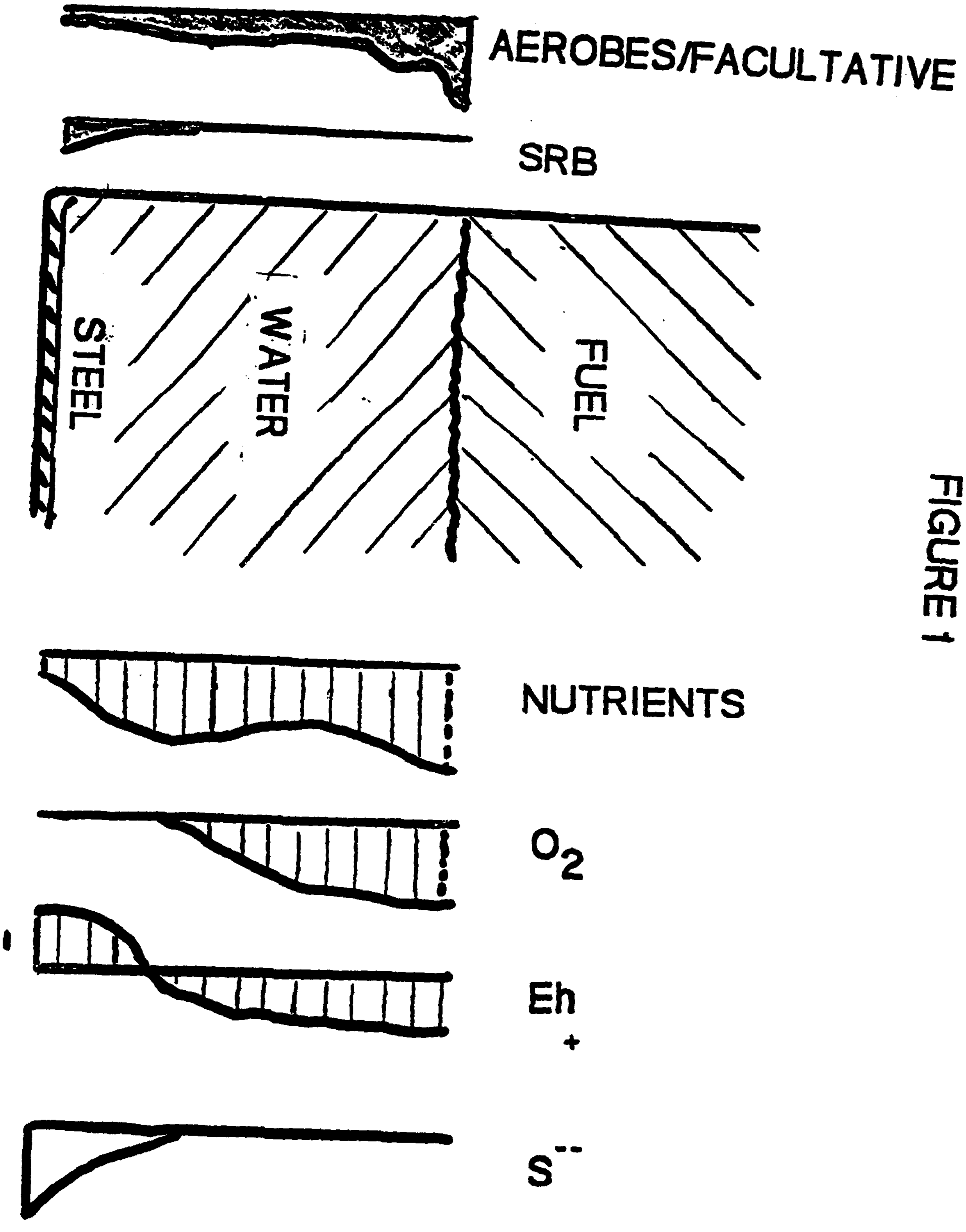


FIGURE 1

FIGURE 2

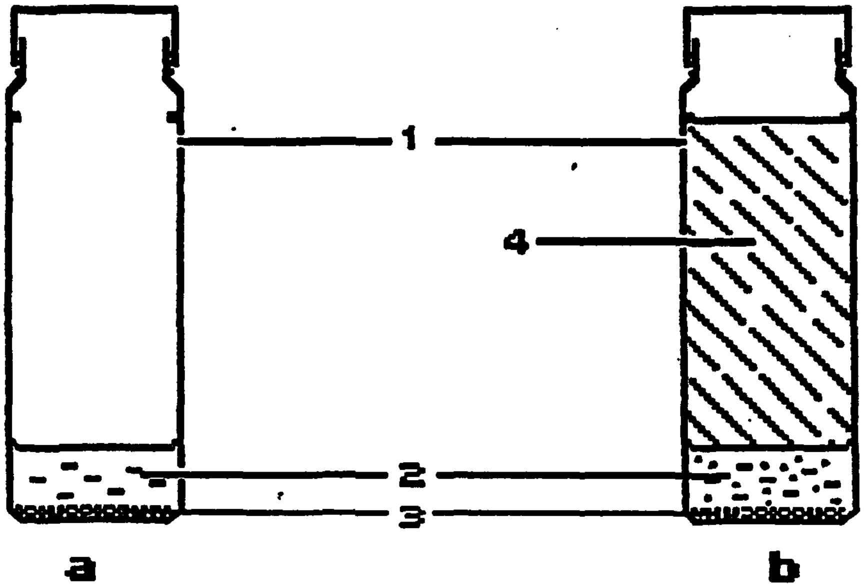
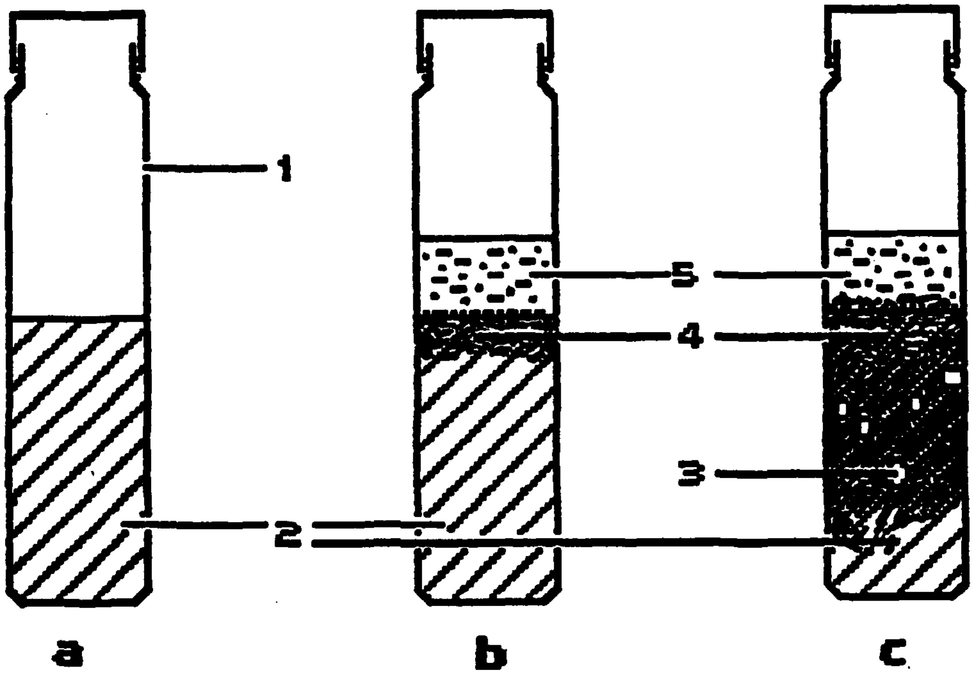


FIGURE 3



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BIOCIDES FOR MICROBIOLOGICAL CONTAMINATION CONTROL IN NAVAL DISTILLATE FUEL

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ABSTRACT

Microbiological contamination (MBC) in naval fuels can cause serious operational problems, particularly if coalescers are used for water removal and if the fuel is to be used in gas turbine engines with their intricate fuel control units which are easily blocked.

In order to identify a biocide which could be used to treat MBC problems in fuel on ships, five commercial biocides have been evaluated. These biocides include compounds based on benzimidazoles, pyridinethiol-1-oxide, dioxaborinanes, morpholines and isothiazolones. The degree of susceptibility of microorganisms, in naval distillate fuel, to the specific biocides was evaluated. Pure cultures of Cladosporium resinae, Yarrowia lipolytica, Pseudomonas aeruginosa and mixed cultures in fuel/water mixtures were treated with the manufacturers recommended concentrations of the biocides.

Results indicated that none of the biocides tested were able to inhibit all of the culture types, under the experimental conditions.

Reinoculation trials were carried out on select biocides using pure cultures of C. resinae. Also, bottle scale trials involving the removal and replacement of the water layers were carried out to imitate the use of water displacement-type fuel systems.

INTRODUCTION

Problems related to microbiological contamination (MBC) have occurred in several Canadian naval vessels over the last few years, causing operational problems by rapid coalescer element blockage. The presence of microbiological contamination in naval fuel systems, which results in blockage of fuel filters and fuel coalescers has been attributed to the mat-forming fungus Cladosporium resinae. This fungus has a number of unique characteristics that make it a persistent problem in fuel systems. The ability of this microorganism to proliferate in petroleum fuels in the absence of other carbon sources and under relatively anaerobic conditions has made it a potential problem in virtually any fuel storage system [1-3]. In fact, C. resinae has been identified as the primary MBC component in a number of studies of naval and aviation fuel supplies [4-11]. In a recent survey of Canadian Forces ships [12], all fuel tanks sampled contained detectable fungi and yeasts. The amount of MBC in each tank varied with the amount of water and particulate present. Although these ships do not currently employ water displacement in the fuel delivery, water ingress, both fresh and salt, has been noted through a variety of means and is next to impossible to prevent. Thus, a treatment program which could control the proliferation of C. resinae would be beneficial to the management of MBC in naval fuel systems.

The application of chemical biocides to eliminate or reduce the development of MBC has been proposed as one of the preferred methods of control of the problem [13,14]. Due to the limited amount of experience with the use of biocides for the control of MBC, a study was undertaken to address a variety of points associated with MBC control.

The efficacy of six candidate biocides/biostates in suppression of growth of several microorganisms was determined using pure and mixed cultures. In addition the following factors were also investigated to determine their impact on growth of MBC in naval distillate fuel: 1) the persistence of activity of selected biocides after reinoculation with fresh microbiological components, and 2) the replacement of the water bottoms on continued suppression of microbiological growth.

PROCEDURE

Test Units

The test system consisted of 250 mL glass culture bottles, containing 95 mL of sterile naval distillate fuel (NATO F-76) and 5 mL of sterile synthetic seawater (Instant Ocean: Aquarium Systems, Mentor, Ohio) supplemented with 0.05% of each of potassium dihydrogen phosphate (KH_2PO_4), magnesium sulfate ($MgSO_4 \cdot 7H_2O$), ammonium sulfate ($(NH_4)_2SO_4$), potassium monohydrogen phosphate (K_2HPO_4) and yeast extract. The bottles and seawater were sterilized by autoclaving. The fuel was sterilized by filtration through 0.45 µm membrane filters (Millipore Ltd.). Controls (membrane-filtered fuel over salt solution) showed no microbiological growth over a three-month period.

Biocides, as supplied by the manufacturers, were added directly to sterilized fuel at manufacturer's recommended concentrations.

Inocula

Stock cultures were maintained in fuel/supplemented seawater medium, as described above, at 20°C in the dark until required. Several species were evaluated including *Cladosporium resinae* (ATCC 22712), *Yarrowia* (formerly ATCC-listed as *Candida*) *lipolytica* (ATCC 16617), *Pseudomonas aeruginosa* (ATCC 9027) and a 1:1:1 mixture (by volume) of *C. resinae*, *Y. lipolytica* and *P. aeruginosa*.

For inoculation of test bottles, interface samples were removed from these stock cultures and as much distillate fuel as possible removed by blotting. The interface cultures were combined and macerated aseptically in a Waring blender and 1.0 mL aliquots of this macerate was used as inocula in the test units.

Estimation of Growth

Test units were maintained at 20°C without agitation for periods up to 10 weeks. Growth was monitored as changes in biomass at 2-3 weekly intervals. Six replicate bottles were analyzed for each determination, in order to estimate variability between samples.

Growth of pure and mixed cultures of the microorganisms studied was estimated as weight of cellular soluble protein per bottle, using the spectrophotometric method of Lowry *et al.*[15]. This method measures peptide bonds and tyrosine residues in sodium hydroxide-extracted interface growth and is sensitive in the range of 10-300 μg protein per 0.5 mL when compared to the standard curve obtained with crystalline bovine albumin.

At specific times during the trial as much fuel as possible was removed from each test bottle with disposable pipettes and the underlying water layer removed by suction to leave approximately 15 mL of interface growth. The sample was either analyzed immediately or stored frozen for later analysis.

To test for possible interference from residual fuel, a British Standard Association (BSA) standard was prepared with approximately the same concentration of protein as the extracts. A portion of the standard was shaken with an equal volume of fuel prior to assay. A comparison between this standard and the BSA standard not exposed to fuel showed no interference from the fuel on the spectrophotometric determination of soluble protein. Dilution of samples and standards during preparation would reduce residual fuel in the aqueous phase to 1:10 or 1:100.

To establish the correlation between soluble cell protein and total dry weight of interface growth, eight replicates inoculated with 1.0 mL macerates of C. resinae (ATCC 22712) were evaluated after six weeks incubation. Four samples were analyzed for protein as described above. The remaining four were filtered through preweighed 0.45 µm membrane filters to collect all growth. The cells on the filter were washed repeatedly with hexane to remove distillate fuel, rinsed with 95% ethanol and oven-dried. The dried samples were weighed and results expressed as mg dry weight/bottle.

Correlating protein weight and dry weight for C. resinae, cellular soluble protein was calculated as 5.5 ± 1.04% of dry cell weight.

BIOCIDE TRIALS

Assessment of microbiological activity involves a variety of factors, such as immediate killing effects, biostatic effects, long-term effect on growth rate and production of biomass, degree of residual toxicity, inhibition of germination and range of species inhibited, singly or in mixed populations. Biocide efficacy trials and related studies are generally carried out under small-scale (e.g. bottle, flask) or large-scale (e.g. flask, tank, drum) laboratory conditions. Inferences derived from these experiments are applied to the much larger scale, complex microbiological ecosystem found in bulk fuel storage containers.

For maximum predictive value, laboratory scale experiments need to be reproducible, with large sample sizes to permit statistical treatment or, at a minimum, estimates of variability between replicates. Different research groups have employed different protocols for media selection, preparation of inocula, incubation and estimation of growth over periods ranging from hours or days to weeks or months [2].

For our studies on the efficacy of biocides against pure and mixed cultures we have employed a simple procedure for incubation and growth estimation (outlined under procedure of this paper) which yields consistent, quantitative results in bottle-scale tests [16].

In order to determine the effect the candidate biocides had on cultures of various microorganisms, sterile bottle-scale efficacy trials were conducted.

A study to determine the ability of selected biocides to suppress microbiological growth after a reinoculation of an additional 1.0 mL of fresh inoculum after the end of two weeks was conducted using pure cultures of Cladosporium resinae. In addition, bottle-scale trials were conducted involving the removal and replacement of the water layer in the biocide treated bottles in an attempt to imitate the use of a water displacement-type fuel system. The water layer was removed after the second week by pipet, taking care not to introduce or remove any biogenic material, and a volume of supplemented water equal to the volume removed was introduced back into the bottles.

The chemicals that were evaluated were all commercial biocide/biostate preparations. These products, hereafter described by numbers, were based on benzimidazoles (**1**)[1], pyridinethiol-1-oxide (**2**)[2], dioxaborinanes (**3**)[3], isothiazolones (**4**)[4], morpholines (**5**)[5], and glycol ether (**6**)[6].

RESULTS AND DISCUSSION

The advantages of the cellular soluble protein method described here are its applicability to large numbers of replicates and to either fresh or frozen samples, and the

---

[1] A fungicide containing 50% methyl-1-(butylcarbamoyl)-2-benzimidazolecarbamate, E.I.duPont de Nemours & Co., Wilmington, Delaware.

[2] A broad spectrum microbiostate which contains the 1,1-dimethylethaneamine adduct of 2-pyridinethiol-1-oxide, Olin Corporation, Stamford, Connecticut.

[3] A fungicide containing 95% 2,2'-oxybis-(4,4,6-trimethyl-1,3,2,-dioxaborinane) and 2,2'-methyl-trimethylenedioxy-bis-(4-methyl-1,3,2-dioxaborinane), U.S. Borax & Chemical Corp., Los Angeles, California.

[4] A microbiostate containing 8.6% 5-chloro-2-methyl-4-isothiazoline-3-one and 2.6% 2-methyl-4-isothiazoline-3-one, Rohm & Haas Company, Philadelphia Pennsylvania.

[5] An antimicrobial agent containing 70% 4-(2-nitrobutyl)morpholine and 20% 4,4'-(2-ethyl-2-nitrotrimethylene)dimorpholine, Angus Chemical Company, Northbrook Illinois.

[6] A biostate containing 100% diethylene glycol monomethyl ether, Aldrich Chemical Co. Inc., Milwaukee, Wisconsin.

absence of interferences from residual fuel in the determinations. There are disadvantages, particularly in analysis of mixed cultures, since the pattern of amino acid residues and the percentage of extractable protein vary from species to species so that attention must be paid to possible shift in species' composition during successional growth or as a result of biocide treatment [12,17]. Preferably, correlations between protein level and dry weight, and identification of major components, will be conducted at the start and end of trials using mixed cultures.

The number of replicates chosen depends on the level of precision required [18]. In the experiments reported here all determinations were done in replicates of six, at 4, 6 and 8 weeks. The variability between replicates was low in the single-species cultures but higher in the mixed cultures.

The data for the biocide efficacy trials is presented in the form of comparison graphs (Figure 1), in which the mean value for mg protein/bottle is plotted on the X-axis for control and on the Y-axis for treated cultures for each time point; the 45 degree equivalence line is indicated. Points falling on the equivalence line indicate no difference in biomass between control and treated samples, while points falling below the line indicate a degree of inhibition associated with treatment, with total inhibition being demonstrated by points falling on the X-axis.

As can be seen in Figure 1, biocide **1** demonstrated inhibition of the C. resinae component; however, it had little to no effect on the Y. lipolytica and P. aeruginosa. Biocide **2** demonstrated good control of the pure cultures of C. resinae and Y. lipolytica. Due to the loss of vigor of growth in the P. aeruginosa inocula, this biocide was not tested against that bacterium. Biocide **3** exerted no measurable suppression of growth of any of the three

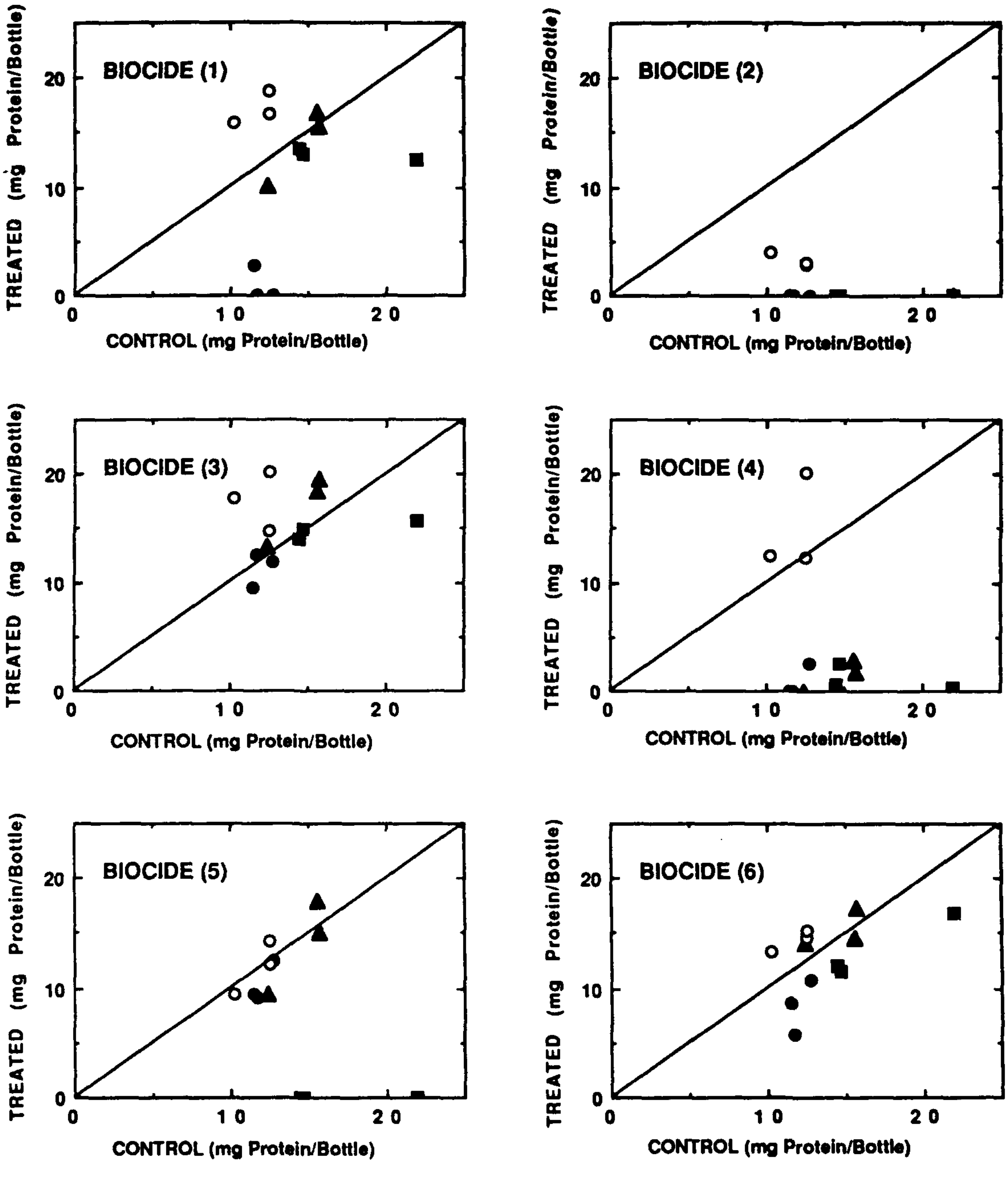

Figure 1. Comparison plots of mg protein/bottle for the three culture types (● C. resinae, ■ Y. lipolytica, and ▲ P.aeruginosa) and o a mixed inoculum vs. six biocides/biostates (1 to 6).

microorganisms. Biocide **4**, on the other hand, demonstrated relatively good control for the pure cultures of C. resinae, Y. lipolytica and P. aeruginosa. Biocide **5** demonstrated negligible to no inhibition of the C. resinae and P. aeruginosa. However total control of the Y. lipolytica was obtained. Biocide **6** demonstrated effects similar to biocide **3**, in that, no measurable suppression of growth was noted for the cultures.

Chemical control of the growth of the mixed inoculum (a 1:1:1 mixture by volume of C. resinae, Y. lipolytica and P. aeruginosa) was not achieved (Figure 1) by most of the biocides evaluated. Biocide (**2**) was the only biocide which demonstrated any inhibition, albeit minor, of the three species mixture. This unfavorable response to chemical treatment may be due to a synergistic factor. In fact, the presence of P. aeruginosa in mixed bacterial cultures has been reported [21] to induce increased resistance of sulphate reducing bacteria to some nitroparaffin, mercural and phenolic growth inhibitors.

The reinoculation and water replacement experiments were conducted with only three of the biocides (**2**, **4**, **5**) and a different response for each of the biocides was demonstrated when compared to untreated cultures of C. resinae .

The reinoculation of the bottles was done two weeks after the start of the trials. Biocide **2** demonstrated good residual biocidal activity after the reinoculation. Some minor increase in the protein level was noted the first week after the reinoculation. Biocide **4** demonstrated a resurgence of protein production within a few week after the reinoculation. In fact, the initial regrowth rate was found to be similar to the growth rate initially observed in the untreated control systems. Biocide **5** did not demonstrate any supression of growth under any of the monitored regimes. The results for the reinoculation experiments are shown in Figure 2.

The results for the water replacement trials were similar to those observed for the reinoculation study, in that, biocide **2** demonstrated good residual efficacy, biocide **4** showed a drop in inhibition of the growth and biocide **5** had no measurable effect. These results could reflect the relative partitioning of the active component into the water phase; that is, if the initial (first two weeks) partitioning into the water is relatively slow then replacement of the water phase will have little effect on the prolonged supression effect.

CONCLUSION

Control of microbiological growth was demonstrated by several of the biocides/biostates when tested against pure cultures of C. resinae, Y. lipolytica and P. aeruginosa. The lack of response of the mixed inoculum to the biocides could be due to a synergistic factor.

Results of the reinoculation trials reflected the ability of some biocides to possess prolonged suppression effects, while the water replacement results could reflect the relative partitioning of the active component to the water phase.

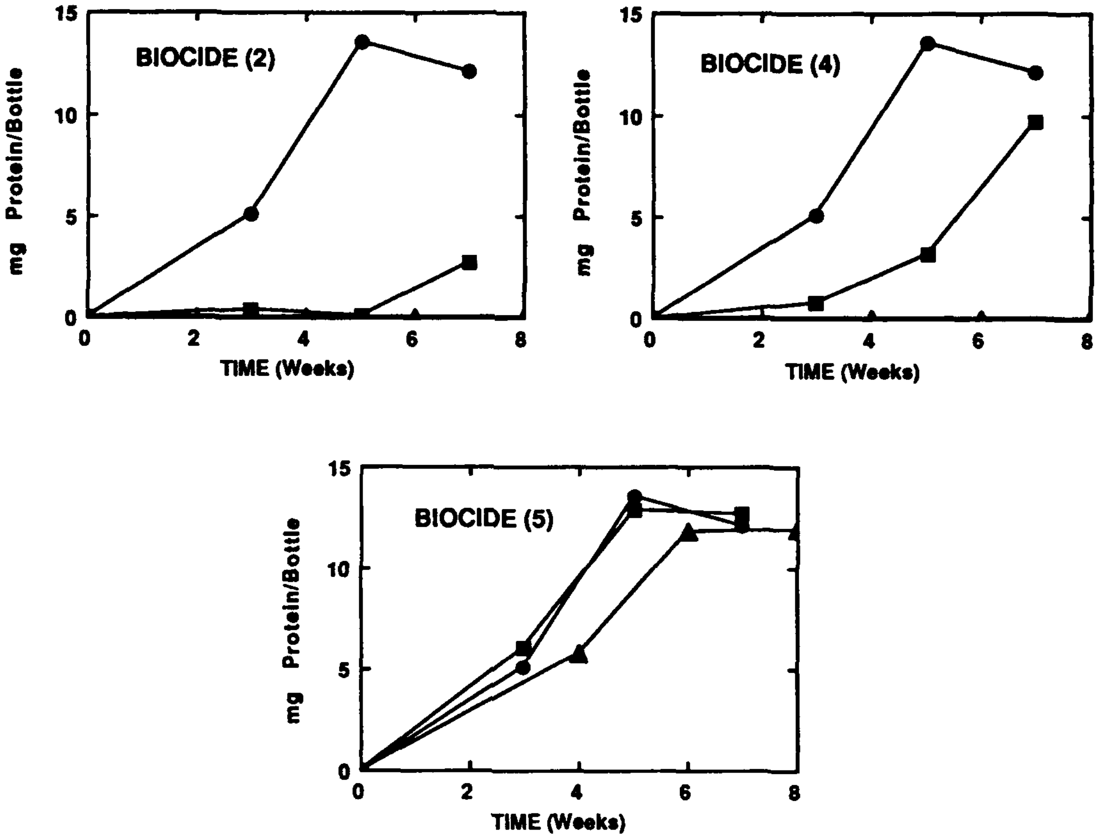

Figure 2. Comparison plots for reinoculation with C. resinae at two weeks for the three biocides (**2**, **4**, & **5**). (● Control-untreated, ■ Treated-reinoculated, and ▲ Treated-control).

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EVALUATION & COMPARISON
OF
MICROBIAL GROWTH
IN DISTILLATE FUELS

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ABSTRACT

Microbial contamination of fuel tanks and systems has been blamed for fuel system corrosion, filter and line plugging, and fuel degradation. Of the fuel samples in this evaluation, bacterial growth has been isolated from as many as 56% of stored fuel systems in the United States. Since most storage tanks were underground and maintained a relatively constant temperature year-round, microbial proliferation was neither regional nor seasonal.

Although microbial growth in fuel systems is an area of concern involving both users and suppliers of distillate fuels, this study limits its scope primarily to users of distillate fuel and further attempts to categorize microbial isolates of fuel systems and their deleterious effects to fuel by:

* Frequency of appearance
* Colony forming units per milliliter (cfu/ml) quantitated
* Amount of growth byproduct generated, and
* Physical appearance of the water, fuel, and interfacial phases.

Samples of fuel were collected from a twenty-three state geographical area east of a line from New Mexico to the Dakotas. The states sampled most heavily were Indiana, Ohio, Michigan, Kentucky, Illinois, Tennessee, New Jersey, Florida, and Texas.

This study limits its attention to aerobic organisms, initially cultured and isolated on Tryptone, Yeast, Dextrose agar, then subcultured to appropriate media for identification. Inoculation, culturing, identification and isolation were performed according to guidelines established for clinical pathogens. Statistical evaluations were used to compare specific organisms isolated (genus and species) along with amount of colony forming units generated to amounts of growth by-products, physical appearance of the fuel, and physical appearance of the water phase in samples collected (if present).

By isolating specific organisms from fuel which have been statistically shown to affect the condition of stored distillates, the fuel user can select treatment methods most effective against those organisms.

DISCUSSION

The role of microbial organisms in the degradation of even such durable substances as metals, rubber, and plastics has been thoroughly explored in research. For over 90 years (Miyoshi, 1895), micro-organisms have been found to utilize hydrocarbons in petroleum products. For more than 60 years, these findings only served to prompt speculation as to their origin. By the 1950's, however, micro-organisms in petroleum products - specifically distillate fuels - had begun to cause some concern, not specifically because of their presence, but related to consequences of their growth (Rogers and Kaplan, 1964).

When matting and other by-products of their growth was observed to completely clog fuel systems, causing equipment dysfunction due to fuel starvation (Rogers and Kaplan, 1982), microbes in distillate fuels first began to prompt anxiety. Fuel pumps and filters became strangulated with slimy matting, capacitance guage malfunctions occurred and eventually vital parts became involved and engine failure resulted. In short, microbial contamination presents a triple threat to any fuel consumer by: (1) system blockage from excessive growth by-products, (2) tank surface corrosion, (3) acceleration of fuel oxidation and resultant carbon residue deposition.

Microbial-initiated problems in the oil industry could be classified into three main groups: bacteria, fungi, and algae. However, since algae requires light for growth, they are generally not a problem in closed (underground tank) systems. Where a layer of free water is present, micro-organisms proliferate by their access to oxygen from the fuel and hydrocarbons as a food source (Holmes, 1986).

Contamination of a fuel system is a fact that is impossible to eliminate. Sources of contamination can be reduced thus minimizing the chances for productive inoculation, but the possibilities for contact given the air, liquid and solid-borne presence of bacteria are too numerous to completely eradicate. In the course of fuel handling from the refinery to the end-user, foreign matter including water, surfactants, resins, dust, sand, dirt, metal chips, cellulose fibers, and other particulate contamination will be found in any system (Littmann, 1981). In addition, any water present (even in very small amounts) in a petroleum product will harbor bacteria, yeast and fungi which in turn will grow through exponential reproduction into dense masses of colonies, organism excrements and byproducts - microbiological contamination/growth which can generally cause severe filter plugging, corrosion, fuel instability complications, and also (through metabolic by-product production) water/fuel emulsions (LePera, et al, 1983).

Any free water as droplets or thin films is sufficient for microbial growth and allows the development of biologically induced corrosion that, due to its electrochemical nature, needs an aqueous environment to develop. Although good housekeeping procedures are mandatory to avoid the presence of water and particulate contamination, it is an almost impossible task to eliminate water from the fuel during its processing, transport and storage (Reinoso, et al, 1986). Therefore, the presence of water is a prime factor in providing an environment conducive to microbial proliferation. The water/fuel interface is the most attractive area for microbial multiplication, providing a medium for growth directly proportional to the size of the interfacial area.

Although by-products of microbial growth are the primary causes of microbiologically related engine dysfunctions, their growth may extend from the water/fuel interface to tank surfaces, where acid by-products and cell concentration differentials result in tank corrosion and possible deterioration through cathodic depolarization (Reinoso, E. H., et al, 1986). The presence of water in a fuel system, coupled with microbial consumption and degradation of the hydrocarbon fuel, will result in oxidation of the fuel, where the hydrocarbon chains decompose, leaving carbon as a dark precipitate only adding to the already-existent contamination with particulate matter.

As of this writing, we are unaware of any research that has been compiled relating fuel deterioration, amount of by-products generated, and colony-forming unit quantities to specific genus and species. However, such an evaluation would enable the fuel consumer to intelligently deal with the problems of microbial contamination.

Microbial growth in distillate fuel systems is a widespread problem that has attracted significant attention since its effects were first published. In our study, positive growth has been isolated from as many as 56% of all fuel storage systems surveyed. (Since most storage tanks are underground and maintain a relatively constant year-round temperature, microbial proliferation tends to be neither regional nor seasonal.)

To minimize the presence of bacteria, good housekeeping practices are imperative. Frequent removal of tank water bottoms, periodic analysis and quantitation of microbial growth coupled with conscientious use of an effective fuel-soluble biocide can eliminate the presence of microbial growth and harmful side-effects. By submitting a sample of the microbiologically infested tank bottom to a reputable laboratory with capabilities to quantitate microbial growth present, the fuel consumer can then effectively target a biocide and judge its effectiveness in killing the micro-organisms.

This study limits its attention to aerobic organisms. Claims of anaerobic microbial degradation of hydrocarbons have been published from time to time but have not been overwhelmingly substantiated (Schwartz & Leather, 1976). Some, in fact, have been retracted. The available evidence appears to be overwhelmingly in favor of the description of hydrocarbon oxidation as an aerobic process.

This would tend to eliminate anaerobic microorganisms from being associated with primary infestations of fuel systems. Their role as secondary infestors, existing due to favorable conditions resulting from the primary infestation, has not been substantiated either although the possibility exists. The claim that oxidation of hydrocarbons is limited to aerobic organisms does not necessarily eliminate anaerobic organisms from consideration, however, as they may exist as a secondary infestation utilizing by-products from the primary organisms as sustenance.

In the interest that subsequent studies would specialize into different areas of consideration, this study's scope was not substantially narrowed.

MATERIALS AND METHODS

Sample Collection: The observation specimens encompassed a period of twelve months. 74% of this study's samples were taken from in-ground storage tanks using a Bacon Bomb Fuel Sampler (a gravity/vacuum-fed sampler supplied by Kohler Instruments). The remaining 26% of the samples were obtained within the first 20 seconds of fuel drop from a delivery transport hose into a storage tank. Samples were then appropriately labelled and, within one to four days of collection, delivered to the laboratory via parcel service.

Collection of fuel samples was made by AMALGAMATED COAL & PETROLEUM SPECIALISTS, INC. from a twenty-three state area east of a line from New Mexico to North Dakota. Most of the samples originated from Indiana, Ohio, Michigan, Tennessee, New Jersey, Florida, and Texas. 87% of the samples came from #2 diesel fuel systems with the remaining 13% from gasoline, kerosene, and jet fuel systems.

Sterile techniques in acquisition of samples was accomplished within reasonable guidelines given the wide geographical area of samples evaluated. Upon receipt in the laboratory, they were processed under strict sterile protocol.

53% of the samples submitted consisted of a visible water/fuel interface in a 16 oz. polypropylene or glass jar. The remaining 47% consisted of fuel with amounts of sediment and particulate matter varying from none to copious.

Laboratory Receipt: Upon receipt in the laboratory, samples were coded numerically and any results obtained either visually from the specimen or through repeated incubations and isolations bore the numeric code.

Before preliminary visual evaluation, samples were allowed to settle for one hour. They were then visually examined according to the following criteria:

Growth By-Products - The water/fuel interface was described as:

LIGHT: (thin film between phases, with no clumps or projections),
MODERATE: (film greater than 1mm in thickness but not more than 3mm, with three or less clumps projecting into either phase), or
HEAVY: (film thickness greater than 3mm with four or more clumps projecting into either phase).

Fuel Phase - The fuel phase was described as:

CLEAR: (newsprint legible through sample in pint-size glass jar) or
CLOUDY: (newsprint illegible under same criteria).

Water Phase - The presence or absence of free water was recorded as follows:

MINUTE WATER: In the cases where the water content was minute, the sample was homogenized and a Karl Fischer water titration was performed.
CONTAINING WATER: Specimens with water content of greater than 0.05% were reported as containing water.
NO WATER DEFINITION: Samples with less than or equal to 0.05% were not reported as containing water.

Sample Preparation, Isolation, and Quantitation: A portion of the sample was removed with a sterile, disposable transfer pipette. In specimens with water/fuel interface, the portion was collected at the interface. When visible sediment only was present, the portion was collected from the area of heaviest concentration. In samples with no visible particulates or interface, a portion of the sample was taken from the bottom of the container.

As of this writing, to our knowledge, there is no prescribed ASTM procedure for the quantitation of microbial growth in diesel fuels nor an ASTM fuel specification limit therein. Therefore, using an in-house method derived directly from the clinical laboratory to quantitate pathogenic aerobic bacteria and fungi (procedure taken from the Food and Drug Administration, Division of Microbiology, Aerobic Plate Count), a portion of each fuel sample was discharged, dropwise, over a sterilized 0.1ml calibrated inoculating loop. The loop was then streaked in a quantitation pattern onto SMA (a nutrient media of Standard Method Agar: Tryptone/Yeast/Dextrose), reconstituted according to manufacturer's directions.

The plates were incubated in ambient atmospheric conditions at 37 degrees Celcius in an Equatherm Incubator (Curtin Mathesin Scientific, Inc.). If growth was apparent at 24 hours, colonies were counted on a Coulter Colony Counter at that time. If not, they were kept for a total of 48 hours and then re-examined for growth and quantitiated.

Organism Isolation and Identification: Following quantitation, distinct colonies were taken off the initial incubation plate and streaked for isolation, again of SMA. The number of isolation streak plates necessary for separation of all types depended upon how heavily the colony was mixed. Upon isolation into pure colonies, the colonies were transferred to appropriate media for identification by standard microbiological techniques. All cultured growth groups were isolated and identified by the Bacteriology Department at the Lutheran Hospital, Inc., Fort Wayne, Indiana.

GRAM STAIN CATEGORIES

Gram stains were performed on all pure isolates and, based on morphology and Gram's reaction, were evaluated by the following criteria:

I **Gram Positive Cocci (GPC)**
- A. Catalase:
  - 1. Positive
    - a. Staphylococcus sp.
      - i. Coagulase to speciate
    - b. Micrococcus sp.
      - i. Morphological differentiation by Gram's Stain-large GPC's and tetrads.
  - 2. Negative
    - a. Streptococcus sp.
      - i. Hemolysis reaction to speciate. Group A-Esculin; Group B-Streptex

II **Gram Negative Cocci (GNC)**
- A. Oxidase for preliminary evaluation.

III **Gram Positive Bacillus (GPB)**
- A. Corynebacterium sp.
  - 1. Identify from moyphology on Gram's Stain
- B. Oxidase
  - 1. Positive
    - a. Bacillus sp.
  - 2. Negative
    - a. Further differentiation necessary

IV **Gram Negative Bacillus (GNB)**
- A. Oxidase
  - 1. Positive
    - a. Differentiate by Nonfermetor Strip, API
  - 2. Negative
    - a. Differentiate by VITEK (automated instrumentation)

Fungi (yeasts and molds) were isolated on SMA and subcultured to Sabauraud's Agar. These in turn were identified by microscopic evaluation of slide cultures and macroscopic evaluation of colonial morphology.

RESULTS

Demographic Distribution: 63% (184 samples out of the 293 total evaluated) were found to contain active microbial growth. The groups isolated were broken down into four groups: (1) Gram Positive Organisms, (2) Gram Negative Organisms, (3) Molds, and (4) Yeasts. Their distribution and frequency of occurrence is expressed as a percentage of the total in the following table:

TABLE I DEMOGRAPHIC DISTRIBUTION OF ISOLATED ORGANISMS

Gram Positive Organisms:		36.41%
Corynebacterium		15.76%
Bacillus		11.41%
Staphylococcus		5.98%
Staphylococcus epidermidis	(4.89%)	
Staphylococcus aurecularis	(1.09%)	
Micrococcus		2.17%
Nocardia		1.09%
Gram Negative Organisms:		45.11%
Pseudomonas		16.85%
Pseudomonas testosteroni/alcaligenes	(7.06%)	
Pseudomonas aeruginosa	(3.25%)	
Pseudomonas cepacia	(1.09%)	
Pseudomonas diminuta	(1.09%)	
Pseudomonas maltophilia	(1.09%)	
Pseudomonas putrefaciens	(1.09%)	
Pseudomonas stutzeri	(1.09%)	
Fluorescens	(1.09%)	
Alcaligenes		5.98%
Alcaligenes faecalis/odorans	(4.89%)	
Alcaligenes denitrificans	(1.09%)	
Achromobacter		5.98%
Achromobacter zylosoxidans	(4.89%)	
Achromobacter Group V-D	(1.09%)	
Moraxella	(4.89%)	5.98%
Moraxella urethralis	(1.09%)	
Serratia marcescens		4.89%
Pasteurella		2.16%
Acinetobacter calcoaceticus bio. lwoffi		1.09%
Citrobacter amalonaticus		1.09%
Flavobacterium		1.09%
Molds:		14.67%
Monosporium apiospermium	(13.58%)	
Cladosporium	(1.09%)	
Yeasts:		3.81%
Candida fomata	(2.72%)	
Torulosis candida	(1.09%)	

Gram Negative Organisms were found to be present in the highest concentration, accounting for over 45% of all organisms isolated. Not surprisingly, the genus of highest concentration within this group was Pseudomonsa sp. representing over 30% of all Gram Negative Organisms present and more than 16% of the total population. The species of highest concentration were four: Achromobacter xylosoxidans, Alcaligenes faecales/odorans, Pseudomonas testosteroni/alcaligenes, and Serratia marcescens. Each represented over 10% of all Gram Negative Organisms present and almost 5% of the total microbial population.

Gram Positive Organisms were present in the second highest proportion, representing over 36% of the total population. Corynebacterium sp. accounted for over 43% of the Gram Positive Organisms population and nearly 16% of the total population. Bacillus sp. followed with 31.3% of the Gram Positive population and over 11% of the total population.

Molds were overwhelmingly represented by Monosporium apiospermium, accounting for more than 92% of all molds isolated and 13.58% of the total population. The only other mold isolated was Cladosporium sp. which accounted for 7.43% all molds isolated and only 1.09% of the total population.

Yeasts accounted for the least representation - 3.73% (Candida fomata).

Additional results: Quantitative Distribution (Table II), Growth By-Products (Table III), Fuel Appearance (Table IV), Water Appearance (Table V), and Water Phase (Table VI) appear in the Appendix Section.

CONCLUSIONS AND RECOMMENDATIONS

In order to effectively deal with it, the problem must be approached scientifically. The objective of this study was four-fold to:

(1) Survey common infestions in fuel systems

(2) Establish correlations between specific organisms with effects on fuel systems

(3) Prompt further research with these specific areas in mind, and

(4) Provide consumers with information that hopefully will enable them to effectively cope with the very real problems of microbial contamination in fuel systems.

Some general conclusions can be drawn from the data presented. The fungi groups appeared to be predominately responsible for the majority of high cfu/ml counts, large amounts of growth by-products observed, and the cloudy appearance of both the water and fuel phases of the samples collected. Specifically, both molds and yeasts were heavily represented in those cultures whose colony counts exceeded 500,000 cfu/ml. Molds appeared to be representative of the generators of high amounts of growth by-products. Both molds and yeasts were associated with fuel deterioration but only yeasts appeared to heavily contaminate the water phase together with Gram Negative Organisms.

The Gram Negative Organisms were most heavily represented by the Pseudomonas species, the molds by Monosporium apiospermium and Cladosporium sp., and the yeasts were exclusively represented by Candida fomata. Thus, one may conclude that, within the limitations of this study, these organisms in the fuel system are responsible for fuel damage due to colony infestation. Although this claim would certainly need to be substantiated through further research, a conclusion could be drawn that a relationship exists between cfu/ml quantitated and amounts of growth by-products generated.

As mentioned before, the scope of this study was kept broad to provide a base for hypotheses for further studies. If one basic conclusion is to be drawn from this study, it would be that further studies need to be conducted in order to either substantiate or disprove the claims of this one. Several suggestions might be incorporated into further research:

* Sterile sampling techniques should be employed in the field collection and handling of samples prior to their receipt in the laboratory.

* Certain nutrient-based preservatives might be added to the sample in order to ensure the sustenance of all strains present until it can be cultured in the laboratory.

* Specific collection and culturing techniques might be employed if the study was limited to one specific group of organisms. Growth characteristic observations might be adjusted to include all (or only those) characteristics proven to be deleterious in fuel systems, (i.e., tank surface corrosion, etc.).

* Additionally, specific field-sampling procedures need to be established to eliminate inherent variables associated with obtaining fuel samples.

* Simultaneous inoculations of several types of media to provide an ideal growth environment for all possible types of organisms, together with a similar variety of incubation temperatures and atmospheres would allow for accurate representation of all organisms present.

* A detailed ASTM procedure for the culturing and quantitation of microbial growth needs to be developed and utilized uniformly throughout the fuels' industry.

Further studies would be helpful to the consumer to substantiate the hypostheses regarding which specific organisms are the most deleterious to fuel systems.

ACKNOWLEDGEMENT

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APPENDIX

QUANTITATIVE DISTRIBUTION

Specific organisms were further evaluated by amount of colony-forming units (cfu's) isolated from the quantitative evaluation phase and the distribution is indicated in the following table:

TABLE II **BREAKDOWN BY AMOUNT OF CFU/ML GROWTH QUANTITATED**

Organism:	Less than 50,000	50-100,000	100-500,000	More than 500,000	N/S
Corynebacterium					
Diphtheroids	4		9	16	
Bacillus	9		2	10	
Staphylococcus					
S. epidermidis	2		2	5	
S. aurecularis	2				
Micrococcus	2			2	
Nocardia	2				
Pseudomonas					
P. testosteroni/alcaligenes			5	5	3
P. aeruginosa			2	2	2
P. cepacia				2	
P. diminuta				2	
P. maltophilia				2	
P. putrefaciens				2	
P. stutzeri				2	
Fluorescens	2				
Alcaligenes					
A. faecalis/odorans				9	
A. denitrificans				2	
Achromobacter					
A. xylosoxidans				9	
A. Group V-D	2				
Moraxella		2		7	
M. Urethralis				2	
Serratia marcescens	2			7	
Pasteurella				4	
Acinetobacter calcoaceticus bio. lwoffi	2				
Citrobacter amalonaticus	2				
Flavobacterium		2			
Monosporium apiospermium			3	22	
Cladosporium		2			
Candida fomata				5	
Torulosis candida				2	

N/S = Not Specified.

Distribution was most heavily represented in the "more than 500,000" colony forming units column.

GROWTH BY-PRODUCTS

Specific organisms that were present in samples which contained varying amounts of growth by-products are indicated in the following table:

TABLE III AMOUNT OF GROWTH BY-PRODUCTS

Organism:	Small	Medium	Heavy	N/S
Corynebacterium				
Diphtheroids	4	9	16	
Bacillus	2	2	15	2
Staphylococcus				
S. epidermidis	4		5	
S. aurecularis			2	
Micrococcus		2	2	
Nocardia			2	
Pseudomonas				
P. testosteroni/alcaligenes	4	3	4	2
P. aeruginosa			3	3
P. cepacia				2
P. diminuta			2	
P. maltophilia			2	
P. putrefaciens			2	
P. stutzeri			2	
Fluorescens		2		
Alcaligenes				
A. faecalis/odorans	4		5	
A. denitrificans		2		
Achromobacter				
A. xylosoxidans	3			6
A. Group V-D		2		
Moraxella	3			6
M. Urethralis			2	
Serratia marcescens	3		4	2
Pasteurella			4	
Acinetobacter calcoaceticus bio. lwoffi	2			
Citrobacter amalonaticus			2	
Flavobacterium	2			
Monosporium apiospermium		2	21	2
Cladosporium			2	
Candida fomata		2	3	
Torulosis candida	2			

N/S = Not Specified.

Amount of growth by-products were most prevalent in the "Heavy" category for the majority of organisms. Molds were proportionately highly represented in the heavy growth by-products column. There appears to be a direct relationship between the presence of molds in fuel systems and the amounts of by-products observed within the limitations of this study.

FUEL APPEARANCE

The appearance of the fuel phase is related to specific organisms in the following table:

TABLE IV — **FUEL PHASE**

Organism:	Light/ Clear	Dark/ Cloudy	N/S
Corynebacterium			
Diphtheroids	9	20	
Bacillus	2	11	8
Staphylococcus			
S. epidermidis		2	7
S. aurecularis			2
Micrococcus	4		
Nocardia		2	
Pseudomonas			
P. testosteroni/alcaligenes	5	5	3
P. aeruginosa		2	4
P. cepacia			2
P. diminuta		2	
P. maltophilia		2	
P. putrefaciens		2	
P. stutzeri		2	
Fluorescens			2
Alcaligenes			
A. faecalis/odorans		9	
A. denitrificans			2
Achromobacter			
A. xylosoxidans			9
A. Group V-D		2	
Moraxella	2	7	
M. Urethralis		2	
Serratia marcescens		5	4
Pasteurella		4	
Acinetobacter calcoaceticus, bio. lwoffi	2		
Citrobacter amalonaticus			2
Flavobacterium	2		
Monosporium apiospermium	4	16	5
Cladosporium		2	
Candida fomata	2	3	
Torulopsis candida			2

N/S = Not Specified.

Organisms fell predominately within the "dark/cloudy" range. Diphtheroids and molds seem to be leading in the visible deterioration of the fuel phase.

WATER APPEARANCE

The condition of water in the samples submitted is related to the specific organisms by the means of the following table:

TABLE V **WATER PHASE**

Organism:	Light to Clear	Black to Cloudy	N/S
Corynebacterium			
Diphtheroids	7	20	2
Bacillus		12	9
Staphylococcus			
S. epidermidis		2	7
S. aurecularis		2	
Micrococcus		4	
Nocardia		2	
Pseudomonas			
P. testosteroni/alcaligenes	2	7	4
P. aeruginosa	2	4	
P. cepacia		2	
P. diminuta	2		
P. maltophilia		2	
P. putrefaciens		2	
P. stutzeri		2	
Fluorescens			2
Alcaligenes			
A. faecalis/odorans		9	
A. dentifricans	2		
Achromobacter			
A. xylosoxidans	2	1	6
A. Group V-D	2		
Moraxella	2	7	
M. Urethralis		2	
Serratia marcescens		5	4
Pasteurella		4	
Acinetobacter calcoaceticus, bio. lwoffi	2		
Citrobacter amalonaticus	2		
Flavobacterium	2		
Monosporium apiospermium		25	
Cladosporium		2	
Candida fomata	3		2
Torulosis candida			2

Water appearance was predominately "black/cloudy" in the samples observed. Free water was present in all growth classifications; however, two individual fuel samples: Pseudomonas (P. testosteroni/alcaligenes) and Bacillus had no free water visible.

WATER PHASE

The presence of organisms with or without free water in the samples submitted is illustrated in the following table:

TABLE VI

Organism:	FREE WATER Present	FREE WATER Absent	NO FREE WATER Present	NO FREE WATER Absent
Corynebacterium				
Diphtheroids	X			
Bacillus	X		X	
Staphylococcus	X			
S. epidermidis	X			
S. aurecularis	X			
Micrococcus	X			
Nocardia	X			
Pseudomonas	X			
P. testosteroni/alcaligenes	X		X	
P. aeruginosa	X			
P. cepacia	X			
P. diminuta	X			
P. maltophilia	X			
P. putrefaciens	X			
P. stutzeri	X			
Fluorescens	X			
Alcaligenes	X			
A. faecalis/odorans	X			
A. denitrificans	X			
Achromobacter	X			
A. xylosoxidans	X			
A. Group V-D	X			
Moraxella	X			
M. Urethralis	X			
Serratia marcescens	X			
Pasteurella	X			
Acinetobacter calcoaceticus, bio. lwoffi	X			
Citrobacter amalonaticus	X			
Flavobacterium	X			
Monosporium apiospermium	X			
Cladosporium	X			
Candida fomata	X			
Torulosis candida	X			

The relationship between the presence of water and the presence of microbial growth was further substantiated by the study's findings regarding those samples submitted where visible amounts of free water (water more than 0.05%) were found. All samples that contained free water also supported microbial growth.

Approximately 6% of the remaining 47% of total samples (water less than 0.05%) were found to contain microbiological activity. All of the organisms present in the samples with visible free water were also present in the samples with no visible free water.

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

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ABSTRACT

A wide variety of distillate hydrocarbon fuels were characterized as to thermal stability breakpoint (JFTOT, ASTM D 3241) and chemical structure parameters directly measurable by Proton Nuclear Magnetic Resonance (^{1}H NMR). Materials included coal-derived distillates subjected to three levels of hydrotreating severity, specification-quality military diesel and jet fuels, special high-energy density and high-thermal stability jet fuels, and pure hydrocarbons.

Regression modeling resulted in one general model and three sub-models for three distinct temperature regimes. The coefficients of the NMR terms appearing in these equations have provided valuable information on molecular structure factors which enhance or degrade thermal stability.

INTRODUCTION

Background

Thermal stability has historically been a specification property of only jet fuels. In recent years, thermal stability of all distillate fuels has received increasing attention. This is for three reasons:

- Anticipated long-term decreases in crude oil quality
- Definite plans to use the fuel as a heat sink in future-generation, high Mach aircraft (e.g., NASA High Speed Transport, National Aerospace Plane)
- Current development programs for adiabatic diesel engines

The last two will require dramatic increase in thermal stability requirements. The ability to predict thermal stability characteristics of jet fuel and diesel fuel from a knowledge of NMR characteristics would introduce a direct compositional measurement into an area traditionally controlled only indirectly by bench test.

Engine temperatures for the proposed High Speed Transport (HST) have generated a requirement for an increase in minimum acceptable thermal stability from the current commercial and military specification level of 500°F to approximately 750-1100°F. It may be that this criterion can be met by the more exotic future fuels, such as liquid methane and liquid hydrogen, but worldwide logistics are prohibitive. A far simpler and more straightforward solution would be to introduce conventional technology (hydrotreating, clay filtration) in economically upgrading kerosene-type jet fuel. Certainly, Proton Nuclear Magnetic Resonance techniques would be useful in this effort if they can provide insight into those compositional properties of liquid hydrocarbon distillates which correlate with extremely high thermal stability.

Objectives

The objective of this study has been to develop relationships between basic liquid hydrocarbon structures and thermal stability. Such relationships would provide a better understanding of those aspects of thermal stability mechanisms which address effects of molecular configuration upon deposit-forming tendencies. This understanding could then be applied toward future fuels formulated for use in extremely high temperature environments.

Approach

Proton NMR analysis has been used to characterize chemical structure and composition of a variety of liquid hydrocarbon distillates ranging from low-grade diesel fuel to specification-quality jet fuels. In addition, pure compounds and advanced jet fuels of superlative thermal stability have been used. Aromatic hydrogen, alpha hydrogen, methylene hydrogen, methine hydrogen, and methyl hydrogen concentrations derived from NMR analysis have been correlated with thermal stability breakpoint temperature, described in the section below.

Stepwise regression analyses using a variety of variable transformations as possible predictors have been employed to develop logical models which express thermal stability breakpoint in terms of NMR parameters.

In initiating this approach, the authors were well aware of the complicating *influence of trace metallo-organic "heteroatom"* compounds. NMR is blind to these. This present study has, by definition, addressed molecular characteristics of the bulk liquid hydrocarbons. As will be seen, correlative models for the liquids of highest thermal stability (from which heteroatoms are virtually absent) are the most logical and directionally consistent from the viewpoint of both the organic chemist and the statistician.

EXPERIMENTAL MEASUREMENTS AND RESULTS

Apparatus and Procedures

Thermal stability breakpoint was measured using standard Jet Fuel Thermal Oxidation Tester (JFTOT) apparatus per ASTM D 3241-85 procedures. Breakpoint, although not a formally defined term, is widely accepted as "Visual Code 3 inception temperature." A sequence of JFTOT tests is run at increasing (or converging) tube temperatures. The maximum tube deposits are visually rated by comparison to ASTM standards and plotted versus maximum tube temperature. The temperature at which a Visual Code 3 just appears is then the breakpoint. An idealized plot is shown in Figure 1*. Breakpoint repeatability for this technique is considered (by the authors) to be ± 7°F. Military and commercial specifications require a minimum breakpoint of 500°F for JP-4,

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* For purposes of plotting a "breakpoint curve" the ASTM ratings of <4, <3, <2 are taken to be 3.5, 2.5, and 1.5, respectively.

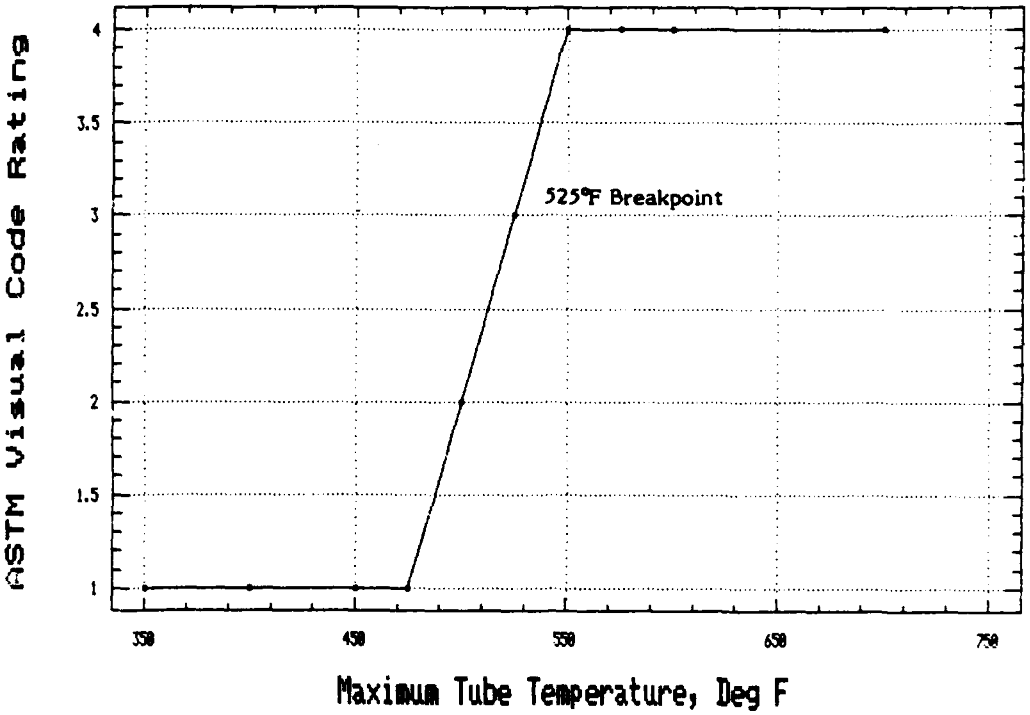

Figure 1. JFTOT Breakpoint Curve (ASTM D 3241-85 Procedure)

JP-5, JP-8, and commercial Jet A.* Military JP-7, used in the SR-71 Blackbird, has a minimum breakpoint requirement of 670°F. Although not a part of the fuel specification, special testing at SwRI indicates that:

- For crudes and residual fuel oils, breakpoint is in the range of 350-450°F
- For marine and automotive diesel fuels, the range is typically 400-500°F

Proton NMR analyses were performed using a JEOL 90Q FTNMR 90 MHz instrument. Fuel samples were diluted to approximately 50% concentration in deutero chloroform and tetramethyl silane (TMS) was added as an internal standard. Operating parameters were selected to provide optimum quantitation of the various proton types. Integrations of the spectra were evaluated according to the assignments given in Table 1.

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* Military specifications for JP-4, JP-5, JP-8 and commercial specifications ASTM D 1655 for Jet A, Jet A-1, and Jet B required the JFTOT test to be conducted for 2.5 hours at 500°F; however, the ASTM specification permits the test to be conducted at 475°F if the test fuel fails at 500°F. This lower test temperature is currently being debated and may be removed from D 1655.

Table 1. Proton NMR Chemical Shift Assignments

Proton type		Abbreviated Symbol	Description	Chemical Shift Region (ppm, Delta)
1.	Alkane methyl	CH_3	Terminal paraffin chain protons	0.5 - 1.05
2.	Gamma methyl	CH_3	Terminal alkyl chain protons at least three carbons from an aromatic ring	0.5 - 1.05
3.	Alkane methylene	CH_2	Mid-paraffin chain protons with no branching	1.05 - 1.4
4.	Beta methyl	CH_2	Terminal alkyl proton exactly two carbons from an aromatic ring	1.05 - 1.4
5.	Gamma methylene	CH_2	Mid-alkyl chain proton at least three carbons from an aromatic ring	1.05 - 1.4
6.	Alkane methine	CH	Mid-chain proton with branching	1.4 - 2.0
7.	Cycloalkane methylene	CH	Cycloalkane (naphthene) proton	1.4 - 2.0
8.	Beta methylene	CH	Mid-alkyl chain proton exactly two carbons from an aromatic ring	1.4 - 2.0
9.	Alpha methyl	ALP	Terminal alkyl chain on carbon adjacent to an aromatic ring	2.0 - 4.4
10.	Alpha methylene	ALP	Alkyl chain proton on carbon adjacent to an aromatic ring	2.0 - 4.4
11.	Alpha methine	ALP	Alkyl proton on carbon adjacent to an aromatic ring with branching	2.0 - 4.4
12.	Aromatic	ARO (DI& MONO)	All aromatic ring protons on di- or mono-ring compounds	6.2 - 9.2

Test Fuels

Twenty seven individual fuels were evaluated for thermal stability breakpoint and NMR properties. Fuel classes included:

- Surface and marine diesel fuels (DF-2 and DFM)
- Navy jet fuel (JP-5)
- USAF/Army jet fuel (JP-4)
- USAF high-thermal stability jet fuels (JP-7 and JPTS)
- Coal-derived distillate fuel (Exxon Donor Solvent process) subjected to 3 levels of hydrotreating severity (EDSB, EDSL, EDSM, EDSH in Table 2)

Table 2 presents SwRI fuel code and fuel class, plus JFTOT breakpoint (BKPT), and the five essential NMR measurements. Breakpoints ranged from 375°F for the base coal-derived liquid prior to hydrotreatment (EDSB) up to 725°F for the high thermal stability jet fuel (JPTS). This is considered to be the range of thermal stabilities for in-use distillates ranging from low-grade diesel to super-refined, special-use jet fuels in use today.

REGRESSION ANALYSIS MODELS

Analysis of thermal stability breakpoint and the several NMR parameters was accomplished by means of a stepwise regression program in the STATGRAPHICS®PC software package. It is a particularly flexible package intended for use in a broad range of industrial, service, and educational applications.

The Stepwise Variable Selection Regression Procedure was used in this study in an exploratory fashion to gain insight into the relationships between breakpoint and NMR variables. (Breakpoint is the dependent or response variable and combinations of the five NMR variables are the independent variables). The procedure begins with no variables in the model. For each NMR variable, or algebraic combination, the procedure calculates F statistics reflecting the variable's contribution to the model if it is included. These F statistics are compared to the F-to-enter value (at the $\alpha = 0.05$ level of significance) specified at the start of the procedure. If no F statistic has a significant level greater than the F-to-enter, the procedure stops. Otherwise, the stepwise procedure adds the variable with the largest F statistic to the model. After a variable is added, however, the stepwise method looks at all the variables already included in the model and deletes any variable that does not produce an F statistic significant at the F-to-enter ($\alpha = 0.05$ level of significance) level. After this check is made and the necessary variables deleted, then another variable can be added to the model. The stepwise procedure ends when none of the variables outside the model has an F statistic significant at the F-to-enter level and every variable in the model is significant at the F-to-remove level.

Table 2. NMR-Thermal Stability Database

Fuel Code	Fuel Type	CH_3	CH_2	CH	ALP	ARO	BKPT
FL-0765-F	EDSB	19.7	24.5	21.8	21.8	12.3	375
FL-0260-F	DF2	31.8	43.4	9.5	9.5	5.8	456
FL-1180-F	EDSL	25.8	26.8	26.6	14.0	6.7	456
FL-0416-F	JP5	50.0	26.0	18.4	3.6	2.0	480
FL-1170-F	DF2	38.5	46.0	8.9	3.3.	3.5	485
FL-0466-T	JP5	35.8	37.1	13.0	9.1	4.9	490
FL-1171-F	DF2	33.0	43.3	9.4	6.9	6.3	500
FL-1172-F	DF2	33.1	40.7	9.4	9.5	6.5	505
FL-0422-T	JP5	44.0	28.6	20.6	5.1	1.7	510
FL-0467-T	JP5	38.0	35.5	15.3	7.1	4.1	510
FL-1302-T	JP-8X	35.1	27.0	24.3	9.5	4.1	510
FL-1303-T	JP-8X	32.5	36.5	10.8	13.9	6.4	510
FL-1304-T	JP-8X	28.6	24.8	34.3	7.9	4.5	510
FL-0260CT	*DF2*	29.8	42.3	11.5	10.7	5.7	535
FL-1183-F	EDSM	30.7	29.5	30.0	6.4	3.3	538
FL-0436-T	JP5	38.8	39.9	11.2	6.7	3.4	540
FL-0448-T	JP5	37.9	39.3	14.2	6.0	2.6	545
AL-10150-S	DFM	29.9	43.9	11.0	10.8	4.4.	550
FL-0470-T	JP5	34.9	43.0	12.2	6.7	3.2	550
AL-9649CT	DF2	30.8	46.5	10.6	7.1	5.1	555
AL-9843CT	DF2	32.1	45.6	9.8	7.3	5.2	560
FL-0468-T	JP5	36.5	43.8	8.9	7.0	3.9	560
FL-1168-F	EDSH	34.8	29.9	29.5	4.0	1.8	563
FL-1235-T	JP4	43.2	32.2	14.6	6.5	3.3	600
FL-0464-T	JP5	37.5	40.9	11.5	6.3	3.7	625
FL-1241-T	JP7	42.9	36.6	10.8	8.0	1.7	685
FL-1242-T	JPTS	37.6	41.1	11.7	9.1	0.5	725

Model Descriptions

1. General Model

All five basic NMR variables were included as possible predictor variables in the stepwise regression procedure used to formulate the general model. The model fitting results are shown in Table 3 along with a a plot of the observed versus predicted break point values as shown in Figure 2. The resulting overall equation was:

$$\text{Breakpoint} = 453 - 36.6(\text{ARO}) + 3.7\,(\text{CH}_2) + 12.4\,(\text{ALP}) \qquad [1]$$

The coefficient of determination, unadjusted R^2, of 0.7034 and standard error of estimation (SE) of 40.1 indicate only a fair linear additive model for explaining the variation seen in the breakpoint values. R^2 measures the proportion of variability attributable to the regression fit while the standard error of estimation is a measure of the standard deviation about the regression model. The smaller the standard error, the more precise will be the predictions. Nevertheless, the constant of 453.279°F plus the algebraic signs of the parameters (ARO, CH_2, ALP) are logical and consistent in that they are of consistent order of magnitude and add to or subtract from the constant value as would be expected from bonding theory.

2. Fuel Class Sub-Categorization

There are three distinct sub-categories for this collection of fuels:

- Lower grade distillate (breakpoints less than 500°F)
- Conventional jet fuel (breakpoints from 500 to 560°F)
- Extremely high thermal stability jet fuels (breakpoints above 560°F)

The database was accordingly sub-divided into three distinct sets. This resulted in the following:

- 5 fuels having breakpoints less than 500°F
- 13 fuels in the mid-range (500-560°F)*
- 5 fuels having breakpoints above 560°F

Stepwise regression models were developed for each of these subgroups with resulting parameter estimates shown in Tables 4 through 6 with their corresponding Figures 3 through 5.

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* Four of seventeen fuels were removed from this set, since they were DF-2 and DFM formulations, not jet fuels, and had been clay-treated and otherwise modified from their original composition.

Table 3. General Model Fitting Results

Independent variable	coefficient	std. error	t-value	sig.level
CONSTANT	453.279348	49.577405	9.1429	0.0000
aro	-36.558279	5.935639	-6.1591	0.0000
ch2	3.699322	1.134277	3.2614	0.0034
alp	12.388014	3.707737	3.3411	0.0028

R-SQ. (ADJ.) = 0.6647 SE= 40.119220 MAE= 31.451221 DurbWat= 0.890

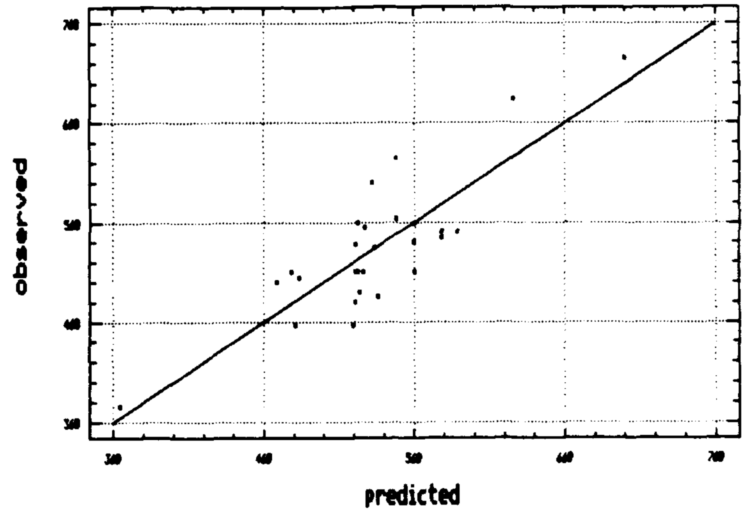

Figure 2. Plot of General Model

Table 4. Low-Grade Distillate Model Fitting Results

Independent variable	coefficient	std. error	t-value	sig.level
CONSTANT	540.970196	12.059029	44.8602	0.0000
aro	-13.338885	1.65307	-8.0692	0.0040

R-SQ. (ADJ.) = 0.9413 SE= 11.166729 MAE= 7.516269 DurbWat= 2.471

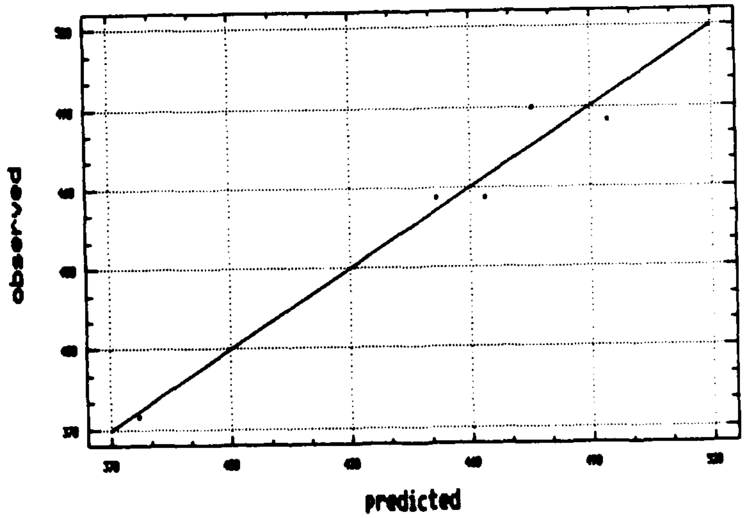

Figure 3. Plot of Low-Grade Distillate Model

3. Low-Grade Distillate Model (<500°F)

The first of these, Table 4 and Figure 3, is for the five fuels of lowest thermal stability from 375°F to 490°F. The resulting equation was:

$$\text{Breakpoint} = 541 - 13.3\ (\text{ARO}) \qquad [2]$$

The multiple R^2 of 0.9560 and standard error of 11.167 are an indication of a good statistical fit. Note also the negative coefficient for the aromatic hydrogen term, indicating that this molecular characteristic is the predominant compositional factor in hydrocarbon makeup. For this sub-class, heteroatom presence is undoubtedly also a major factor.

4. Conventional Jet Fuel Model (500-560°F)

The 13 fuels which comprise the intermediate group with breakpoints from 500° to 560°F are virtually all military specification JP-4, JP-5, and JP-8X fuels. Stepwise modeling resulted in the coefficients and constants shown in Table 5, the observed vs. predicted plot in Figure 4, and the following equation:

$$\text{Breakpoint} = 303 - 10.0\ (\text{ARO}) + 3.2\ (\text{ALP}) + 3.0(\text{CH}) + 5.2\ (\text{CH}_2) \qquad [3]$$

Here again, the R^2 of 0.9393, the standard error of 5.797, and the algebraic signs of the coefficient for the several NMR terms are logical and consistent, with the aromatic hydrogen term (ARO) again having deleterious effect on thermal stability. The other three terms (ALP, CH, CH_2) tend to enhance thermal stability.

5. High Thermal Stability Jet Fuels (>560°F)

The final grouping of extremely high thermal stability fuels resulted in model parameters and curves as shown in Table 6 and Figure 5, and the following equation:

$$\text{Breakpoint} = 817 - 33.7\ (\text{ARO}) - 6.6\ (\text{CH}) \qquad [4]$$

The R^2 of 0.9894 and standard error of 9.499 indicate excellent fit. Note that only ARO and CH (both with negative coefficients) appeared as significant terms. The negative contribution of aromatic protons is consistent with each of the previous correlation equations. The negative sign on the methine proton coefficient agrees with its relative high free radical stability compared to methyl or methylene protons.

Table 5. Conventional Jet Fuel Model Fitting Results

Independent variable	coefficient	std. error	t-value	sig.level
CONSTANT	303.407983	29.56802	10.2614	0.0000
aro	-10.045985	2.122683	-4.7327	0.0015
alp	3.181133	1.238982	2.5675	0.0333
ch	2.945933	0.481024	6.1243	0.0003
ch2	5.235639	0.553327	9.4621	0.0000

R-SQ. (ADJ.) = 0.9089 SE= 5.796602 MAE= 4.160738 DurbWat= 1.516

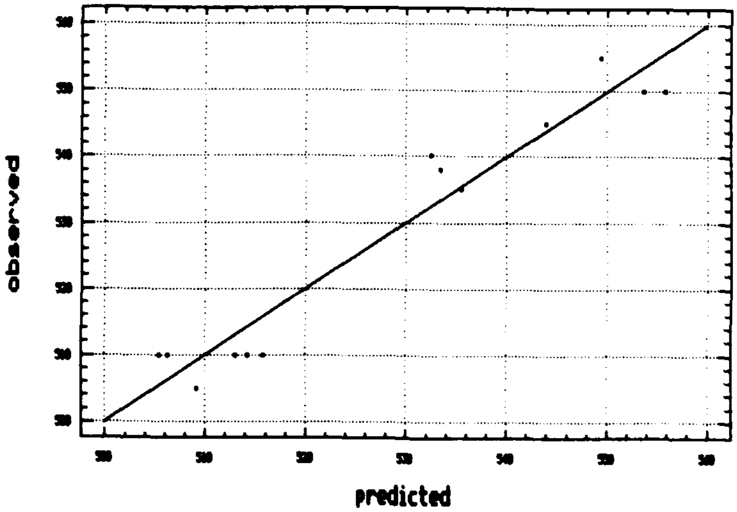

Figure 4. Plot of Conventional Jet Fuel Model

Table 6. High Thermal Stability Jet Fuels Model Fitting Results

Independent variable	coefficient	std. error	t-value	sig.level
CONSTANT	816.668556	13.649195	59.8327	0.0003
aro	-33.672087	3.668997	-9.1775	0.0117
ch	-6.593468	0.604209	-10.9126	0.0083

R-SQ. (ADJ.) = 0.9788 SE= 9.498862 MAE= 5.001040 DurbWat= 3.402

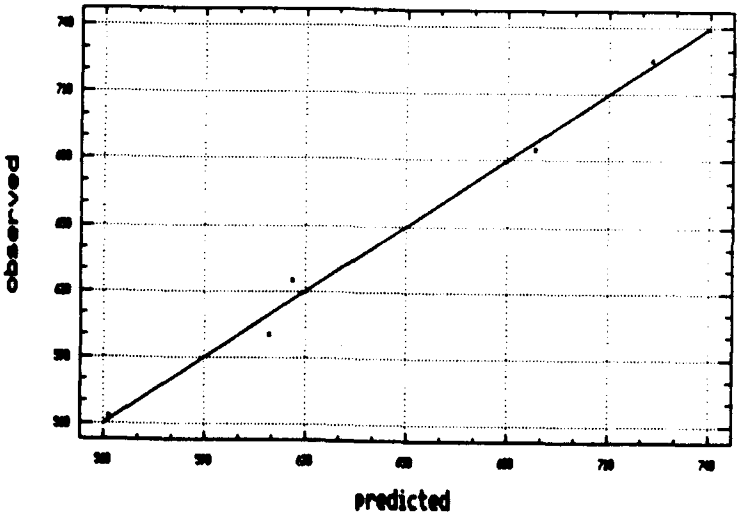

Figure 5. Plot of High Thermal Stability Jet fuels Fuels Model to Three Severities

SPECIAL LIQUIDS

Coal-Derived Liquids

Three distillate materials had been prepared at SwRI under the U.S. Department of Energy Alternative Fuels Utilization Program (AFUP). The base liquid was a low-grade distillate derived from the Exxon Donor Solvent (EDS) process. These fuels were particularly valuable since they stemmed from the same base stock. Breakpoint and NMR data were obtained for the base stock and the three products produced at three distinct levels of hydrotreating at the DOE Synthetic Fuel Center at SwRI. Complete data for the caustic-treated feedstock (EDSB) and three products (EDSL, EDSM, EDSH) are given in Table 7. Since hydrotreating has a positive effect on thermal stability, it was particularly advantageous to generate JFTOT and NMR data on the three hydrotreated samples. These are shown in Figure 6, wherein the caustic-treated base stock had a breakpoint of 375°F, followed by breakpoints of 456°, 538°, and 563°F, indicating that the four curves shown are separated significantly. Figure 7 shows JFTOT breakpoint temperature as a function of hydrotreating severity (hydrogen content).

Figure 8 presents the five principal NMR parameters for the EDS feedstock and products plotted as a function of JFTOT breakpoint temperature. Note that the alkane protons (CH, CH_2, CH_3) increased with level of hydrotreating (i.e., with increasing breakpoint), while the protons associated with aromatic rings (ARO, ALP) decreased dramatically. Note also the inverse relationship between aromatic protons and thermal stability. This implies that aromatic compounds have lower thermal stability than saturated structures in distillate fuels. This may also be an indirect measure of other elements and structures not represented in the proton NMR data (but related to aromatic proton content) which are being removed through hydrotreatment. In either case, the NMR correlation is still statistically valid.

Pure Hydrocarbon Compounds

Various studies of pure compounds report deposit formation to both increase as well as decrease with concentrations of normal paraffins, isoparaffins, cycloparaffins, aromatics, and olefins (1-8*). The results show definite contradictions where deposits increase in one report and decrease in another as shown in Table 8. References listed in Table 8 were cited in a literature search conducted by the Coordinating Research Council (CRC).

The thermal stability of several pure hydrocarbons was measured in the current study after clay-treating**. Results are summarized in Table 9. A variety of chemical structures similar to the type of information available from NMR analysis were assessed in this procedure, including straight-chain alkanes, branched-chain alkanes, cycloalkanes, olefins, mononuclear aromatics, and polynuclear aromatics. With the exception of the mixed methyl naphthalenes, the only polynuclear aromatic tested, all of the hydrocarbon types displayed a visual code deposit of 2 or less at 750°F. Methyl naphthalenes had a <4

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* Denote references listed at the end of the paper.
** ASTM Method D 2550, Annex A4

Table 7. Caustic-Washed EDS Middle Distillate Hydrotreated to Three Severities

Property	Method	EDSB Feedstock Caustic Treated	EDSL Low Severity	EDSM Medium Severity	EDSH High Severity
Identification Number	-	FL-0765-SP-F	FL-1180-SP-F	FL-1183-SP-F	FL-1168-SP-F
Specific Gravity, 60°F	D 1298	0.9254	0.9013	0.8844	0.8729
API Gravity		21.4	25.5	28.5	30.6
Distillation, °F	D 86				
IBP		412	369	377	272
5 V%		424	416	407	388
10		431	424	415	404
20		440	433	425	420
30		449	441	432	430
40		461	453	441	440
50		473	464	450	453
60		489	479	464	466
70		509	499	480	484
80		534	519	504	506
90		573	552	533	537
95		611	582	561	565
FBP		649	624	591	609
Recovery, V%		98.0	99.0	99.0	99.0
Residue, V%		2.0	1.0	1.0	1.0
Loss, V%		0.0	0.0	0.0	0.0
Cetane Number	D 613	23.5	29.0	34.2	38.2
Cetane Index	D 976	22.6	26.4	28.2	31.8
Viscosity, 20°C, cSt	D 445	4.08	3.78	3.47	3.44
40°C		2.53	2.33	2.29	2.19
Hydrocarbon Type, V%	D 1319				
Saturates		18.3	53.3	77.3	88.9
Olefins		6.5	1.2	1.1	0.9
Aromatics		75.2	45.5	21.6	10.2
Aromatic Carbon, M%	UV				
Monocyclic		22.46	16.18	8.07	3.73
Dicyclic		6.36	1.92	1.03	0.42
Tricyclic		1.31	0.19	0.05	0.09
Elemental Analysis, M%					
Carbon	D 3178	88.5	87.7	87.1	86.5
Hydrogen	Modified	10.9	11.9	12.7	13.1
Sulfur	D 2622	0.01	0.01	0.01	0.01
Oxygen	Microcombustion	0.46	0.22	0.15	0.03
Nitrogen	Visible Chemiluminescence	0.028	0.0006	0.0005	0.0005
Heat of Combustion	D 240				
Gross, BTU/lb		18788	19018	19284	19375
MJ/KG		43.701	44.236	44.855	45.067
Net, BTU/lb		17794	17930	18129	18183
MJ/KG		41.388	41704	42.168	42.293
BTU/gal.		137,134	134,583	133,525	132,181
Existent Gum, mG/100mL	D 381				
Unwashed		372.7	2.2	4.0	1.4
Washed		371.1	1.5	1.0	0.7
Accelerated Stability, mG/100 mL	D 2274	1.39	0.17	0.14	0.17
Flash Point, °F	D 93	199	96	124	81
Pour Point, °F	D 97	-48	-47	-	-52
Refractive Index*	D	1.5149	1.4941	1.4808	1.4703
Surface Tension, Dyne/cM	D 971 MOD (Air/Fuel)	33.0	30.69	32.0	31.4

* Result from National Research Council Canada, Division of Mechanical Engineering

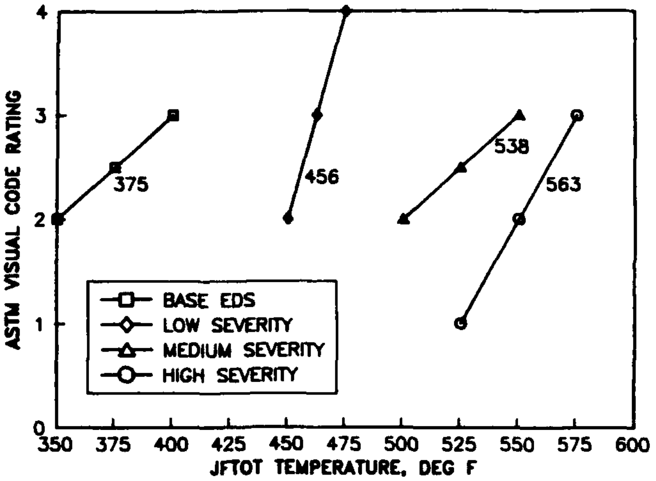

Figure 6. Thermal Stability of Hydrotreated EDS Coal Liquids

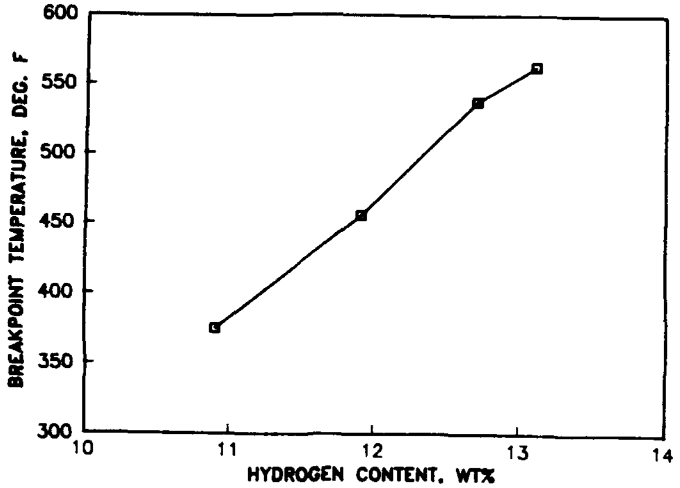

Figure 7. Thermal Stability of EDS Coal Liquids with Fuel Hydrogen Content

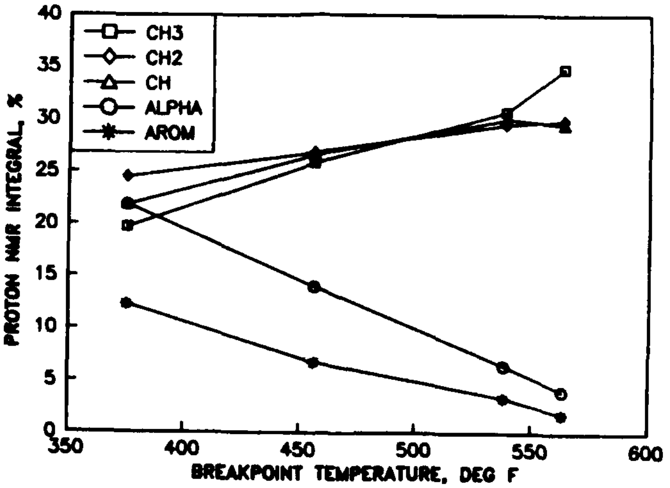

Figure 8. Proton NMR Response to Hydrotreated EDS Coal Liquids

Table 8. Effects of Hydrocarbon Structure on Deposit Formation

Hydrocarbon Type	Proton NMR Structures	Deposit Increase	Deposit Decrease
n-paraffins	CH_2, CH_3	relative to iso-paraffins(6)*	with molecular size(1) relative to iso-alkanes(1)
iso-paraffins	CH_2, CH_3	relative to n-alkanes(1)	relative to n-paraffins(6)
cycloparaffins	CH	100% increase with aromatics(6)	modest inhibition(1) 50% decrease in deposits(6)
aromatics	ARO, ALP	tetralin, acenaphthene drastic(4) napthalenes sharply(5) contribute significantly deposits(3) slight increase(6) 100% increase with cycloparaffin(6)	significant reduction(1) fluorene/diphenyl methane - 10X at 10 wt%(1) deposit inhibitor(3) alkyl-benzene little(5)
Olefins	**	at 10 wt% 3-35X in n-C_{10} alphamethyl styrene(1), indene marked by higher deposits(7) indene copolymerizes with oxygen(2) diolefins, greatest(1)	mono olefins no increase(7) some diolefins no change(8)

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* Reference Number

** Olefins in fuels are generally not detected with proton NMR because of low concentration; in high concentrations olefinic protons are observed between 4.4. and 6.2 ppm on the Delta scale.

Table 9. JFTOT Deposit Ratings of Clay-Treated Pure Hydrocarbons

Temperature, °F	450	500	600	625	650	675	700	750
Alkanes								
Isooctane	-	-	-	-	-	-	-	1
Dodecane	-	-	-	-	-	-	-	2
Heptamethyl Nonane	-	-	-	-	-	-	-	1
Hexadecane	-	-	-	-	-	-	-	2
Cycloalkanes								
Decalin	-	-	1	-	-	-	<2	1
Aromatics								
Tertiary Amyl Benzene	-	1	1	-	-	-	1	<2
Methyl Napthalenes	-	1	9	<3	3	3	<4	-
Olefins								
Indene	-	-	1	-	-	-	-	<2

visual code at 700°F (estimated visual code 4 at 750°F), resulting in the lowest thermal stability of the compounds tested. These results are graphically illustrated in Figures 9 and 10, wherein it can be seen that the mixed methyl naphthalenes are the only compound type having (by definition) a "breakpoint" (625°F).

Indene, which has been reported to be very unstable (2,7), gave surprising results. Heat was generated during clay-treatment. Infrared spectra of the as-received indene showed carbonyl species and other indications of oxidation, but the clay-treated indene sample matched the literature infrared spectra. It was therefore concluded that the oxidized portion was adsorbing to the clay and releasing the heat of adsorption with no further reaction taking place.

The thermal stability of blends of pure compounds was also investigated at 700°F. These results are presented in Table 10. Blends of methyl naphthalenes resulted in the heaviest deposits. Blend deposits were greater than expected from unblended results for combinations of isooctane and decalin, tertiary amyl benzene and indene, and blends of methyl naphthalenes. These results are illustrated in Figure 11.

It is concluded from the hydrocarbon type studies that polynuclear aromatic structures may be especially detrimental to thermal stability. Indications of polynuclear aromatic content should be emphasized in NMR structural analysis and in correlation development. Polynuclear aromatic protons are indicated in the NMR spectra in the region above 7.2 ppm, but it is not very quantitative due to the low concentration in most fuels.

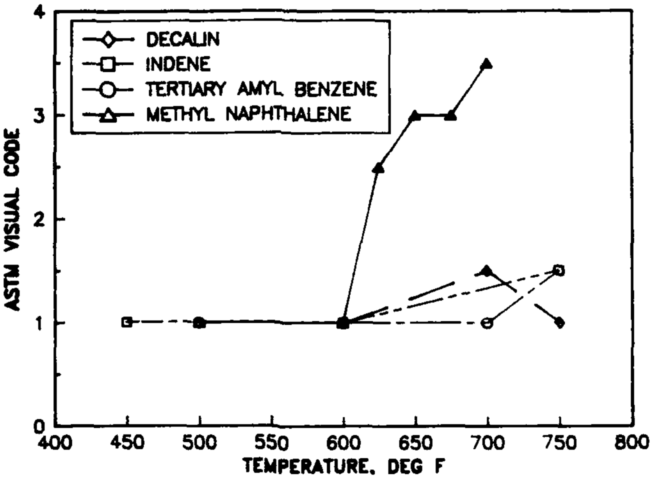

Figure 9. JFTOT Deposit Ratings for Clay-Treated Pure Hydrocarbons

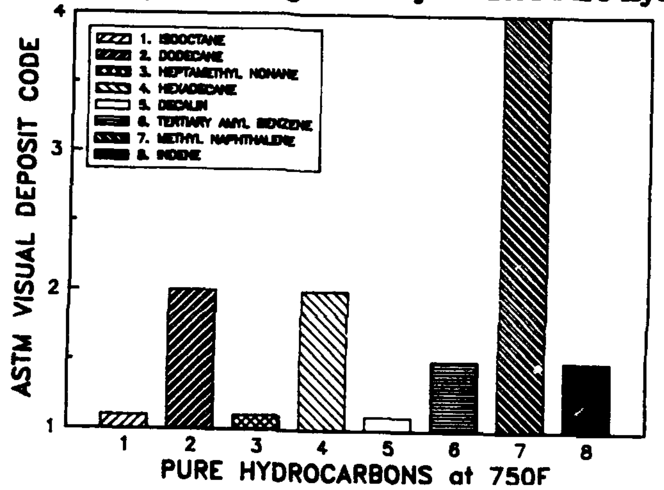

Figure 10. JFTOT Deposit Ratings for Clay-Treated Hydrocarbons

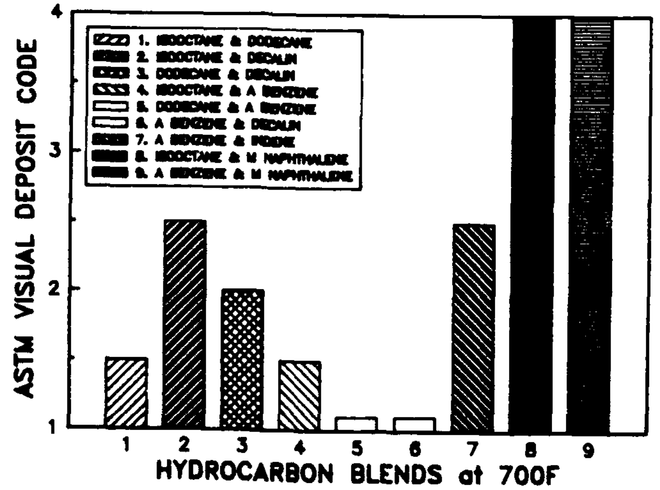

Figure 11. JFTOT Deposit Ratings for Clay-Treated Hydrocarbon Blends

Table 10. JFTOT Deposit Ratings of Clay-Treated Pure Hydrocarbon Blends

	ASTM Visual Code at 625°F	ASTM Visual Code at 700°F	Component Comparison (of ASTM Visual Code) at 750°F(**)	Blend Deposit Synergism
Alkane Blends (*)				
Isooctane: Dodecane	-	<2	1:2	-
Isooctane: Decalin	-	<3	1:1	increase
Dodecane: Decalin	-	2	2:1	-
Tertiary Amyl Benzene Blends (1)				
Isooctane: Amyl Benzene	-	<2	1:<2	-
Dodecane: Amyl Benzene	-	1	2:<2	-
Amyl Benzene: Decalin	-	1	<2:1	-
Amyl Benzene: Indene	-	<3	<2:<2	increase
Methyl Napthalene Blends (1)				
Isooctane: Methyl Napthalene	-	>4	1:<4	increase
Dodecane: Methyl Napthalene	<3	-	2:<4	-
Amyl Benzene: Methyl Napthalene	-	>4	<2:<4	increase

(*) All blends made in a 4:1 volume ratio as listed.
(**) Except methyl napthalene measured at 700°F.

CONCLUSIONS

For all four regression models, the following generalizations may be observed:

- The constant values in all four equations are of an appropriate order of magnitude and all of positive algebraic sign.
- The highest thermal stability model (Table 6, Figure 5, equation [4], probably reflects the true conditions of the structures moreso than the other models where heteroatom contamination may cloud the issue.
- The four equations consistently indicate that molecules containing aromatic protons (ARO) tend to degrade thermal stability.
- Polynuclear aromatic hydrocarbons may be especially detrimental to thermal stability, while single ring aromatic compound may actually enhance stabilty.

This last may, indeed, prove to be most important implication from this study: that low concentrations of mononuclear aromatic compounds can improve thermal stability. This will require considerable more experimentation before generalizations can be attempted.

ACKNOWLEDGMENTS

The fuels and breakpoint data provided by R.A. Kamin of the Naval Air Propulsion Center and S. Anderson of the USAF Propulsion Laboratory were of great value in this work.

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

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ABSTRACT

The Jet Fuel Thermal Oxidation Tester (JFTOT) is normally operated under standard conditions required by international specifications for qualification of production batches of jet fuel. Because the test can discriminate between fuels of poor and good high temperature stabilities, it has a valuable role in its present form for quality assurance of fuels. However, it can also be used under a wider range of operating conditions for research into high temperature thermal stability behaviour of aviation fuels. Some typical research investigations are reviewed in the paper to illustrate this point.

When used in the research mode, several shortcomings of the JFTOT become evident, particularly in the areas of tube deposit assessment and tube surface metallurgy. Improvements are proposed to overcome these shortcomings, eg. measuring tube deposits quantitatively by carbon burnoff, or by recently developed methods utilising light interferometry and breakdown of dielectric potential. JFTOT breakpoint temperature is a very important concept for establishing the level of fuel thermal stability quality, and this is discussed in detail. Some single test predictive methods for measuring breakpoint temperature are outlined, which are aimed at shortening the usual lengthy multi-test determination of this parameter.

INTRODUCTION

The Jet Fuel Thermal Oxidation Tester (JFTOT) provides data characterising high temperature instability properties of aviation kerosines. Instability manifests itself through the occurence of autoxidation reactions that lead to formation of insoluble deposits, and the quantities of such deposits, measured in the JFTOT, describe the deposit-forming tendency of a fuel. International specifications for aviation fuel state that the deposits must not exceed specified values under given operating conditions, and the test result is reported as a "pass" or "fail" with respect to these requirements. It is in this role - the qualification of production batches of jet fuel against specification quality requirements - that the JFTOT by necessity finds its greatest use.

But use is also made of it in fuels research , when it is operated over a wider range of test conditions, and there is a need to study deposits in greater detail so that conclusions may be drawn about fuel degradation mechanisms, and the function of specific chemical components.

Research into thermal stability is becoming increasingly important as higher performance, energy efficient engines are being developed. Before being burnt, the fuel on an aircraft is exposed to ever higher thermal stress conditions within heat exchangers, fuel metering and control units, and finally the burner arm pipework. In any of these areas, high temperature breakdown of unstable fuel components could cause deposits to be lodged that would contribute to malfunction of the system. Thermal stability quality of fuels therefore not only has to be maintained, it should preferably be improved, and adequate measurement techniques should be available to meet new demands.

The JFTOT is not an ideal research tool, nevertheless it is familiar and available throughout the world, and it can easily be adapted to produce results valuable for the investigation of fuel stability. Some typical research results are described in the paper. Existing methods for assessment of tube deposits may suffice for evaluating fuels for specification purposes, but they lack the ability to quantify deposits in the greater detail demanded for research work. Some recently-developed deposit measurement techniques are outlined in the paper to address this issue.

TEST APPARATUS AND METHOD

The JFTOT apparatus and procedure are described in detail in ASTM D3241. In the test prefiltered, aerated fuel flows under a pressure of 3.4 MPa through an annulus formed between the outer housing and an aluminium inner heater tube, and then out through a test filter. Residence time in the annulus is approximately 13 seconds. A temperature profile is obtained along the length of the heater tube; its maximum value is recorded as the JFTOT temperature. The usual operating conditions laid down in specifications are 260 °C temperature and 150 minutes test duration. If the fuel is unstable, it can produce varnish-like deposit on the heater tube, and/or sediment that increases pressure drop across the test filter.

Filter pressure drop is recorded during progress of the test, and heater tube deposit is checked at the end of the test. Depositsare rated either by eye in the Visual Rating Method, where the tube is examined in a light box against a background of ASTM standard colour codes; or in the Alcor Tube Deposit Rater (TDR) designed to overcome the subjectivity of the human eye by means of a lamp and photocell arrangement. Ratings are measured in this instrument by scanning along the length of the tube, which is spun about its axis.

JFTOT breakpoint temperature is a measurement quoted throughout this paper - this is the temperature at which a fuel fails specification rating criteria. Its determination is discussed in more detail in a later section.

THERMAL STABILITY RESEARCH WITH THE JFTOT

Some examples from the literature will serve to illustrate the adaptability of the JFTOT to fuels research work.

Stability of future hydrocarbon fuels were characterised by their JFTOT breakpoint temperatures in a study of oil-shale and coal-derived fuels (1). Fuel-bound nitrogen content was varied by hydrotreating the fuels to different degrees of severity. The effect of nitrogen on stability was found to be significant, with breakpoint temperature dropping from 330 °C to 220 °C with increasing nitrogen content. It was evident that total nitrogen in excess of 100 ppm would reduce breakpoint temperature to levels below 260 °C. Breakpoint was also measured as a function of hydrogen content, again showing a good correlation. A 260 °C breakpoint generally required at least 13 wt % hydrogen content. Another factor that affected breakpoint was the final boiling point of jet fuels, with a decreasing trend as final boiling point was increased. With these results, it was possible to define the general severity of refinery processing that would be required to produce synthetic fuels with stabilities comparable to those of current jet fuels.

The influence of specific nitrogen compounds found in petroleum crudes was evaluated in a series of tests on Jet A, with individual solutions of pyrrole, indole, quinoline and pyridine, in concentrations ranging from 100 ppm to 1000 ppm nitrogen (2). JFTOT breakpoint was defined as the temperature at which maximum spun TDR of 13 was reached. The results showed that even at the 100 ppm concentration level, all compounds caused significant changes in stability. Indole and pyrrole gave breakpoint temperatures of 250 and 235 °C respectively; whereas pyridine and quinoline results were both around 275 °C. However, solutions of the latter two compounds gave deposits beyond the test section, ie. there was a more rapid rate of buildup in the final filter. The given breakpoints were therefore not accurate. It was concluded that for most fuels, which contain a mixture of nitrogen types, the JFTOT breakpoint results will have to be evaluated on the basis of filter pressure drop as well as on tube deposit.

A modified JFTOT procedure was used by NASA Lewis to evaluate deposit formation for four aerated pure hydrocarbon fuels over the tube temperature range 150 to 450 °C (3). Stainless tubes were used here to permit higher test temperatures and to increase the deposition rate, thereby reducing test time. Four distinct fuel types were studied : a normal alkane (n-decane), an alkene (1-hexene), a naphthene (cyclohexane) and an aromatic (benzene). Results were expressed as TDR values plotted against tube position. At the lower temperatures of 150 and 250 °C, all four fuels produced only small amounts of deposit during the 40 minute run, with TDR values less than 5. At 350 °C the olefinic fuel, 1-hexene, formed the largest amount of deposit, consistent with its susceptibility to oxidation and polymerisation. At the higher temperature of 450 °C all fuels except benzene formed large amounts of deposit with TDR values of 40 to over 50. This confirmed the oxidation stability of the benzene structure. The results were useful in formulating the composition of simulated jet fuel bases for thermal stability studies on added components.

An altogether different application of the JFTOT was made by Hazlett et al (4) to study the sequence of reactions that lead to deposit formation during thermal stress of jet fuels. Pure n-dodecane, representing a major component of jet fuel, was selected as the test fluid. A sample take-off tee, located downstream of the heater section, directed a portion of the flow to a liquid sampling valve on a gas chromatograph. In this way, the formation of soluble degradation products could be measured.

The primary oxidation product was found to be dodecyl hydroperoxide, which was stable at tube temperature conditions up to 290 °C. Above this temperature the hydroperoxide decomposed, reacting completely by 400 °C. Fundamentally different reaction regimes were discovered at different temperature levels. Thus decomposition yielded aldehydes and primary alkyl radicals between 340 and 400 °C, then reactivity slowed down to a modest rate between 400 and 480 °C. Above this temperature, thermal cracking occured, explained by standard hydrocarbon pyrolysis theory.

Similar use of the JFTOT apparatus was later made to study degradation chemistry of n-dodecane doped with nitrogen and sulphur compounds (5). The soluble decomposition products of samples stressed between 200 to 400 °C were analysed by gas chromatography and mass spectrometry, and reaction mechanism information obtained.

CRITIQUE OF THE TEST METHOD

Influence of Tube Surface Metallurgy

The metallurgy of the JFTOT heater tube surface clearly exerts a rate-determining effect on the process of deposit laydown. Significantly greater amounts of deposit are ususally produced on stainless steel tubes than on the standard aluminium ones. Figure 1 shows a comparison of steel versus aluminium deposits from a series of fuels tested at the same temperature. Deposits were quantified by carbon burnoff, the weights obtained being typically twice as high on the steel tubes (6). The deposits produced by low sulphur fuels on steel tubes were much more visible than the very light deposits given by these fuels on aluminium tubes.

A very far-reaching discovery about JFTOT tube metallurgy was made by BP Research, who found that magnesium, which is present as an alloy element in 6061 aluminium, can migrate to the surface of the tube under the influence of high temperature (7). Auger Electron Spectroscopy (AES) was used to analyse the surface of a JFTOT tube heated to 365 °C in dodecane. Since the dodecane would not be expected to decompose, the test could be regarded as studying the effect of heat on the tube alone. The surface layer of oxide was found to contain a surprisingly high level of magnesium (about 25 At %) compared to the bulk concentration in the aluminium of about 1 At %. The presence of magnesium on the surface was found to cause strong inhibition of carbon deposition from the fuel, a fact that was corroborated by performing a test on an aluminium tube which had been coated with magnesium.

The extent of magnesium migration is very temperature-dependent, as shown in Figure 2, depicting AES analyses in the temperature range 245 - 320 °C (8). Surface enrichment of magnesium was observed in all cases, with concentrations ranging from 8 to 12 At %. This raised doubts about the validity of using aluminium tubes in the JFTOT and the TDR for deposit assessment, particularly for research studies at high temperatures.

Deficiencies in Deposit Assessment

Quantifying the amount of JFTOT tube deposit by either of the specified optical reflectance methods can never be completely satisfactory, since both are limited to the specific wavelength range of the human eye or TDR photocell system. The deficiencies of the TDR stem from its insensitivity to deposits in the blue end of the colour spectrum, and the somewhat primitive optical system. An improved TDR would incorporate a new optical system designed to cover different wavelengths of light and a means of separating reflectance and interference effects caused by thin films. There is also no way of knowing whether a deposit rated low by light reflectance is actually a thin dense film, or a thick translucent film.

Furthermore, there is evidence that reflectivity of the JFTOT tube itself may be altered by the action of heat applied during the course of the test. It was found that the mixed aluminium/magnesium oxide layer formed at high temperature on aluminium tube surfaces as a result of magnesium migration had a low optical reflectivity (9). In this case the TDR test suggested the presence of a thick carbonaceous deposit, whereas Auger spectroscopy proved that there was in fact relatively little carbon present.

TDR results have frequently revealed inconsistencies with other forms of deposit measurement, in particular that of total weight by carbon burnoff. For test fuels from three different sources, deposit weight and max. spun TDR both increased with JFTOT temperature (Figure 3). However, quite different correlations were obtained for each fuel, demonstrating that there was no general correlation between TDR and deposit weight (10). Other work also showed TDR failing to respond proportionally to deposit weight (Figure 4). Thickness profile measurements obtained by dielectric and light interference methods gave instances where the TDR was disproportionately influenced by thin, highly coloured deposits (11).

Usefulness as Aircraft Fuel System Simulator

From the general absence of problems directly attributable to thermal degradation products depositing in aircraft fuel systems, it must be concluded that the JFTOT has been very successful in the role of a fuel specification device. It has therefore been an adequate model for prevalent operating conditions in gas turbine engines in service to date. However, newer aero engine designs are tending to place great emphasis on fuel efficiency and this inevitably results in higher fuel system temperatures. Whether or not the 260 °C JFTOT will still adequately model the greater thermal stress conditions to which fuels will probably be exposed in future generations of high efficiency engines, is a question that should now be contemplated.

The JFTOT was designed as a smaller, accelerated version of the Fuel Coker (ASTM D1660), which in turn was designed in the 1950's to simulate the fuel manifold conditions that led to the first aircraft operating problems caused by fuel instability. When fuel flow conditions in the JFTOT are compared to those in a modern engine system, the following shortcomings in the test device are revealed :

a) Lack of a fuel preheating stage. Bulk fuel temperatures in excess of 100 °C can be found in practice.
b) Very slow laminar flow over the heated test section, compared to turbulent flow through actual heat exchangers and fuel management systems.
c) Long residence time, with 13 seconds to traverse the heater test section from inlet to outlet. Typically it takes less than 1 second for fuel to pass through the hottest parts of a heat exchanger.

NEW WAYS OF USING THE JFTOT

New Methods of Deposit Assessment - Thin Deposits

The extreme thinness of the deposit layers formed on JFTOT tubes at test temperatures around 260 °C makes it difficult to interpret them in a quantitative scientific manner. The human eye can detect quite subtle variations in deposit appearance, including 'peacock' shades and colours other than the normal browns. That is probably why the Visual Rating Method, dating back to the Fuel Coker Test, remains as the definitive standard in fuel specifications.

An interesting new method based on light interferometry has been developed by Geo-Centers Inc. (12). It comprises a specially designed holder for fibre optic probes, which replaces the standard JFTOT heater tube holder. A series of probes, each containing both source and detector optics, are located in a spiral arrangement around the tube between stations 18 and 48. Monochromatic light directed at the tube reflects back off the tube/deposit interface and is attenuated on its way through the deposit. Interference between the reflected and incident light waves becomes dependant on the thickness of the deposit layer; this is analysed by a microprocessor, resulting in a final measurement of deposit thickness. A great advantage of this system is that it can be used on-line to give information about the rate of deposit buildup, or off-line as a post test tube deposit reader. On-line operation has the additional facility of furnishing data about deposit formation at multiple temperatures from one JFTOT run.

Unfortunately, the interferometry technique in its present form is not completely suitable for evaluation of the very thin films, of the order of 0.01 microns thickness, that make up JFTOT deposits corresponding to normal Visual Ratings between Codes 1 and 4. It was reported that the technique could only be successfully used on JFTOT deposit layers in the range of 0.14 to 1.5 microns thickness (13). A practical way of utilising the apparatus for fuels research was found in the comparison of different fuels by the JFTOT running time required to reach the first minimum of reflected light intensity (equating to film thickness of 0.14 microns).

Another potential candidate assessment method is photo electron emission, which works by exposing a surface to UV radiation, causing the emission of electrons. The electron flow is attenuated by surface coatings, resulting in a very sensitive technique for detecting and measuring thin layer deposits. Equipment is commercially available (14) and has for example been applied to detect contamination in various production stages in the electronic industry. Its application to the curved metal surfaces of JFTOT tubes has yet to be demonstrated.

New Methods of Deposit Assessment - Thick Deposits

For research purposes, it has become accepted practice to adjust JFTOT running conditions so as to generate relatively heavy layers of tube deposits, which can then be probed and analysed by a variety of techniques. Heavier deposits are promoted by increasing running time beyond 150 minutes; raising the operating temperature well above 260 °C; and using stainless steel in place of aluminium tubes.

The best established method for quantifying thick deposits is by carbon burnoff, inferring total weight of deposit from the volume of carbon dioxide liberated. Accuracy of this determination hinges upon most of the deposit consisting of carbon; fortunately this appears to true for the majority of JFTOT tube deposits. Only small proportions of other elements such as oxygen (1-2 %) and sulphur (0.5 -1 %) were measured in typical deposits(10).

The fibre optic light interference measurement already described would probably be more suitable for thick than for thin films. However, this is constrained by the fact that for very thick deposits, absorption of light by the deposit material dominates, limiting measurement to thicknesses below approx. 2 microns (11).

A novel technique for determining volumes of tube deposits was developed at Southwest Research Institute, based on the electrical insulating properties of the deposit (15). The voltage required to "break down" the dielectric insulation of a deposit was found to be related to its thickness. A prototype Deposit Measuring Device (DMD) was built, which gently lowers an electrode onto the deposit, applies increasing voltage, then detects and displays dielectric breakdown voltage. Measurements are taken along the length of the tube, indexed at four quadrant positions. The resulting four thickness profiles can then be translated into total volume of the deposit. Since the potential is applied through a stylus, the method loses sensitivity with very thin deposits. Deposits of Visual Rating Code 3 and greater can be evaluated with good precision.

The Role of JFTOT Breakpoint Temperature

Regardless of which method is eventually used to rate tube deposits, determination of a JFTOT at a single fixed temperature can provide no more than limited information about thermal stability qualities of different fuels. This is where the concept of JFTOT breakpoint temperature becomes important. In contrast to the conventional pass/fail result at 260 °C, the specification breakpoint of a fuel actually reveals its level of thermal stability quality in quantitative terms. Breakpoint is defined here as the temperature at which the fuel fails specification rating criteria. This can occur in different ways, and also vary with different specifications.

Thus failure for civil jet fuels can be any of the following criteria - Code 3 Visual Rating or 25 mm Hg filter pressure differential (DERD 2494 and ASTM D1655) or 15 spun TDR value or Abnormal Colour (DERD 2494). For the sake of accuracy, it is obviously desirable to quote a fuel's breakpoint in terms of temperature and failure mode.

Regrettably, there are no precision statements for JFTOT ratings in any of the specification methods. Experience shows that reproducibility of 5 °C in breakpoint temperature between two JFTOT machines is not uncommon. For pass/fail qualification of production fuels, the definition of precision is less important since the majority of fuels have a comfortable margin of quality above 260 °C breakpoint temperature. For more detailed research into high temperature stability performance, precision of the method becomes imperative.

Direct measurement of the breakpoint simply involves carrying out a number of JFTOT determinations at different temperatures, until it becomes clear where the specification failure temperature lies. An obvious drawback of this procedure is the time, effort and fuel volume required to run multiple JFTOTs. It would therefore be very desirable to predict breakpoint from a single test, and and much effort has been aimed at this objective. Two indirect approaches are possible - extrapolation from a single JFTOT determination; and/or prediction from the result of a related fuel stability test which correlates with breakpoint temperature.

The principle of an extrapolative method is to run one JFTOT at such a high temperature level that it will certainly fail the specification criteria. Depending on whether failure is due to excess tube deposit or excess pressure drop, a suitable empirical method can be developed to project the test results back to the breakpoint temperature.

A method for extrapolating TDR results was proposed in 1973, utilising the inherent temperature profile along the length of the tube (16). TDR results are plotted on the temperature profile obtained from a single test, as illustrated in Figure 5 for a fuel run at 300 °C. A line is drawn between the temperature at the 50 mm position and the point on the tube at which a 15 TDR first occurs from the fuel inlet end of the tube. Then the temperature profile tangent to this line is observed, which in this example is the profile for T_{max} of 286 °C. This T_{max} is the predicted TDR breakpoint. Substitution in a further empirical formula was necessary to predict breakpoint temperature for Code 3 Visual Rating from the TDR breakpoint.

A different approach is used for extrapolating pressure drop results. The change in delta P versus JFTOT running time is plotted as illustrated in Figure 6 and the breakpoint calculated from the following formula which takes into account the rate of change in delta P.

$$T_b = T_{max} - .0075(150 - t_{25})(t_{25} - t_5)$$

where T_b = delta P breakpoint temperature, °C
T_{max} = JFTOT test temperature, °C
t_{25} = time to reach 25 mm pressure drop, mins
t_5 = time to reach 5 mm pressure drop, mins

In the example given, breakpoint temperature comes out at 270 °C.

Both of the above prediction methods were evaluated on a number of Jet A-1 fuels from various sources; reproducibilty with conventionally determined breakpoints was surprisingly good.

Breakpoint prediction from related tests is illustrated by two examples. Weights of carbon deposited at 350 °C JFTOT operating temperature were found to correlate with fuel breakpoints in the range 265 - 310 °C (Figure 7) (6). Experimental results from a fibre optic modified JFTOT showed that in-situ "time to reach 0.14 micron thickness" measurements for a series of test fuels could be correlated against their breakpoints in the range 220 - 270 °C (13).

Equipment Modifications

Variations of the basic JFTOT apparatus, designed to operate over a wider range of temperature and flow conditions, have long been commercially available. In the 1970's various heated reservoir attachments were built to preheat the bulk of fuel before it reached the heater tube. A Mini Heated Reservoir (MHR) was designed to fit into the standard JFTOT cabinet, and procedures for using this device were proposed by CRC (17). An unavoidable drawback of heated reservoirs is that they tend to make fuels produce greatly increased amounts of filter deposits, without affecting the tube deposits. Also available is a quartz heater tube enclosure coupled to a remote readout TDR, which permits real time observation of the rate of tube deposit buildup.

The above modifications certainly have their uses for studying kinetics of high temperature fuel breakdown reactions and evaluation of thermally unstable fuel components, but they still fall short of better simulation of aircraft fuel systems. Fluid dynamic calculations show that the creation of turbulent flow in the heater section of the existing JFTOT is a practical impossibility. The only way of achieving turbulence would be by redesign of the entire fuel flow setup, for example by pumping fuel through the inside of a heated capillary tube at high velocity. Only then would sufficiently high Reynolds Number be sustained. The practical feasibility of such a system, using 100 micron bore steel capillary tubing, is currently being investigated in the UK (18).

CONCLUSIONS

- Because the JFTOT has an unquestioned track record in disriminating between fuels of good and poor high temperature stabilities, it is likely to continue in its present role in jet fuel specifications.

- New methods of rating tube deposits are becoming available that will challenge the Visual Rating and TDR methods used up to now. These include techniques based on light interferometry and on dielectric breakdown.

- The new rating techniques can provide information not previously available, eg. thickness profiles and rate of deposit buildup. They work particularly well with heavier deposits, and are therefore suited for stability research at conditions beyond specification requirements.

- Measuring a fuel's JFTOT breakpoint temperature is essential for establishing its thermal stability quality level. It is important to agree upon a standard definition of breakpoint temperature and the procedure by which it is determined.

- Breakpoint temperatures could be measured on a more routine basis if the number of required JFTOT test runs were minimised through use of prediction procedures. Some relevant procedures are outlined in this paper.

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FIGURE 1 : INFLUENCE OF TUBE METALLURGY ON JFTOT RESULTS (6)

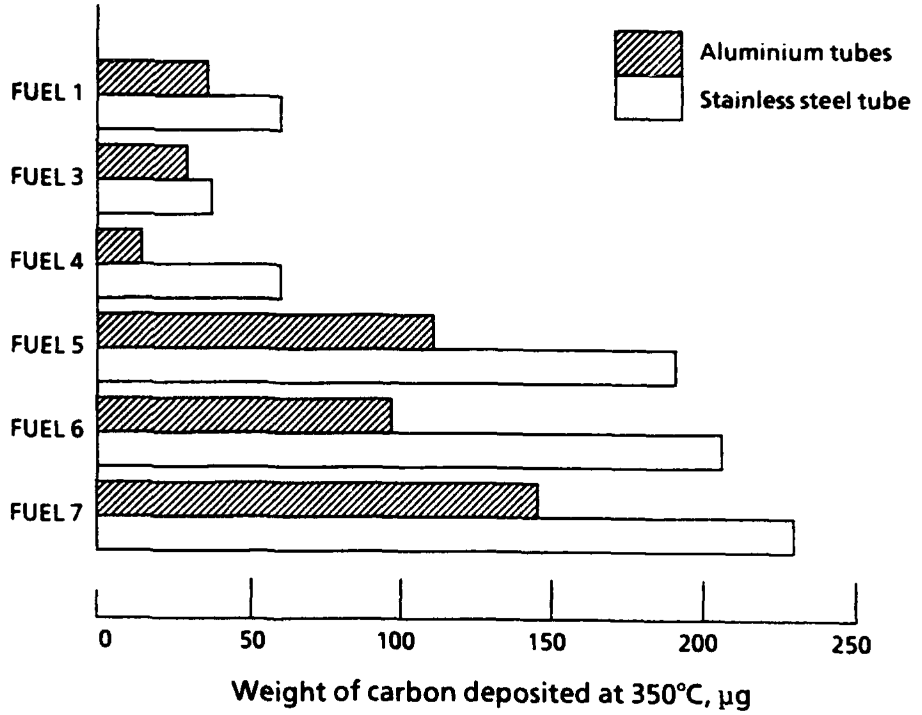


FIGURE 2 : TEMPERATURE DEPENDANCE ON MAGNESIUM DIFFUSION (8)

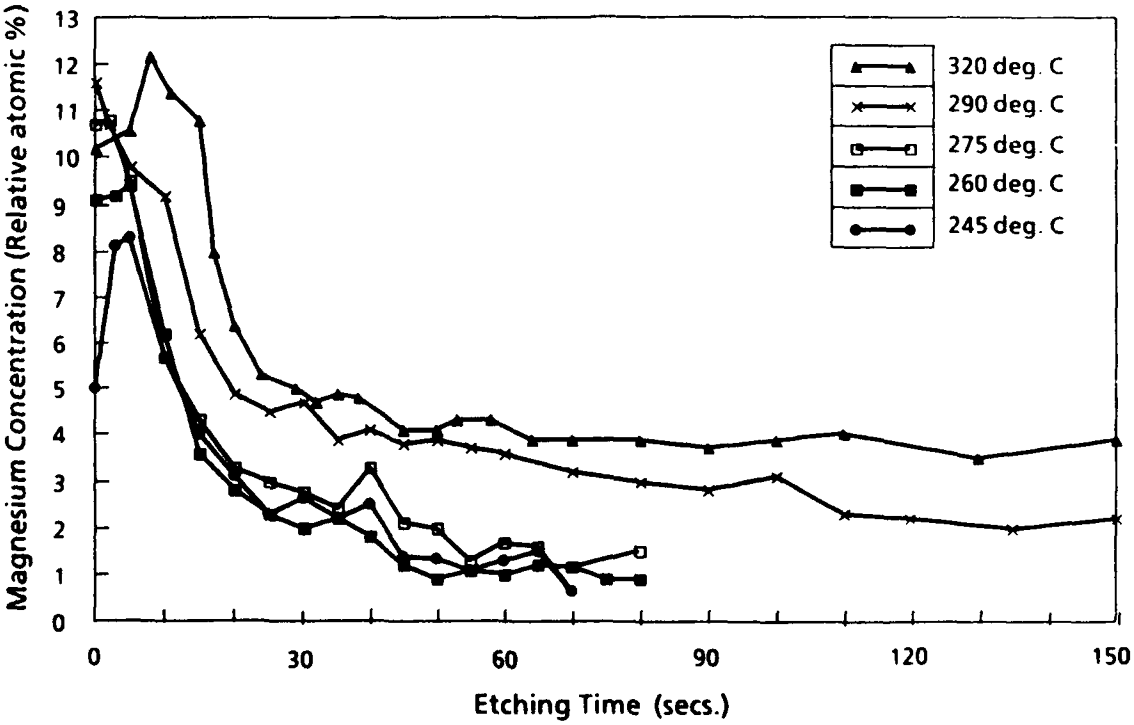


FIGURE 3 : CARBON BURNOFF RESULTS ON THREE FUELS [10]

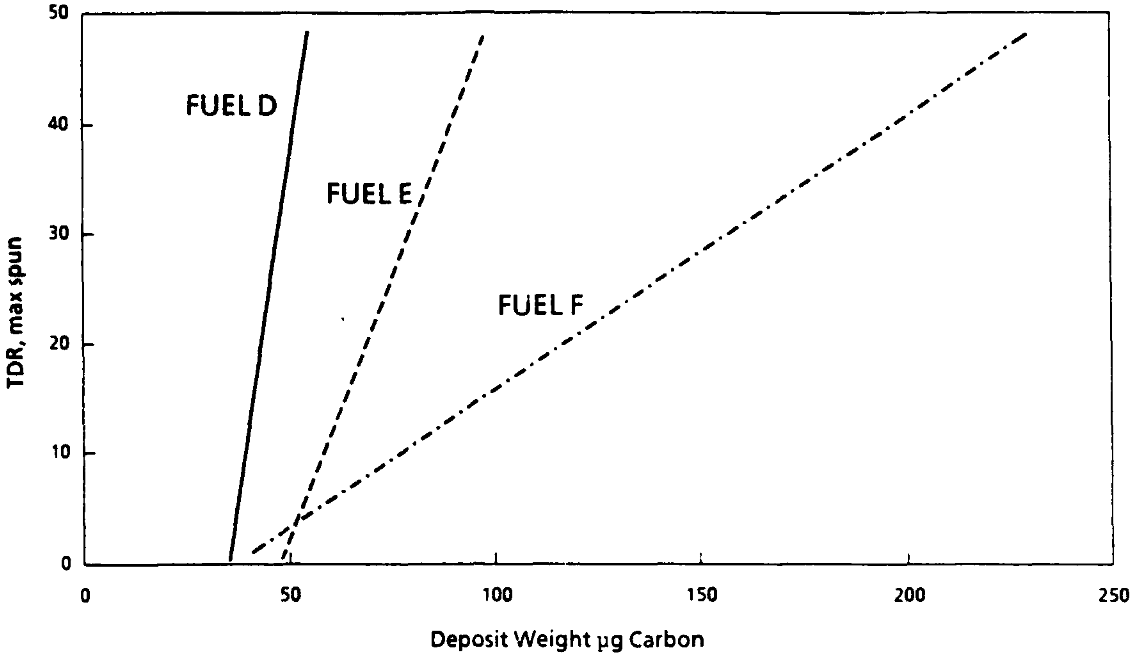


FIGURE 4 : CARBON BURNOFF VERSUS TDR DATA [11]

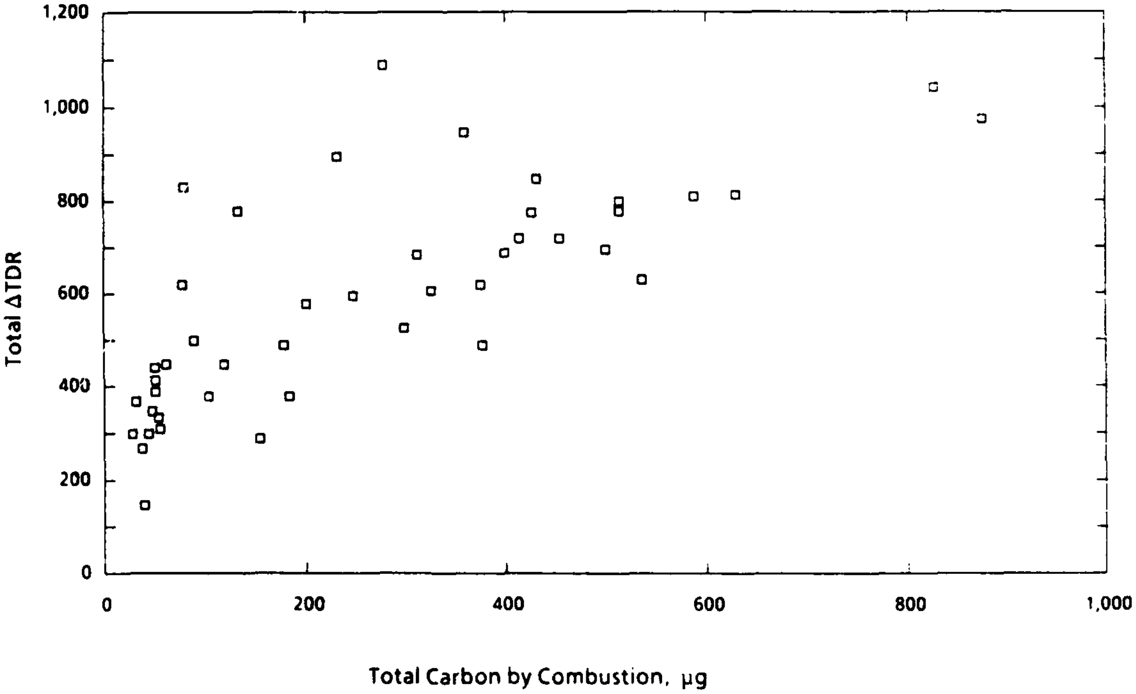


FIGURE 5 : EXAMPLE OF TDR BREAKPOINT TEMPERATURE PREDICTION

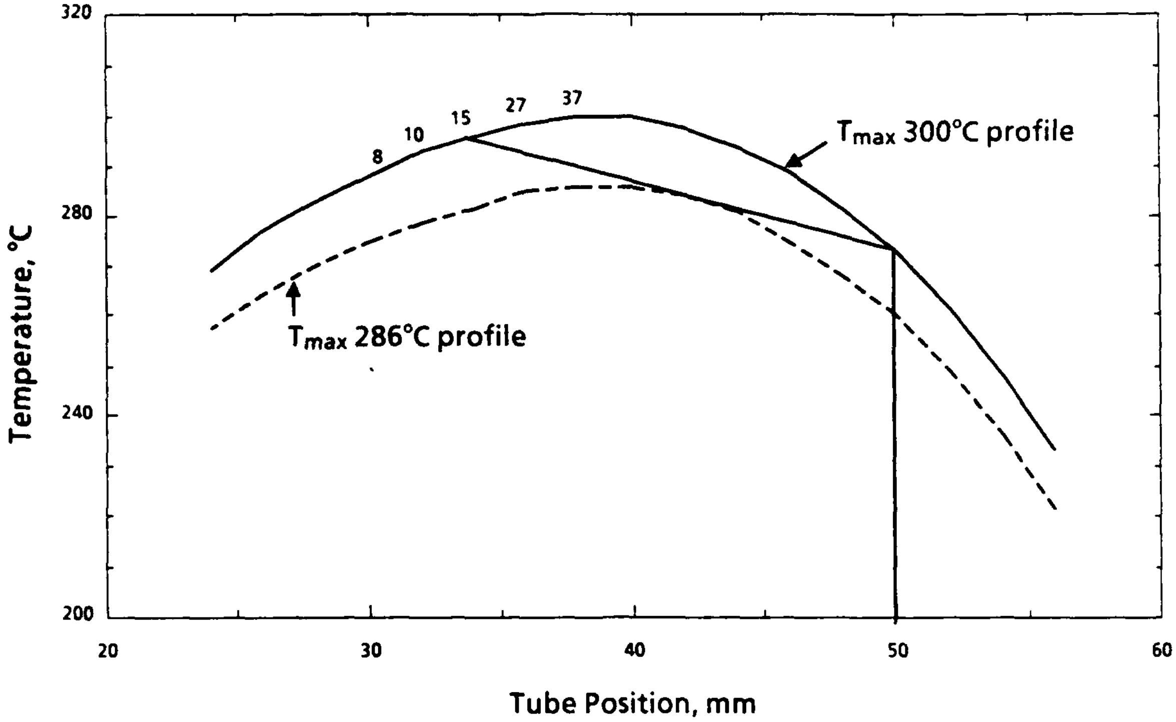


FIGURE 6 : EXAMPLE OF DELTA P BREAKPOINT TEMPERATURE PREDICTION

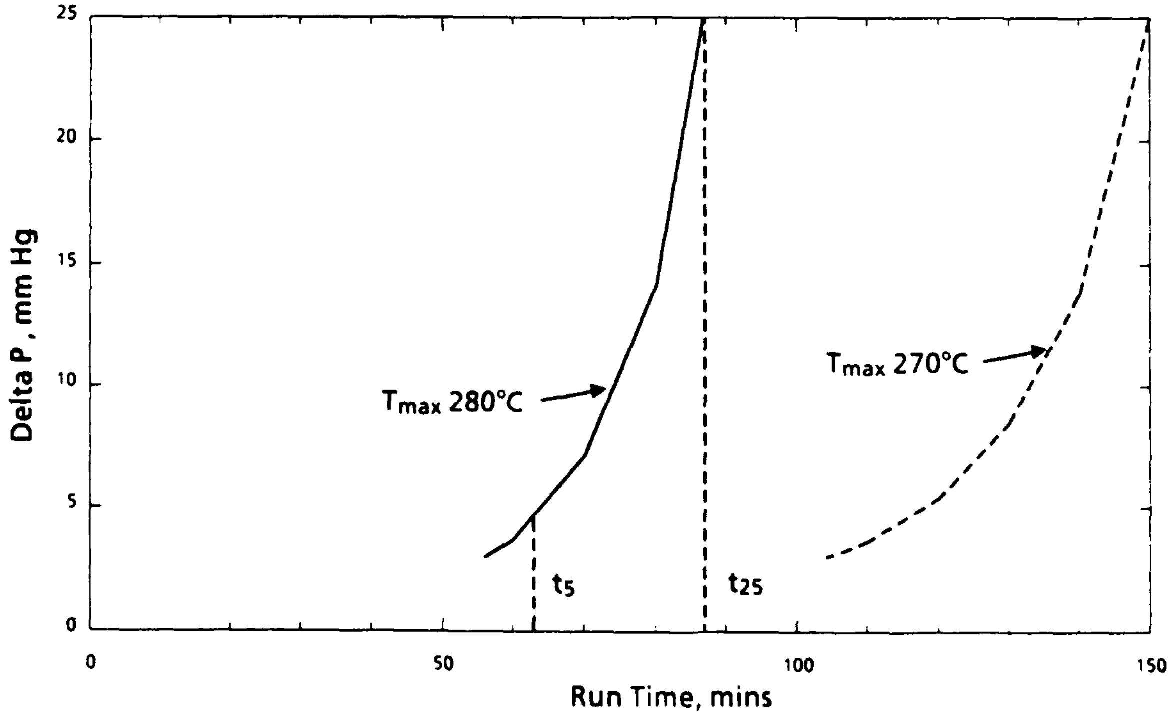
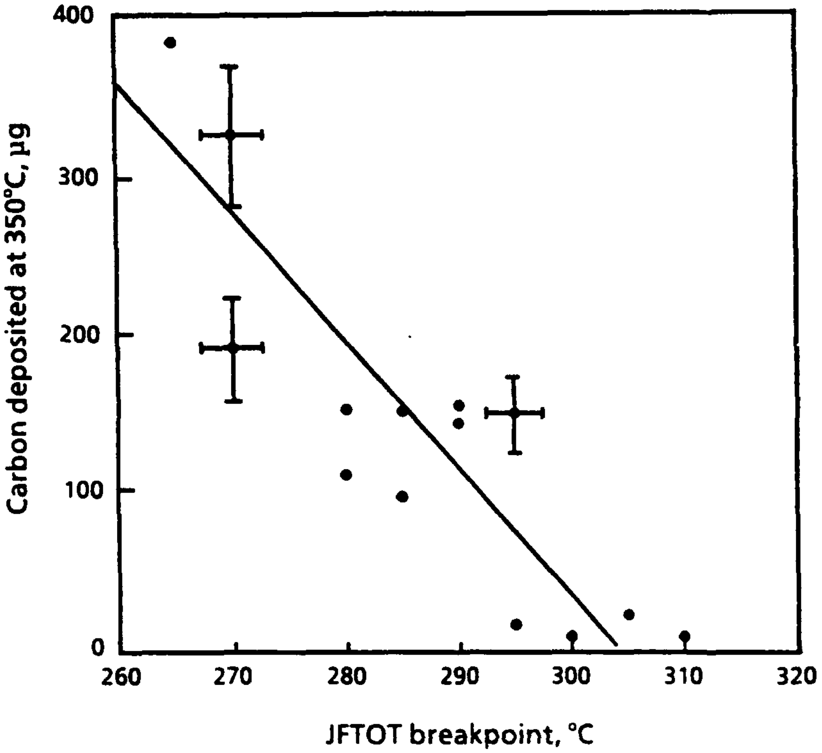


FIGURE 7 : RELATION BETWEEN CARBON DEPOSITION AND BREAKPOINT TEMPERATURE (6)



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

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ABSTRACT

The quantification of deposits formed on heated metal surfaces is used as one measure of thermal stability by the JFTOT procedure. Empirical methods widely employed entail either visual comparisons or measurements of reflected light (TDR), both of which are sensitive to deposit color. We have found that measurements of total carbon content by combustion are more reliable and have compared a number of deposits formed on stainless steel JFTOT heater tubes by the TDR and combustion methods. In addition, two novel techniques based on measurements of dielectric strength and the interference effect produced upon reflectance of monochromatic light have been examined. It was found that the dielectric and interference methods correlated well with the combustion analyses and each other, while the TDR often yielded misleading results. The correlations between the various methods will be discussed in addition to the consequences of method choice on the interpretation of experimental data.

INTRODUCTION

The thermal oxidation of liquid fuels is often accompanied by the formation of insoluble reaction products, either as suspended particulate or as gum which adheres to container surfaces. Modern aircraft engine designs and aerodynamic heating of wing surfaces place more severe thermal stress on the fuel, increasing the likelihood of the formation of insoluble deposits. Aircraft fuel system deposits can be responsible for a variety of problems including decreased efficiency of engine heat exchangers, seizing of fuel control valves and injector fouling.

It is known that thermally initiated fuel degradation is accelerated by the presence of oxygen through autoxidative processes involving free radical chain reactions. The Jet Fuel Thermal Oxidation Tester (JFTOT) is widely used to characterize the thermal oxidation stability of a fuel. In the JFTOT, aerated fuel is pressurized with nitrogen and passed over a heated metal tube so that the fuel is stressed under conditions of high oxygen availability and slowly increasing temperatures. The quantities of insoluble products formed under these conditions constitute a measure of the deposit forming characteristics of the fuel. In accordance with standard ASTM D3241 test procedures [1], the formation of filterable insolubles is detected from changes in pressure differential across a standard test filter downstream of the heated tube and the adherent insolubles deposited on the hot tube are characterized by visual comparison with color standards. The highly subjective nature of the visual method of rating heater tube deposits was revealed in a round-robin effort conducted by the Coordinating Research Council [2]. The poor precision of visual ratings from unusual and highly colored deposits resulted in random errors which were in excess of the differences between the values, thus eliminating any statistical significance. To increase the reliability of the measurement, the Tube Deposit Rater (TDR) was developed. The TDR is based on the measurement of the attenuation of reflected white light by a photocell; thicker coatings increase the TDR while a clean tube surface gives a reading of zero. From comparisons with measurements of deposit thicknesses by Auger spectroscopy, neither the Visual Rating method nor the TDR were found [3] to be adequate in rating tube deposits. While less subject to operator judgement than the visual rating method, the TDR can be influenced by the optical properties of the deposit.

Quantification of tube deposits by combustion of carbon to carbon dioxide has been investigated, with the assumption that the deposit is composed primarily of carbon. Measurements of total carbon contents per unit area per unit time have been employed [4] to study the influence of dissolved oxygen on the rates of deposit formation from thermally stressed jet fuels on 316 stainless steel tubes. These studies were later extended to examine the effects of trace amounts of sulfur- and nitrogen-bearing compounds [5,6] on deposition rates. Combustion analyses have been utilized [7] to quantify deposition rates from jet fuels stressed under a wide variety of experimental conditions in a special test apparatus. Carbon was determined from deposits on sintered stainless steel filters and from the inner walls of heated 316 stainless steel tubes. A lower limit of 200 micrograms carbon on the tube sections was reported. The precision of combustion analyses conducted on standard JFTOT heater tubes has been shown [8] to be limited by the difficulty with which quantitative removal of carbon from the aluminum surface could be attained. This behavior seems related to the relatively thick porous layer of aluminum oxide which coats aluminum metal surfaces. It had been found [8] that the amount of carbon formed on stainless steel tubes thermally stressed in the JFTOT generally exceeded that from aluminum tubes by a factor of two. In addition, migration of magnesium in 6061 T6 alloy aluminum heater tubes at elevated temperatures has been reported to inhibit deposition. Heater tubes comprised of 304 stainless steel do not form porous oxide coatings, allowing much lower detection limits, nor is magnesium inhibition possible. Besides these limitations associated with the use of aluminum tubes, the tubes are destroyed during the combustion analysis and it provides no detailed information concerning the spatial distribution of the deposit.

Two novel techniques for determining the volumes of heater tube deposits have been developed. One technique [9] is based on measurements of the electrical insulating properties of the deposit. The other method [10] is based on the interference effect produced when monochromatic light is reflected off the tube surface through the deposit. Since these methods are non-destructive, we were able to obtain deposit measurements from the TDR, dielectric, interference and combustion methods on each JFTOT heater tube. The initial findings were described earlier [11] on a limited number of samples. In this study, the results from the four methods are compared from a greater number of heater tubes and refinements in the use of the optical interferometry apparatus were investigated.

EXPERIMENTAL

Thermal stressing of fuel samples was performed using the modified JFTOT described earlier [12]. The same Jet A fuel was used in all experiments. Five-inch 304 stainless steel heater tubes were employed to achieve a more gradual increase in temperature, greater reactive metal surface area and to facilitate the combustion analysis. In order to ensure sufficient quantities of material for combustion analysis, run times were increased to 300 minutes. Under these conditions, at a maximum fuel flow rate of approximately three milliliters per minute, the residence time of the fuel in the heater tube holder was approximately 28 seconds. Since appreciable amounts of filterable insolubles would substantially reduce the fuel flow rate through the test filter and increase the contact time of the fuel with the heated tube surface, the test filter was bypassed when the flow rate dropped below 2.5 mL/min. Tests were conducted at maximum heater tube temperatures of 260, 270, 280 and 310°C.

Spun TDR measurements were taken with an Alcor Mark 9 tube deposit rating device. The instrument was calibrated in accordance with the manufacturer's instructions, using a calibration tube supplied with the instrument. Readings were taken from heater tubes before and after stressing at 2 mm intervals over the 120 mm heated length. To obtain a measure of the changes in reflectance due to the deposit, differences between the initial and final TDR values at each location were calculated and reported as the delta TDR. The sum of the delta TDR constituted the total delta TDR, which was used as an indication of the total amount of deposit on the tube. The highest spun delta TDR at any one location was taken as the maximum delta TDR.

Volume measurements were performed by Southwest Research, Inc., using their dielectric measuring device. This technique relies on the assumptions that an organic deposit will behave as an electrical insulator and that all "normal" deposits have similar dielectric strengths. When a voltage potential is applied across the tube deposit through a stylus, it will act as an electrical insulator until the potential reaches the point at which the organic material comprising the coating breaks down. The coating then ceases to act as a dielectric insulator and current begins to flow between the heater tube and the stylus. Values for the dielectric breakdown were determined by increasing the voltage potential across the coatings at a controlled rate while monitoring the current. Deposit thicknesses were calculated from an empirically determined [9] proportionality factor, which relates the dielectric breakdown voltage to deposit thickness. The precision of the measurement is reduced with very thin coatings. The dielectric measurements are taken at specific points on the tube, so that spinning cannot be employed to average out variations in thickness around the tube. The side of the tube facing the fuel outlet was taken as a reference point i.e., zero degrees. Measurements were obtained at 2 mm intervals down the tube at 0, 90, 180 and 270 degrees, providing four sets of thickness measurements for each tube. At each location, the readings were averaged and used to define a thickness profile from which the total deposit volume was calculated.

Deposit volumes were determined by Geo-Centers, Inc. with the fiber optic JFTOT tube scanner which they developed. Additional interferometry measurements were taken in our laboratory using a similar instrument, supplied by Geo-Centers. In this method, monochromatic light having a wavelength of 680 nm was directed onto the coated tube in a direction perpendicular to the surface through a fiber optic assembly which contained both the source and detector optics. The intensity of reflected light represents the quantity of light which emerges through the coating after reflecting off the metal tube surface. Since there is a large difference in the refractive indices between the air and the deposit, the reflected light wave undergoes a phase change. As a consequence, the emergent wave interferes constructively or destructively with the incident wave, depending on the thickness of the deposit. As the detector is scanned across a deposit, the light intensity changes periodically as the deposit thickness passes through multiples of the wavelength of the incident light. At thicker deposit thicknesses, absorption of the light by the coating dominates, limiting measurement to thicknesses below approximately two microns. Like the dielectric method, the interference method is also a static measurement which is conducted at four points around the tube circumference, using the side facing the fuel outlet as the reference. The interference measurements are treated as follows. The thicknesses at each tube location are averaged and a table compiled of the locations at which the average coating thicknesses pass through multiples of the incident light wavelength. The deposit depth at each location is then corrected for the refractive index of the deposit and the source-detector geometry. The thickness profiles thus determined are fitted to the appropriate functions and integrated to obtain the deposit volume.

Total carbon contents of the tube deposits were determined after completion of the other measurements. Combustion analyses were performed with a Perkin-Elmer model 240 elemental analyzer. After calibration of the analyzer with known compounds, blank values were obtained from cleaned, unused heater tube sections. The grip ends of the heater tubes were removed and the heated section was cut into two equal lengths, cleaned in toluene, vacuum dried and analyzed.

RESULTS

The quantities of total carbon from each JFTOT heater tube, the TDR values and the deposit volumes from the dielectric breakdown and interference methods are given in Table 1. The scatter plot of TDR values vs total carbon in Fig. 1 illustrates that, although there is a tendency for the heavier deposits to exhibit higher TDR readings, there was a high degree of uncertainty. This illustrates the deficiency of the TDR when used quantitatively in research efforts undertaken with the JFTOT.

A plot of the deposit volumes calculated from the dielectric and interference measurements vs total carbon (Fig. 2), indicates that these quantities are more linearly related to carbon content than the TDR. Light absorption by the thicker deposits limited the useful range of the interference measurements to coatings containing less than 400 micrograms of carbon. There was a tendency for the deposit volumes to be somewhat less by the dielectric method at very thin deposits, i.e., less than 1×10^{-4} cu.mm. This is understandable in light of the fact that the precision of the dielectric measurements would be expected to decrease on very thin coatings.

Both of these two new non-destructive techniques provide a convenient means of measuring deposit thicknesses at known locations on non-spinning tubes. Such techniques could be employed to determine the relationships between deposit thickness variations and experimental variations. Thickness profiles from interferometry along four sides of a typical heater tube are illustrated in Fig. 3. In this example, the thickness measured at 0° was nearly twice that at 90 and 180°, where the side of the tube having the thickest deposit was designated as 0° and the other profiles were taken by indexing the tube in 90° increments. In those instances where there are large radial variations in thickness, increasing the number of measurements around the circumference would increase the precision of the volume calculation. However, the high degree of correlation with the combustion data indicates that, in these experiments, the precision of the deposit volumes from measurements at four locations was comparable to that of the combustion data.

The agreement between tube deposit measurements from these methods can be quantitatively expressed by performing regression analyses and considering the linear correlation coefficients. From the regression correlation coefficients given in Table 2 the deposit volumes by the dielectric breakdown and the interference methods are shown to correlate extremely well with total carbon contents and with each other. The TDR values did not correlate with any of the other measurements.

Typical TDR profiles from two heater tubes were found to have maximum TDR values of 47 and 28 at the locations of maximum tube temperatures. The TDR scan of the heavier deposit also contained a secondary maximum at approximately 80 mm. Corresponding maximum dielectric breakdown potentials of 828.3 and 17.2 volts were measured from the same two tubes. This illustrates the increased range of the dielectric measurement over the TDR for a case where changes in TDR were not proportional to the actual quantities of tube deposits. Carbon contents of the entire deposits on these two tubes was 381 and 27 micrograms, respectively. The random nature of the correlation between TDR and carbon contents or deposit volumes renders the existence of any systematic non-linear relationship very unlikely. A secondary maximum TDR value at 80 mm was also not apparent from the dielectric measurements. This type of effect may have been caused by light absorption by a thin, highly colored deposit which resulted in an erroneously high TDR. There is also the possibility of interference effects arising from thin coatings with thicknesses in multiples of the dominant wavelength of the incandescent lamps used in the TDR rating device.

The interference measurements were obtained down the length of the heater tube by manually moving the fiber optic probe. The increments between measurements must be reduced in order to sufficiently resolve the point at which the coating thickness passes through a multiple of the incident light wavelength. In order to facilitate interference measurements taken at NRL, the fiber optic probe was fixtured to the photocell transport assembly of our Alcor Mark 9 TDR rater. The probe could be manually positioned in the TDR rater with a resolution of 2.5 mm. In addition, a motor drive was fitted onto the positioning mechanism of the TDR rater and the output signal of the fiber optic probe was applied to a chart recorder, providing a continuous plot of reflected light intensity vs location. Comparison of plots of intensity vs location from the discrete measurements with the continuous chart recordings revealed that taking readings each 2.5 mm was not sufficient to resolve the coating thickness gradient. It was therefore necessary to obtain the data in a continuous manner. Continuous acquisition of the reflected light intensity was accomplished by input to a suitable analog-digital interface to a desktop microcomputer. The translation rate of the probe across the tube was calibrated to provide a means for determining the position of the probe by the timing of the signal.

A computerized method of converting the raw measurements to deposit volumes would allow for a nearly automated procedure, which would facilitate the use of this technique in routine specification testing. As a first step, a computerized method was applied to fitting the unequally spaced thickness measurements to a smooth curve. Integration of the resulting thickness profile yields the deposit volume. One approach was the application of a cubic spline to fit the data to a smooth curve that passed through all the data points. The curves derived from spatial distributions of deposit thicknesses from dielectric and interference measurements of the same deposit are shown in Figure 4. Good agreement was found between the volumes calculated from the spline fit and the values originally reported. It is not surprising that the volumes calculated from the dielectric data agreed so well, since the dielectric data points are regularly spaced. The agreement between the spline fit and the methods used by Southwest Research and Geo-Centers indicates that at least in some cases, automatic measurement and reporting of volumes is possible, providing a means for utilization of these techniques for routine specification testing.

DISCUSSION

Within their respective useful ranges, both non-destructive methods described here provided measurements of deposit volumes which correlated equally well with each other and with measurements of total carbon. Since these measurements are obtained at discrete points, they also describe the distribution of deposits around the heater tube circumference. Comparison of deposit thickness profiles for each quadrant around the tube, it was found that in many cases the deposits were not evenly distributed around the tube circumference. Generally, the thickness was greater on the surface facing the fuel outlet. This unevenness contributed significantly to the uncertainty in the average thicknesses calculated from the four points around the circumference. It may be possible to minimize this unevenness somewhat by reducing the test duration, it may also be necessary in certain instances to increase the number of measurements that are taken around the tube surface to improve the precision of the computed average.

The dielectric method is limited to coatings which are thick enough to electrically insulate the stylus from the tube, thus limiting its use with very thin coatings. A lower limit of 20 volts for the dielectric breakdown potential, which represents a coating 0.05 microns thick, has been indicated by Southwest Research as the point below which the readings can be unreliable. The dielectric method may therefore not be applicable for quantifying very thin deposits produced by aviation fuels when tested in accordance with ASTM D3241 [1]. Lower limits and the correlation with visual ratings would have to be established before it can be determined if the dielectric method would be suitable for routine specification testing.

The lower limit of detection of the interference method is mainly a function of the wavelength of the incident light. In this work, light with a wavelength of 680 nm was used, theoretically limiting the lower limit to 0.14 microns and the resolution to 0.07 microns. Absorption of light by the coating imposes constraints on the maximum deposit thicknesses that can be measured by the interference technique. The maximum thicknesses of many of the tube deposits generated in this work were beyond the upper limit of the interference technique, but the experimental conditions in this work were formulated to maximize deposit quantities for combustion analysis. Another factor is the distribution of deposit. In the interference method, data points are obtained only at those locations where the deposit thickness passes through multiples of the wavelength of the incident light. The number of data points will therefore be a function of the length of the deposit thickness gradient. A coating which increases in thickness over a short distance may not provide a sufficient number of data points to accurately fit the thickness profile equations. Tube deposits having a long thickness gradient and which appear under white light to have a peacock appearance, will generally yield more data points. Most of the deposits examined in this study provided a sufficient number of data points on the transition between the fuel inlet and the location of the temperature maximum. The heat transfer characteristics of the stainless steel tubes causes the maximum temperature to occur near the fuel outlet and thus, in many cases, the number of data points for the deposit thickness transition between the hot zone and fuel outlet were limited. It would be expected that the use of aluminum JFTOT tubes would alleviate this problem, since the temperature maximum is further from the fuel outlet. In addition, shorter run times would tend to reduce the likelihood of exceeding the upper limit of the measurable thickness. Therefore, the interference technique shows promise as an applicable tool in nondestructively quantifying JFTOT heater tube deposits produced during specification testing.

A limitation that currently exists to the application of the interference method to routine testing of fuels is the methods for data interpretation. The dielectric measurements provide thickness information at regular intervals and therefore, calculation of deposit volume is a relatively straightforward procedure. On the other hand, the interference measurements provide thickness information only at multiples of the incident wavelength, at uneven intervals. Thus, the calculation of deposit volumes is somewhat more complicated and requires some interpretation on the part of the analyst. The use of a computerized technique to obtain the thickness profile would simplify the analysis procedure and eliminate any operator subjectivity. The spline fitting techniques described above show promise as a non-interpretetive method for fitting and integrating a thickness profile. However, the accuracy of the fitted thickness profile would still be limited by the number of data points upon which it is based, i.e., the thickness gradient. Future efforts will involve refinement of the mathematical methods to provide automatic reduction of the raw measurements to deposit volumes.

CONCLUSIONS

Excellent agreement was obtained between JFTOT heater tube deposit volumes calculated from measurements of dielectric breakdown and from optical interference and the total amount of carbon measured by combustion. Within their respective measurement ranges, both the dielectric and interference techniques could be employed to quantitatively determine JFTOT heater tube deposits from the 304 stainless steel tubes. Since the precision of the volume calculations derived from static measurements can be affected by extreme radial variations in deposit thickness in certain instances, it may be necessary to increase the number of measurements taken around the tube circumference. Although the treatment of the regularly spaced dielectric measurement data to calculate deposit volumes is relatively easy, the technique is nevertheless limited to thicker coatings which can be beyond the range of interest in specification testing. The interferometric method will measure thinner deposits, but the accuracy can be compromised in those situations where the thickness gradient is too short to provide for enough data points. The examination of heater tubes prepared in accordance with standard specification test methods by the dielectric and interferometric techniques would be necessary to assess their potential applicability to specification testing. However, automation of the data collection and analysis procedures would seem to be a prerequisite, particularly for interferometry. The use of spline functions to define and integrate the thickness profiles shows promise as a noninterpretive approach towards automating the data analysis procedure.

As practical alternatives to combustion analyses, the dielectric and interference methods may also allow for the use of aluminum JFTOT tubes in quantitative studies. These techniques could also provide a convenient and practical means with which to study the relationships between fuel flow and deposit characteristics and to determine the influence of heater tube composition without resorting to combustion analyses to quantify deposits. The thickness profiles obtained by these two new methods have also demonstrated instances where the TDR values were disproportionately influenced by thin, highly colored deposits. The failure of the spun TDR method to respond proportionately to certain types of deposits poses limitations on its usefulness as a tool for quantitative measurements.

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Table 1. JFTOT Heater Tube Deposit Measurements

Total Carbon, micrograms	Total Delta TDR	Volume, cu.mm. Interferometry	Volume, cu.mm. Dielectric Breakdown
876.8	965		0.6365
826.0	1044		0.5405
630.1	822		0.5358
618.6	855		0.5107
587.9	819		0.4570
537.3	628		0.4553
514.9	790		0.4962
513.6	780		
493.5	698		0.5035
456.2	731		0.4129
438.1	836		0.3532
430.8	772		0.4057
415.4	727		0.4325
398.5	685		0.4272
385.2	476		0.4149
381.2	634	0.350	0.3752
370.6	660		0.2883
352.5	945		0.2170
321.8	612	0.310	0.2627
319.7	612		
304.1	672	0.330	0.3493
287.7	526		0.2752
266.9	1088		0.2257
237.6	594	0.260	0.2182
221.6	897		0.1790
196.4	570		
163.4	374	0.190	0.1563
158.4	283	0.110	0.1238
156.5	485		
133.8	771		0.0562
121.2	441		0.0785
112.0	609		0.0942
107.3	745		0.1541
106.0	371		
97.2	706		0.0855
96.7	431		0.1006
92.0	660		0.0805
91.2	494	0.086	0.0545
84.9	836		0.0175
83.6	626		0.0469
80.8	433		
79.2	337		0.0511
66.0	443		0.0607
59.4	317	0.055	0.0237
57.9	458		0.0230
55.8	345	0.067	0.0281
55.4	339		0.1610
52.0	445	0.053	0.0233

Table 1, continued

Total Carbon, micrograms	Total Delta TDR	Volume, cu.mm. Interferometry	Volume, cu.mm. Dielectric Breakdown
51.1	304		0.0124
50.8	422		0.1264
50.7	419	0.041	0.0309
50.4	380		0.0197
47.2	365		0.0458
47.0	355	0.041	0.0194
42.8	299		0.0178
39.6	150	0.028	0.0129
37.9	257		0.0700
30.3	362		0.0930
27.2	299	0.016	0.0086
10.3	139		0.013
<10	255		0.0132
<10	244		0.0141

Table 2. Linear Correlation Coefficients from Comparisons of Tube Deposit Evaluation Methods

Independent Variable	Dependent Variable	Correlation	Observations
Total Carbon	Dielectric Volume	0.929	56
Total Carbon	Optical Volume	0.971	14
Optical Volume	Dielectric Volume	0.970	14
Total TDR	Total Carbon	0.561	62
Total TDR	Dielectric Volume	0.473	56
Total TDR	Optical Volume	0.707	14

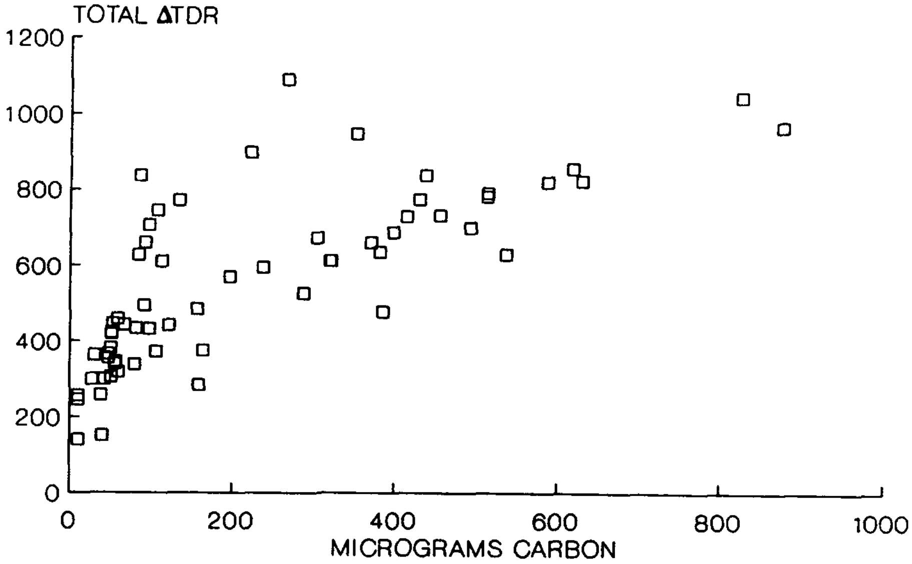

Figure 1. Relationship of TDR values to carbon content.

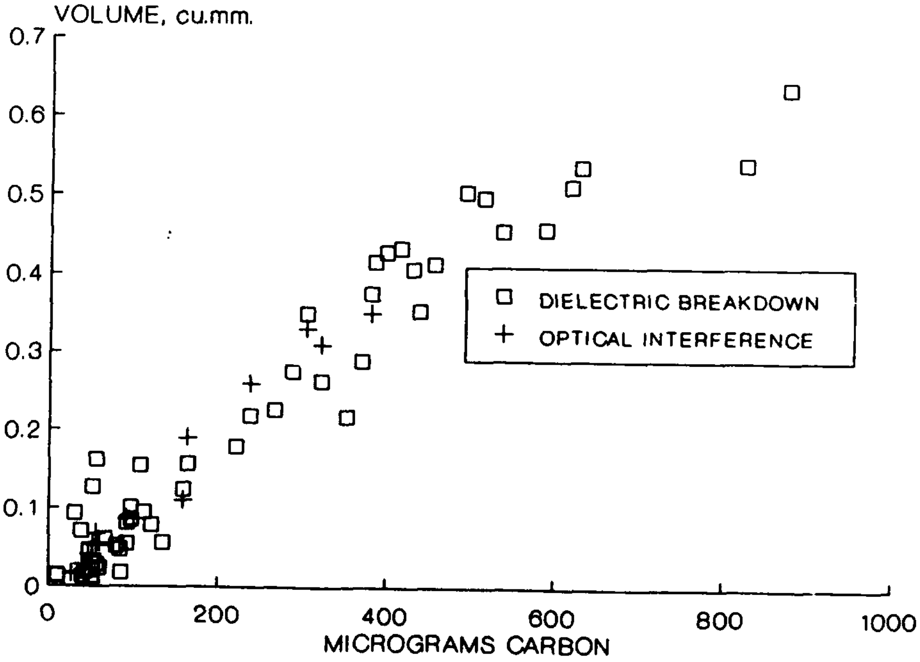

Figure 2. Relationships of deposit volume measurements to carbon content.

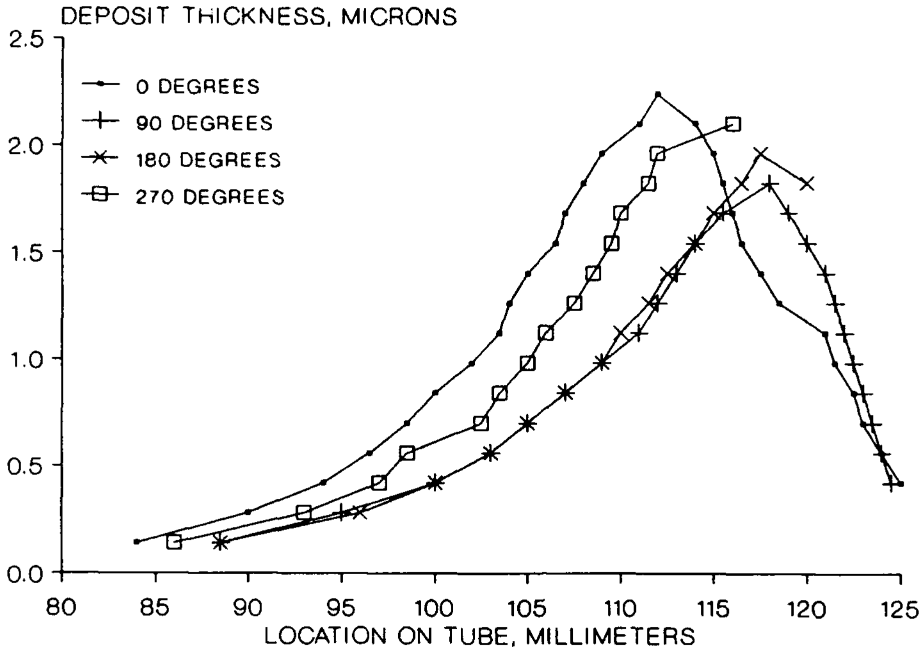

Figure 3. Deposit thickness measurements by interferometry along four sides of heater tube.

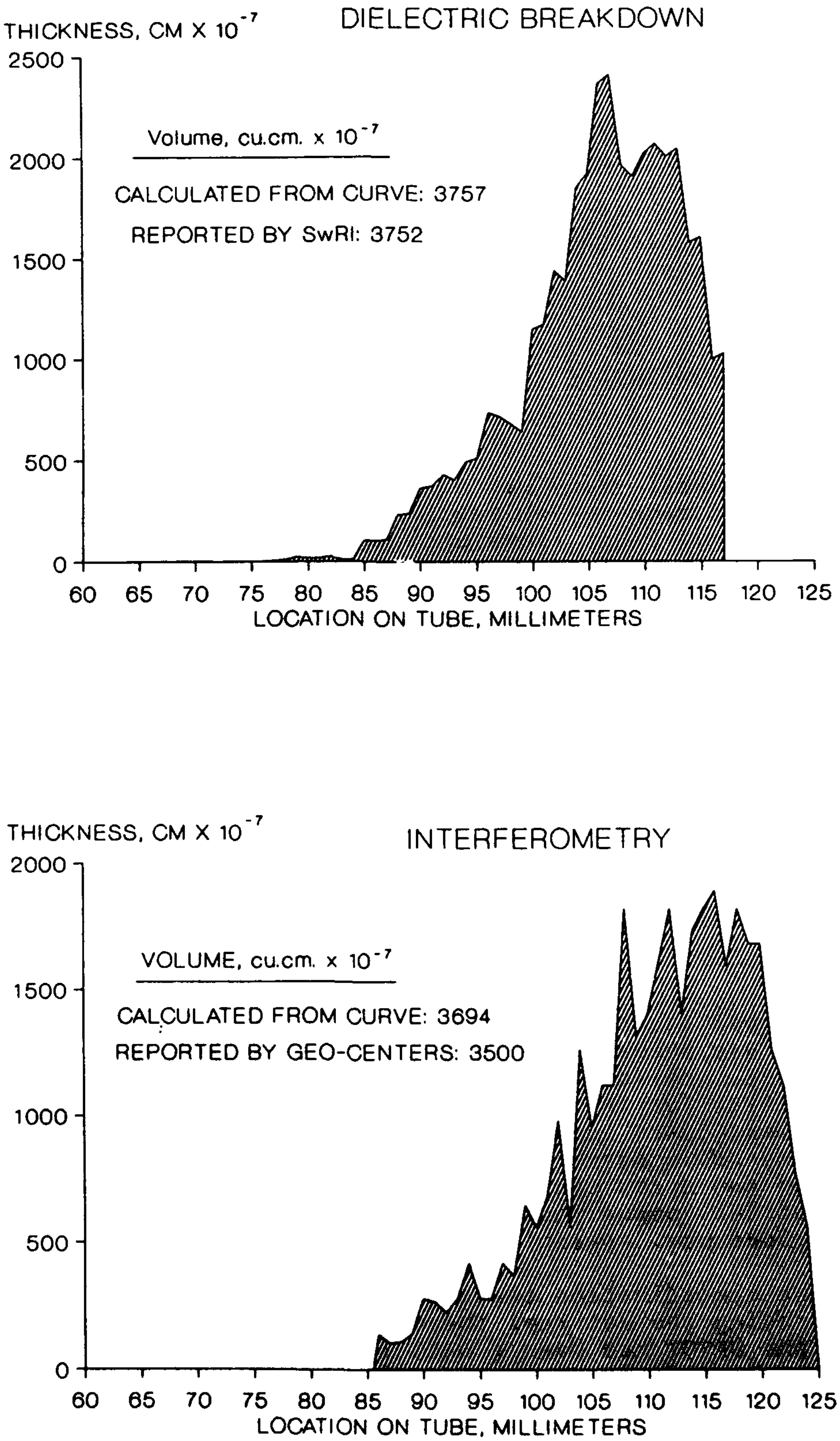

Figure 4. Deposit volumes obtained by integration of thickness profiles derived from cubic spline fitting.

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

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ABSTRACT

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

INTRODUCTION

As advances in engine technology continue to increase the performance of gas turbines by raising their operating temperatures and pressures, the added heat stress placed on the fuel increases the possibility for fuel deposition. This hydrocarbon deposit, caused by inadequate fuel thermal oxidation stability, may foul heat exchangers, obstruct valves and filters and degrade the atomization and spray characteristics of injectors. Consequently a build-up of fuel deposition can lead to substantial degradation of engine performance, operability and durability.

Current specification testing of a fuel's thermal stability is performed using the Jet Fuel Thermal Oxidation Tester (JFTOT). [1] Although the JFTOT has been a satisfactory go-no-go quality control test, its capabilities as a research tool are extremely limited. [2] Fuel performance in the JFTOT is rated according to the visual appearance of the deposits that form on a heated tube as well as the pressure drop across a 17 micron filter. The tube deposit is visually rated in a "tuberator" light box, in which the color of the deposit is compared against a set of ASTM color standards. This method, carried over from the Coker Thermal Stability Test (ASTM D1660), is extremely subjective, particularly when deposit colors deviate from the normal brown or tan and appear peacock or grey.

An alternate method of measuring tube deposit is based on the light absorbance of the deposit as measured by the Mark 8A Tube Deposit Rater (TDR). In this method, white light is reflected from the surface of the JFTOT tube and collected by a photocell. The amount of deposit is measured on an arbitrary scale inversely proportional to the intensity of reflected light. The TDR rating is determined by scanning the length of the tube to obtain a maximum value. This method overcomes the problem of observer subjectivity, but like the "tuberator" provides only a semi-quantitative measurement of the tube deposit. Therefore, a major problem in utilizing the JFTOT as a research tool has been its inability to provide quantitative data relative to the thickness of deposit formed. Quantitative deposit thickness data from the JFTOT would be extremely valuable because it would provide a correlatable link between a fuel's deposition characteristics as measured in the laboratory with its behavior in actual aircraft components.

This paper will discuss the development and the initial test results of the real time Fiber Optic Modified JFTOT (FOMJFTOT) and the Fiber Optic Offline Reader (FOOR). These instruments provide the capability for both on-line and post test quantitative measurements of the thickness of the deposit formed on the JFTOT tube.

THEORY

The FOMJFTOT and FOOR were developed under the assumption that light interferometry, rather than absorption, was the dominant phenomenon influencing the light reflected from the JFTOT tube. When light is reflected from a medium having a refractive index greater than the index of the medium in which it is traveling, it undergoes a phase change. In the case of the thin deposits formed on the JFTOT tube, the refractive index of the film is greater that the refractive index of the surrounding fuel or air and the refractive index of the tube is greater than that of the film. When a light source is directed on the deposit, part of the light is reflected off the deposit surface, while the remaining portion is refracted toward the surface of the tube. This light is then reflected off the tube's surface back through the deposit. If no deposit film is present, the two wave paths are in phase and interfere constructively, thus resulting in a maximum intensity of reflected light (Figure 1A). As the deposit film thickness increases, the phases of the two distinct wave paths become increasingly mismatched. When the deposit becomes one quarter wavelength thick, the two wave paths emerge in opposite phase and interface destructively, resulting in a minimum intensity in the reflected light (Figure 1B). As the deposit thickness increases, the two wave paths repeatedly become in and out of phase and the intensity of the reflected light cycles between maxima and minima (Figure 1C).

The thickness of the deposit film, d, ($d = \frac{m\lambda}{4n \cos\theta}$) is determined where m is the number of inflection points (maximas and minimas observed), λ is the wavelength of the light source (880 nm), n is the refractive index of the deposit film (1.6 assumed) and θ (0°) is the angle from the normal at which the light passes through the film. The design of the FOMJFTOT and FOOR produces inflection points (maximas and minimas) at .14 micron thickness intervals.

Inspection of the FOMJFTOT raw data (Figure 2) revealed smooth oscillations of the reflected light. This verifies the original assumption that for thin layers of deposit, light interference and not absorption was the dominant phenomenon exhibited.

DESIGN

FOMJFTOT

The real time FOMJFTOT operates on a standard JFTOT unit. The only modification is the replacement of the standard tube holder with one on which fiber optic probes are mounted. Internal dimensions of the FOMJFTOT tube holder are exactly the same as the standard unit. The ends of the fiber optic probes fit flush with the tube holder's interior surface and therefore do not interfere with the fuel flow. The modified tube holder's exterior surface is square and has eight threaded metal connectors, used to secure the fiber optic probes, welded in a spiral pattern as shown in Figure 3. Each of the eight fiber optic probes consist of a bundle of seven fibers. The center fiber of the bundle transmits the light from the source, a laser emitting diode (LED) having an 880 nm wavelength. The light reflected back from the tube is transmitted through the six remaining fibers to a photodetector. The light source and photodetector for each probe is contained in a central control unit located external to the JFTOT. Outputs of the eight photodetectors are fed to a processing unit which provides a voltage reading for each probe. Voltage outputs can be manually read from the meter on the source/detector unit or input to a microprocessor for data acquisition and analysis.

FOOR

The FOOR provides a post test measurement of the deposit thickness formed on a JFTOT tube. This unit, based on the same principles as the FOMJFTOT, operates using a modified Mark 8A TDR. The TDR was modified by replacing the standard light source and photocell detector with a fiber optic probe having the same seven fiber design as those used in the FOMJFTOT. Light is transmitted through the probe by a LED, having a wavelength of 880 nm, located in a one channel source/detector unit positioned external to the TDR unit. The light reflected from the JFTOT tube is returned through the probe to a photodetector. The voltage of the reflected light is read from a meter located on the source/detector unit.

The JFTOT tube is read spatially at 1 mm increments along the 60 mm test section. This procedure is repeated at 90° locations radially around the tube to ensure a thorough evaluation. The data is then manually entered into a computer for analysis.

TEST RESULTS

FOMJFTOT

Six fuels (Table I), having breakpoint temperatures ranging from 216°C (420°F) to 263°C (505°F), were tested on the FOMJFTOT over a tube temperature range of 204°C (400°F) to 316°C (600°F). Approximately 10 to 15 tests, ranging in duration from 2.5 to 96 hours, were run on each fuel. Extended test durations were necessary to obtain measurable deposit thicknesses at the lower temperatures. Probe temperature profiles were ascertained by measuring the maximum JFTOT tube temperature (Probe #5) during testing and determining the temperatures of the remaining seven probes from the ASTM D3241 Table of JFTOT Standard Temperature Profiles. Deposition rates were calculated, using Equation (1), at each probe position for the initial .84 microns of deposit formed. Deposition rates at thicknesses greater than .84 microns were difficult to obtain because either the test duration selected was too short or the refracted light path was absorbed to a degree sufficient to mask the light interference pattern.

Due to the apparent strong temperature dependence exhibited by the deposition rates, Arrhenius plots (natural log of deposition rates versus the reciprocal of absolute temperature) were generated to correlate the data for each fuel. Only the data generated by probes 1 through 5 (located at and upstream of the hottest point on the tube) were used to develop the Arrhenius curves. The data generated by the three probes downstream of the hot spot were not included because they were exposed to a more stressed fuel environment than the upstream positions having the same tube temperatures and therefore developed deposition at an increased rate.

A basic structure of six parallel lines, corresponding to the six .14 micron increments of deposit thickness measured, were observed in each Arrhenius graph. Figure 4, an Arrhenius plot developed for a typical aviation fuel (FF-8), shows that the time required to form each layer of deposit was not equal. Specifically, forming the initial .14 micron layer of deposit required the longest period of time while each of the subsequent increments were formed at increasingly faster rates. For FF-8, the time to form the layer of deposit thickness from .70 to .84 microns was 1/3 the time to form the initial .14 micron thickness. This phenomenon of increasing deposition rates was observed consistently for each of the fuels tested. Potential reasons hypothesized for this behavior were: 1. An increase of surface roughness caused by the deposition which increased the collection efficiency of the surface. 2. The hydrocarbon surface formed by the initial layer of deposition was a more conducive material for deposit formation than the aluminum surface of the tube. However, to determine the exact cause of this phenomenon of increasing deposition rates requires additional tests and analyses which were beyond the scope of this study.

A preliminary study, conducted during the development of the FOMJFTOT, approximated the deposit thickness on a tube having a minimum visual code 3 rating (current ASTM Thermal Oxidation Stability specification) to be .10 micron. Although this data did not agree with previous JFTOT and Coker thickness measurements made by both Beta-Ray Backscatter [3]) and Auger Electron Spectrometer/Ion Gun techniques [4], it did correlate well with the thickness measurements made by both electron microscopy [5] and the Deposit Measuring Device (DMD) [6].

Arrhenius curves of the six fuels tested are compared in Figure 5. A thickness of .14 microns was chosen as the deposit thickness level for fuel comparison because it most closely corresponded to the deposit thickness estimated to produce an ASTM visual Code 3 rating. The advantage of using the FOMJFTOT over the current breakpoint temperature method is that it provides a greater amount of data which allows fuel comparison over a wider range of temperatures. As shown in Figure 5, the four test fuels having breakpoint temperatures from 249°C (480°F) to 263°C (505°F) displayed similar deposition behavior over a wide range of tube temperatures. However, this was not the case for the two poorer quality fuels, NAPC-29 and NAPC-35. Although both fuels had a 216°C (420°F) breakpoint temperature, they exhibited increasing divergent deposition behavior at temperatures above and below the breakpoint.

Activation energies calculated from the Arrhenius curves for each fuel ranged from 20.1 Kcal/mole to 29 Kcal/mole. These values all fell within the range of those values typical of homogeneous oxidation reactions [7].

FOOR

FOOR deposit thickness measurements were obtained from the plots of reflected light voltage versus tube position. In order to analyze the plots it was necessary to assume that the JFTOT tube had an area of maximum deposit thickness which decreased to zero at each end. The center of the graph (area of maximum thickness) was determined such that an equal number of inflection points were on either side (Figure 6). Deposit thicknesses were calculated for each inflection point according to Equation (1). Figure 7, a graph of deposit thickness versus tube position, demonstrates the excellent agreement between the FOMJFTOT and the FOOR thickness measurements.

FOOR measurements were taken at 90° locations radially around the tube. This data, Figure 8, indicated that the deposit thickness around the tube was fairly uniform for each of the six fuels tested. From this data it can therefore be assumed, that for the fuels tested, each FOMJFTOT probe provided a representative deposit thickness measurement independent of its radial location on the tube.

CONCLUSION

Initial results indicate that both the Fiber Optic Modified JFTOT and Fiber Optic Off-line Reader have the potential to be valuable research tools. The FOMJFTOT provides a non-subjective, quantitative, real-time test which produces a more thorough and potentially more useful evaluation of fuel thermal oxidation stability than the standard JFTOT. The Arrhenius curves constructed from the FOMJFTOT deposition rates can be used to evaluate a fuel's deposition tendencies over a much wider temperature range than the current JFTOT breakpoint temperature method.

The FOOR provides a post-test method to quantitatively measure the thickness over the entire JFTOT tube. The FOOR can also be used to determine the uniformity of the deposit formation radially around the tube as well as supplement the results obtained by the FOMJFTOT.

The deposit thickness and deposition rates obtained by the FOMJFTOT and FOOR could provide an essential link between the evaluation of a fuel's thermal oxidation stability in the laboratory and its actual behavior in the field. It is anticipated that with further development the FOMJFTOT and the FOOR can produce the type of quantitative data necessary to make the JFTOT a useful research tool.

ACKNOWLEDGMENT

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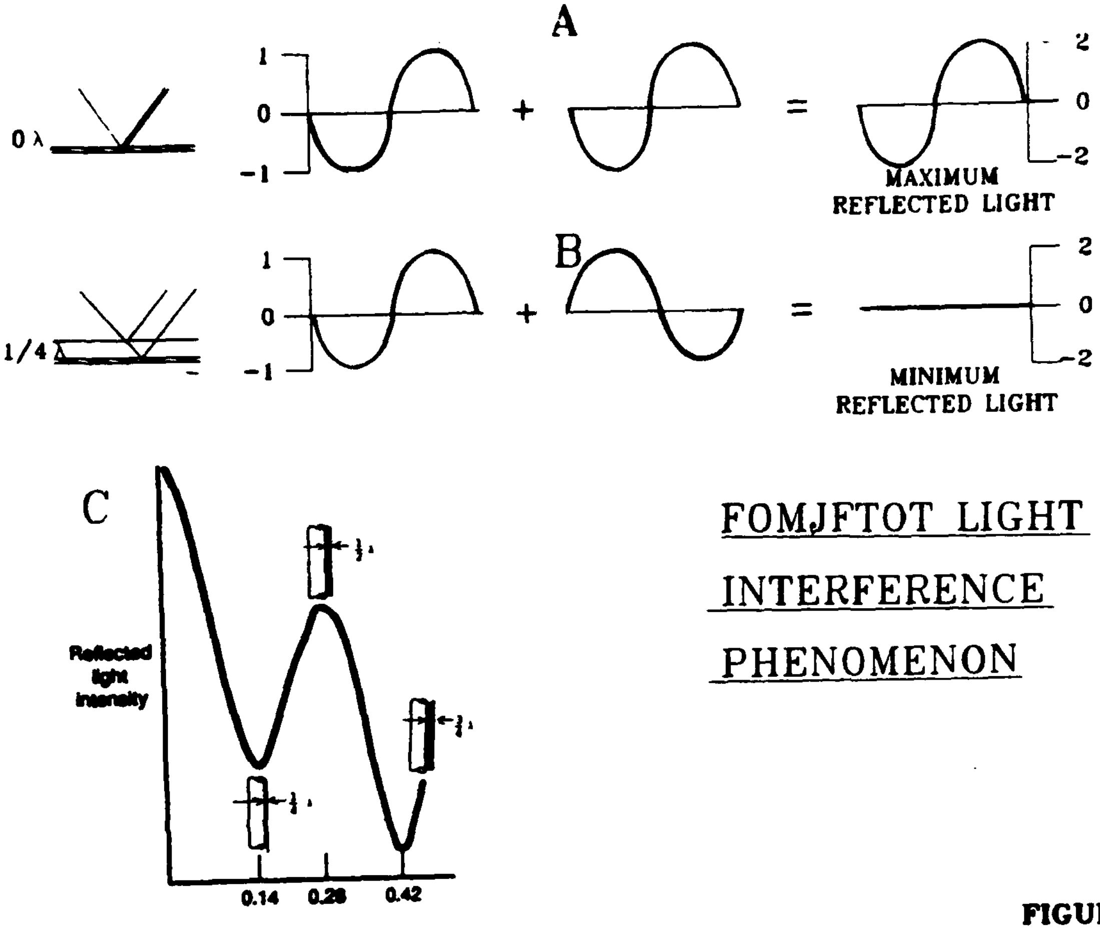
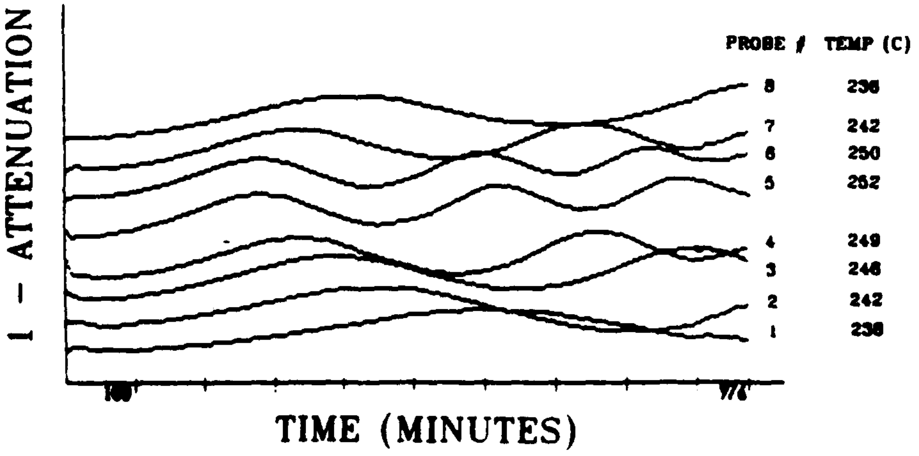


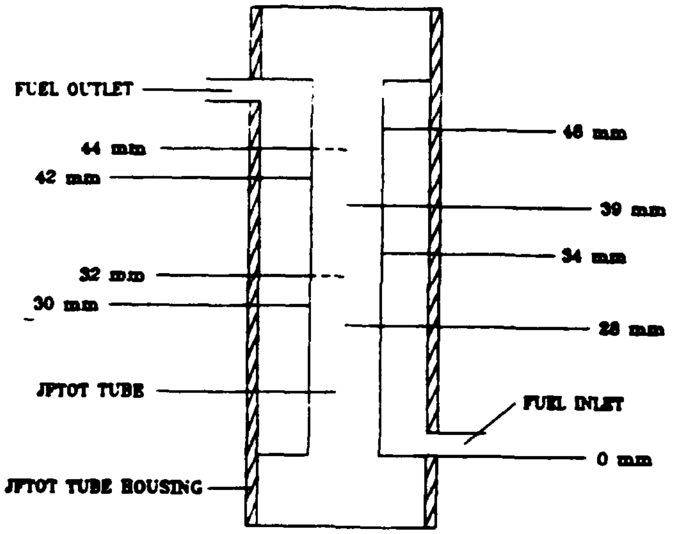
FOMJFTOT LIGHT INTERFERENCE PHENOMENON

FIGURE 1



FOMJFTOT RAW DATA

FIGURE 2



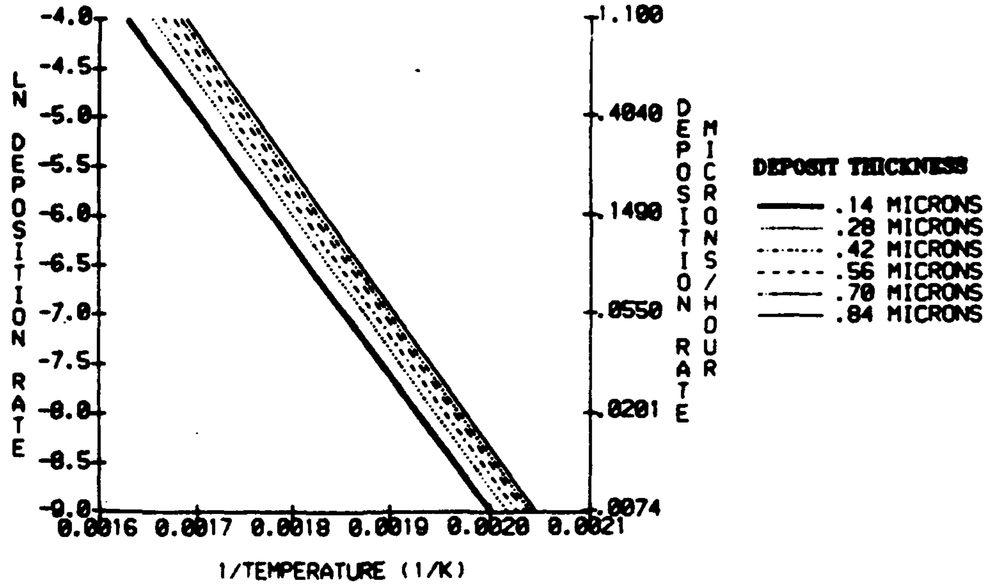
NAPC FOMJFTOT PROBE LOCATIONS

FIGURE 3

FUEL	JFTOT BREAKPOINT TEMPERATURE (C/F)	ACTIVATION ENERGY (KCAL/MOL)
NAPC-19	263/505	26.9
FF-8	260/500	26.7
FF-6	260/500	24.6
FF-3	249/480	29.0
NAPC-29	216/420	20.1
NAPC-35	216/420	26.9

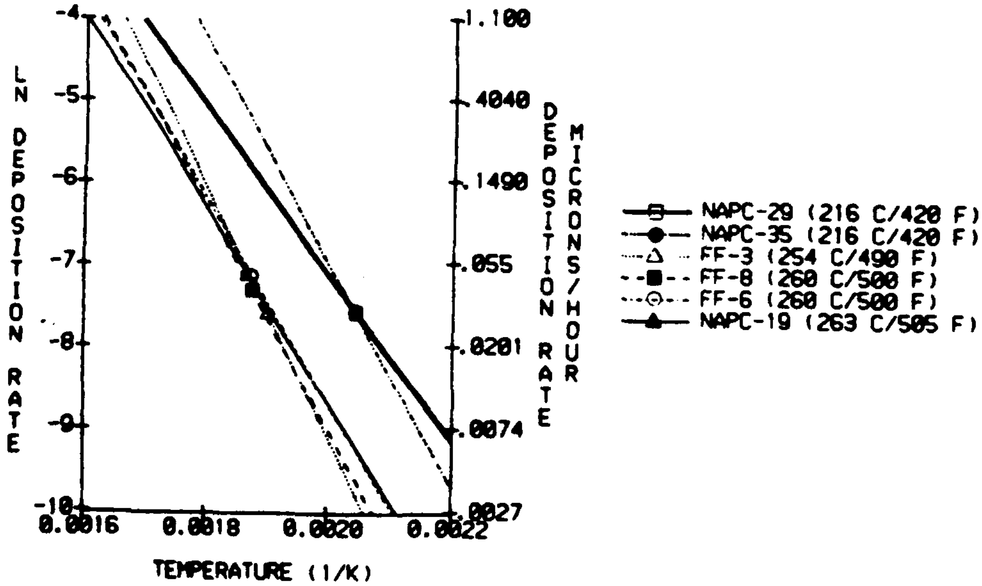
<u>FOMJFTOT TEST FUELS</u>

TABLE 1



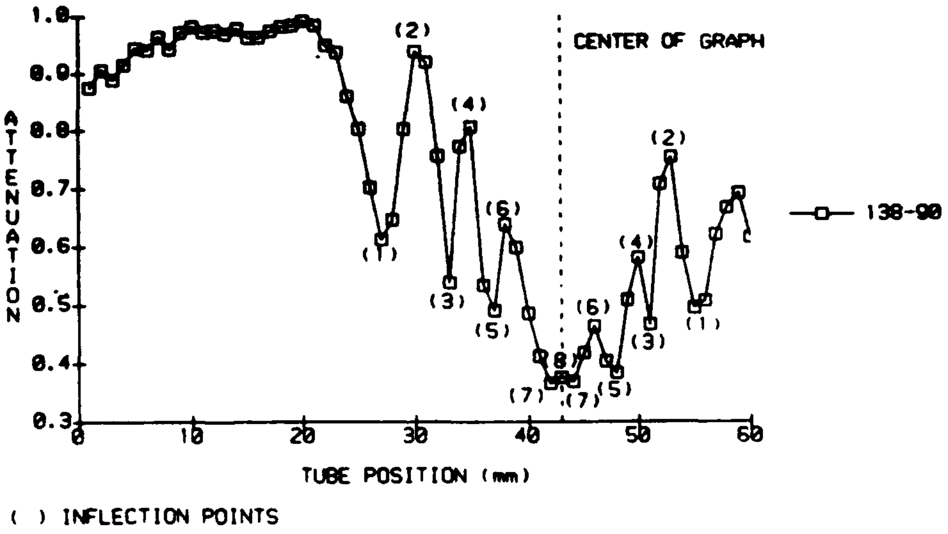
ARRHENIUS GRAPH OF FOMJFTOT DATA FOR FF-8

FIGURE 4



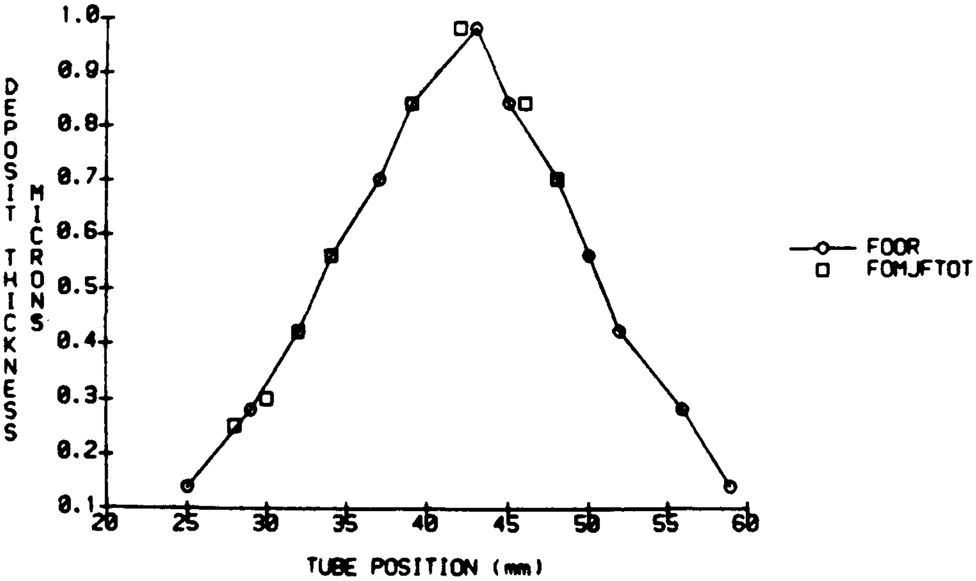
COMPARISON OF FOMJFTOT ARRHENIUS CURVES
(DEPOSITION RATES TO FORM INITIAL .14 MICRON THICKNESS)

FIGURE 5



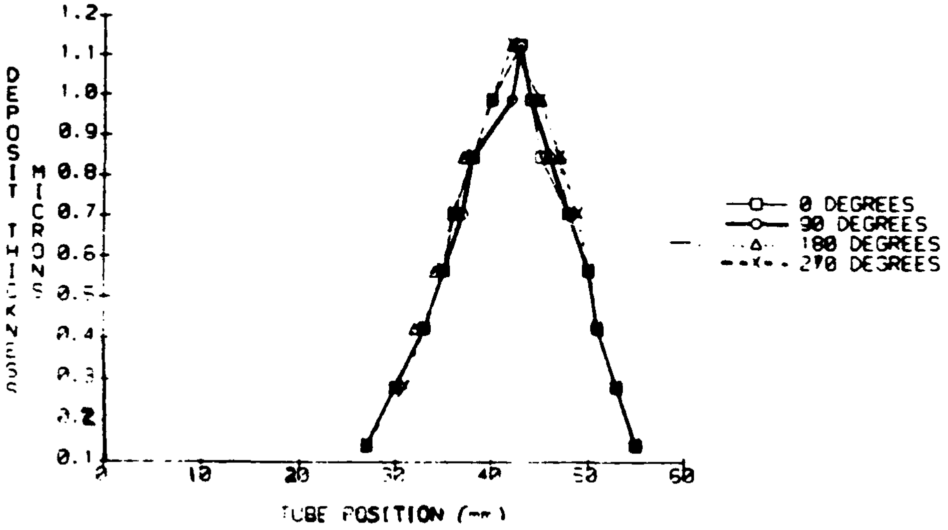
FOOR RAW DATA

FIGURE 6



COMPARISON OF FOMJFTOT AND FOOR THICKNESS MEASUREMENTS

FIGURE 7



DEPOSIT THICKNESS
RADIALLY AROUND THE JFTOT TUBE

FIGURE 8

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The Role of Alkylperoxy and Alkyl Radicals in Fuel Deposit and Gum Formation

[#32]

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ABSTRACT

The thermal stability characteristics of n-dodecane and n-dodecane plus heteroatomic species were studied after aerating the fuels and stressing them on a modified Jet Fuel Thermal Oxidation Tester (JFTOT) facility.

Fuel degradation mechanism(s) were hypothesized, based on the quantification and identification of the soluble degradation products using Gas Chromatography and Mass Spectrometric techniques. The mechanism suggests that in the autoxidation regime ($T \leq 300C$), the alkylperoxy ($RO_2^{\bullet}$) radical reactions appear to dominate the alkyl ($R^{\bullet}$) radical reactions. Conversely, in the intermediate temperature regime ($300 \leq T \leq 400C$), the $R^{\bullet}$ radical reactions appear to dominate the $RO_2^{\bullet}$ reactions.

The predictions of the fuel degradation mechanism were compared with actual fuel derived deposits and gums. Data from similar JFTOT experiments performed at the Naval Research Laboratory and from flask oxidation studies conducted at Stanford Research Institute were used to test the validity of the hypothesized mechanism.

The data correlation showed that the hypothesized fuel degradation mechanism is valid. Thus, if the $RO_2^{\bullet}$ and $R^{\bullet}$ can be suitably scavenged in the appropriate temperature regimes using anti-oxidants, inhibitors, radical scavengers, etc., it may be possible to inhibit fuel degradation.

INTRODUCTION

Fuel stability, or more correctly fuel instability, is a measure of the general chemical reactivity of a fuel; it is specifically the gum, sediment and/or deposit forming tendency associated with exposure of the fuel to long term storage at ambient temperatures (commonly referred to as storage instability) or to short term stress at higher temperatures (commonly referred to as thermal stability). Both storage and thermal instability form degradation products that manifest themselves as harmful deposits in storage tanks, distribution systems, fuel tanks, and combustion systems, ultimately leading to fuel system malfunctions and/or operating difficulties.

Fuel stability problems are expected to become severe in the future due to the anticipated usage of broadened specification and alternative fuels and to increased demands on aircraft performance. Future fuels will tend to have relatively higher contents of heteroatomic species (nitrogen, sulfur and oxygen containing organic compounds) which are reactive constituents and are known to influence fuel degradation. Past work, emphasizing research on actual fuels and dopants, has yielded some information regarding the effects of certain dopants on fuel degradation, but the detailed chemistry is lacking.

Consequently, the study of a single component model fuel, n-dodecane, singly and in combination with selected heteroatomic species, was undertaken [1-3], motivated largely by the simplification in degradation chemistry inherent in such systems. The fuels, n-dodecane and n-dodecane plus heteroatomic species, were aerated and then stressed on a modified Jet Fuel Thermal Oxidation Tester (JFTOT) facility. For the present work, the JFTOT was not used to estimate the amount of deposits (measured as tube deposit rating, TDR) and insoluble products (measured as a pressure drop, Δp) formed in a test, but was modified to study the formation of soluble degradation products for heater tube temperatures from ambient to 400C [1,3]. This modification allowed several stressed samples to be collected with a single filling of the fuel reservoir. It should be noted that the liquid fuel temperatures (bulk average) are 50-75C lower than the measured and reported heater tube temperatures. The residence time of the fuels in the high temperature zone of the JFTOT is approximately 9 seconds.

Analytical protocols were developed to separate the control and stressed fuel samples into several fractions based on a polarity separation and into several reaction product groups (Groups I - V) based on a molecular weight separation [1]. Gas chromatography (GC) using flame ionization detection and GC/mass spectrometry (GCMS) analyses yielded concentrations and identities of stable reaction intermediate and end products within each group and led to reaction mechanism inferences. The reaction intermediates and products consisted mainly of C5-C10 n-alkanes and 1-alkenes (Group I-nonpolar), C7-C10 aldehydes (Group I-polar), tetrahydrofuran derivatives (Group II), dodecanol and dodecanone isomers (Group III), dodecylhydroperoxde products (Group IV), and C24 alkane isomers (Group V).

Based on the neat n-dodecane work, fuel degradation mechanism(s) hypothesized by Hazlett *et al.* [4] were modified and refined by Reddy *et al.* [3].

The mechanism suggests that in the autoxidation regime ($T \leq 300C$), the alkylperoxy ($RO_2^•$) radical reactions which form alkylhydroperoxides (ROOH), C12 alcohols plus ketones, and tetrahydrofurans appear to dominate the alkyl ($R^•$) radical reactions. Conversely, in the intermediate temperature regime ($300 \leq T \leq 400C$), the $R^•$ radical reactions, yielding n-alkanes plus 1-alkenes and C24 isomers, appear to dominate the $RO_2^•$ reactions.

DISCUSSION

In relating the findings of the hypothesized fuel degradation mechanism to actual fuel derived deposits and gums, data from similar JFTOT experiments performed at the Naval Research Laboratory (NRL) by Hazlett [5] and from flask oxidation studies conducted at SRI International by Mayo and Lan [6] were used to test the validity of the hypothesized mechanism. The NRL data consists of TDR, [ROOH], [CO], and [n-alkanes] as a function of JFTOT tube temperature for a model fuel (n-dodecane) and an actual fuel (RAF-177). The NRL conclusions were: (i) in n-dodecane systems, deposits correlated with ROOH decomposition, Fig. 1, while (ii) in the RAF-177 actual fuel system, deposits correlated with ROOH formation, Fig. 2.

Comparison between Hazlett et al. [4] and Reddy et al. [3] using n-dodecane data has shown good agreement in the soluble degradation product distributions (and concentrations). Hence, it is assumed that correlations and comparisons between the modified fuel degradation mechanism hypothesis and NRL deposit data (TDR data) are valid.

In the intermediate temperature regime ($300 \leq T \leq 400C$), the fuel degradation mechanism hypothesizes that $R^•$ radical reactions dominate the $RO_2^•$ reactions. The NRL n-dodecane derived n-alkane and TDR data, Fig. 3, show that all of the $R^•$ radical derived product profiles, i.e., n-C1, n-C3, n-C9 and n-C10 curves, parallel the TDR build-up. The strong correlation between n-alkane and TDR indicates that $R^•$ radical reactions are probably important in the deposit formation process. Furthermore, the n-alkane product profiles correlate very well with TDR in the pyrolysis temperature regime ($T \geq 500C$), indicating that $R^•$ radical reactions are probably important in deposit formation in this temperature regime also. This is not surprising since at pyrolysis temperatures the fuel cracks to form $R^•$ radicals, which decompose further forming n-alkanes and 1-alkenes (Fabuss et al. [7]). Hence, $R^•$ radicals are probably responsible for deposit formation in the pyrolysis range of temperatures.

In the zone of minimum reactivity situated between the intermediate and pyrolysis ranges of temperatures ($400 \leq T \leq 500C$), the TDR curve dips down, while all of the n-alkane curves show a slight increase (or stay the same). This indicates a poor correlation between TDR and n-alkane concentration. A possible explanation for this behavior is that ROOH is depleted to near zero concentrations, Fig. 1. This causes a sharp decrease in the available $R^•$ radical pool, since RH pyrolysis becomes the sole source of $R^•$ radicals.

The relative $R^•$ radical contributions via ROOH decomposition paths (R%) and RH pyrolysis reactions (P%) in the intermediate range of temperatures can be inferred from the Group I-NP (n-alkane and 1-alkene) profiles using the air saturated and nitrogen purged n-dodecane data, Fig. 4. The air saturated Group I-NP data is a summation of the (R+P) data, while the nitrogen purged data includes contributions from P alone. It is observed that both R and P (absolute) increase from 300C to 400C. If the same data is replotted with R% and P% on the y-axis and temperature depicted on the x-axis, it is noted that R% decreases from 100% to 65% while P% increases from 0% to 35% between 300 and 400C, Fig. 5. In the zone of minimum reactivity, it is known that ROOH concentrations are near zero, Fig. 1, implying that R% is also close to 0%. This implies that P% should attain 100% just when ROOH's are completely depleted. Additionally, from available fuel pyrolysis mechanisms, it is known that P% is 100% and R% is zero at temperatures greater than 500C. Therefore, with the additional information regarding the pyrolysis and the minimum reactivity range of temperatures, Fig. 5 can be extended to include all temperatures greater than 300C.

In the zone of minimum reactivity, it is noted that R% decreases sharply from 65% at 400C to 0% when ROOH concentrations reach zero. On the other hand, P% increases from 35% to 100% when the R% contribution goes to zero.

The dip in the TDR data observed in Fig. 2 is probably due to the sharp decrease in the available $R^{\bullet}$ radical pool caused by the elimination of the major $R^{\bullet}$ supplier (R% --> 0) and the absolute P contribution being of a small order relative to the absolute R contribution. Thus, $R^{\bullet}$ radical concentrations appear to correlate with surface deposition (TDR data) in the intermediate, minimum reactivity and pyrolysis range of temperatures ($T \geq 300C$). Additionally, $R^{\bullet}$ radical derived products such as n-alkanes (Group I-NP) are better correlated with TDR profiles than ROOH decomposition as cited in the NRL work. Therefore, n-alkanes appear to be better correlators of surface deposition than ROOH's, with the added advantage of easier detection and quantification.

The postulated fuel degradation mechanism developed from the n-dodecane work at $T \geq 300C$ appears to work reasonably well for the RAF-177 fuel data, since n-alkanes again correlate with TDR between 327 - 382C (620 - 720F). However, beyond 382C (720F), the TDR does not correlate with the n-alkane profiles, possibly due to the presence of several other hydrocarbons, heteroatomic species, metals, natural and artificial inhibitors, etc. These species may react with the n-alkanes or possibly inhibit fuel pyrolysis reactions, thereby skewing the TDR versus n-alkane correlation.

At temperatures less than 300C where autoxidation predominates, the modified fuel degradation mechanism hypothesizes that $RO_2^{\bullet}$ radical reactions are more important than $R^{\bullet}$ reactions. To verify if $RO_2^{\bullet}$ radical reactions are important in fuel deposition processes (at $T \leq 300C$), the NRL data for [ROOH] plotted with respect to TDR for n-dodecane and RAF-177, Figs. 1 and 2, were examined. Figs. 1 and 2 show that, at autoxidation controlled temperatures, the n-dodecane derived ROOH data does not correlate with TDR while the actual fuel data does correlate with TDR, suggesting that the $RO_2^{\bullet}$ radicals probably contribute to deposits in actual fuels. The poor TDR versus ROOH correlation in the case of n-dodecane is attributed to the absence of other fuel constituents (major and minor species) which are probably important and significant in the overall deposit formation process.

In addition to these JFTOT tests, accelerated static systems were used by Mayo and Lan [6] to study the deterioration of both model and actual fuels. They measured the rates of oxygen absorption (Ro) and soluble gum formation (Rg) at 130C in flask oxidation studies, and found that the actual fuels generated more gum for the oxygen absorbed than pure hydrocarbon fuels (high Rg/Ro values). It was concluded that the low Rg/Ro values observed for model fuels is due to the absence of minor constituents in these fuels which are important in the gum and deposit formation processes. Since soluble gums are precursors of insoluble gums and deposits, the relatively lower amounts of gums observed in the case of model fuels [6] agrees with the low TDR observed for n-dodecane at autoxidation temperatures [5]. This implies that the fuel degradation hypothesis developed using a flowing system (modified JFTOT) is applicable to static systems. Admittedly, Mayo and Lan's experiments were performed at 130C while the temperatures cited in the JFTOT studies are much higher. However, as discussed earlier, the actual bulk fuel temperatures in the JFTOT are 50-75C lower than the reported JFTOT tube temperatures, thereby reducing the net temperature differential.

CONCLUSIONS

The RO_2^* radical reactions appear to be important in the deposit formation processes at the autoxidation range of temperatures ($T \leq 300C$), while the R^* radicals appear to be important at $T \geq 300C$. Therefore, if the RO_2^* and R^* can be suitably scavenged in the appropriate temperature regimes using anti-oxidants, inhibitors, radical scavengers, etc., it may be possible to inhibit fuel degradation.

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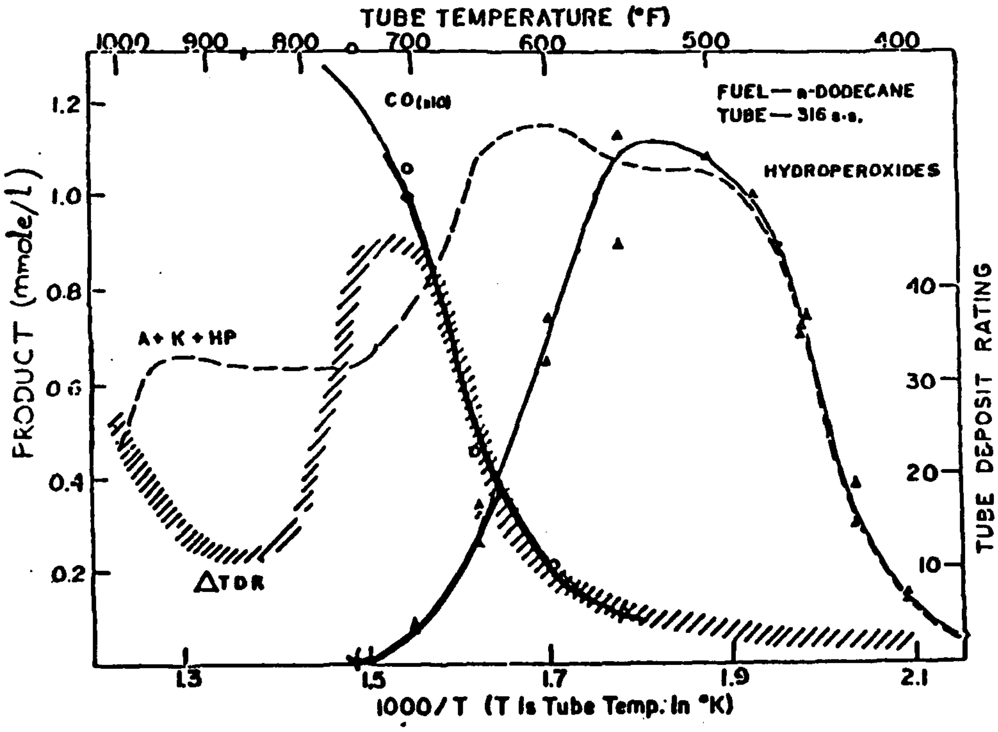

FIG. 1 Hydroperoxide Product Distribution and TDR data for JFTOT stressed n-Dodecane [5].

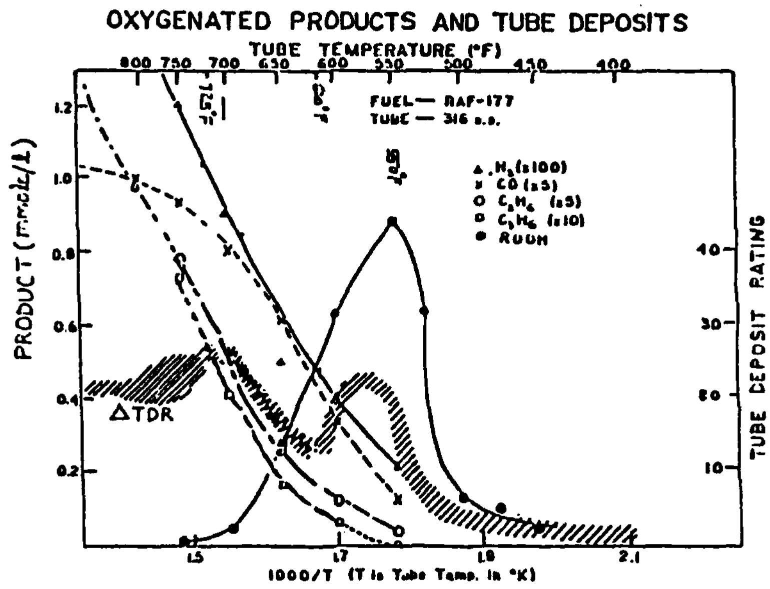

FIG. 2 Reaction Product Distributions and TDR data for JFTOT stressed RAF-177 Fuel [5].

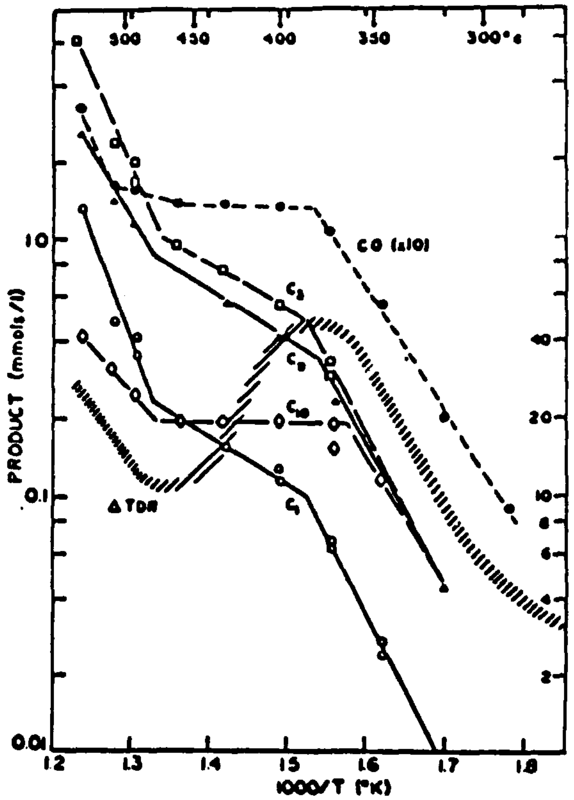

FIG. 3 n-Alkane Product Distributions and TDR data for JFTOT stressed n-Dodecane [5].

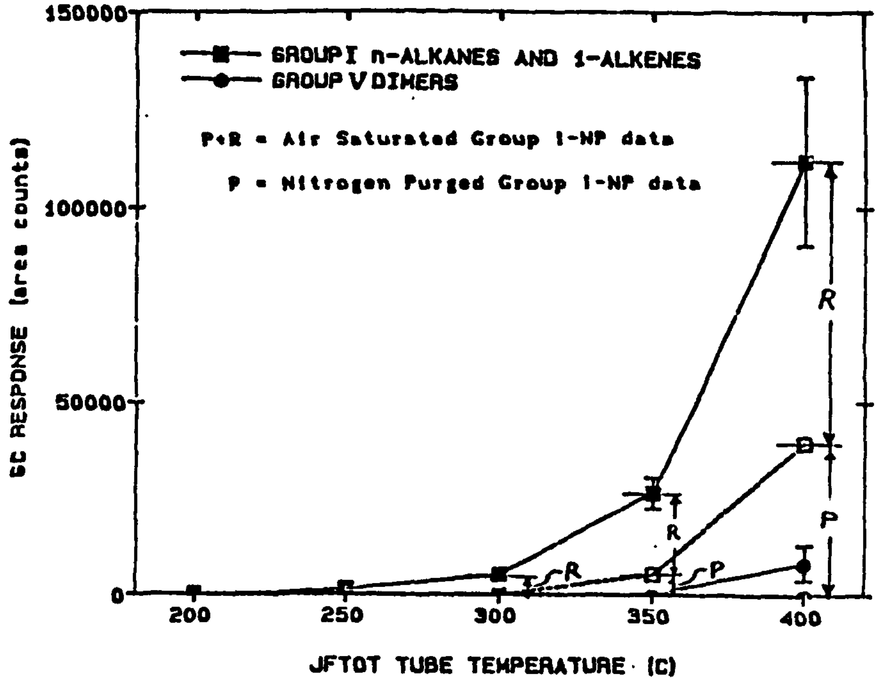

FIG. 4 Effect of Oxygen Concentration on R• Radical Derived Non-polar Products Using GC/Split Injection Analysis of Entire Samples.

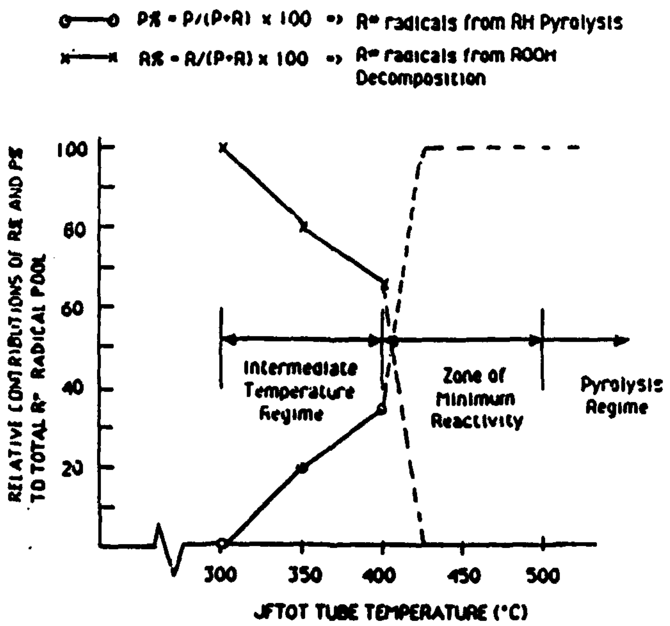

FIG. 5 R• Radical Contributions from ROOH Decomposition (R%) and RH Pyrolysis (P%) Reactions.

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

by

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ABSTRACT

The use of additives to improve the ambient storage stability of aviation fuels has created the need to characterize the influences exerted by these additives at the elevated temperatures of an aircraft fuel system. The behavior of several antioxidant compound types considered representative of those commonly used were examined during thermal stress in a modified JFTOT apparatus. The neat compounds 2,6-di-t-butyl-4-methylphenol and 2,4-di-isopropylphenylenediamine in addition to a tertiary amine, were blended into Jet A at 24 mg/L. A metal deactivator, N,N'-disalicylidine-1,2-diaminopropane was added at 5.8 mg/L as the pure compound and from a multifunctional additive package which contained both the metal deactivator and a tertiary amine, added at 24 mg/L. From experiments conducted with stainless steel heater tubes at temperatures from 200 to 310°C, measurements of heater tube deposits, particulate formation, oxygen consumption and peroxidation were obtained.

All the additives reduced the quantities of heater tube deposits formed at 260°C, compared to the neat fuel. At higher temperatures, the effects of the additives ranged from innocuous to deleterious, with the exception of the metal deactivator, which afforded substantial reductions in insoluble products at temperatures up to at least 310°C. The phenylenediamine was the most effective in reducing maximum peroxide concentrations, but this reduction was accompanied by increases in insoluble products.

INTRODUCTION

The combination of the increasing demand for aviation fuel and newer engine designs which place greater thermal stress on fuel has increased the interest in fuel stability. Both low temperature storage stability and high temperature thermal oxidation are of concern. Storage stability involves oxidation of fuel constituents to form hydroperoxides [1,2,3], which can attack elastomers in the fuel system. Hydroperoxides form more readily in fuels produced by hydrocracking or catalytic cracking followed by hydrotreatment. These refining techniques, while increasing the yield of jet fuel, probably remove natural inhibitors which limit hydroperoxides produced through free radical autoxidation reactions [4]. It is known that hydroperoxides play a key role in thermal degradation processes of aviation fuels by initiating a variety of free-radical reactions [5].

Additives have been used or considered for addressing these stability problems. In this context, one of the aspects of additive behavior that is of concern is the effect of stabilizer additives on thermal stability. Previous examinations of additive behavior on fuel stability at elevated temperatures have produced a variety of results. In the Minex test [6], a metal deactivator suppressed insolubles while phenolic antioxidants did not. At 100°C and 100 psig of oxygen, reductions in insolubles and hydroperoxides were reported [7] in the presence of two different hindered phenols and a phenylenediamine, whereas these same antioxidants were ineffective in long-term storage at atmospheric pressure at 43°C. Mixed results were obtained with a metal deactivator, also depending on test conditions. Phenolic antioxidants have been used with varying degrees of success at storage temperatures ranging from 50 to 160°C, but they have been shown [8,9], to be more effective when added during the early months of storage. N,N-alkylated phenylenediamine antioxidants have been found [10] to be detrimental to stability during storage of hydrotreated jet fuel for six months at 50°C.

Thus, the evidence indicates that the behavior of an additive in stability tests is not only influenced by the age and composition of the fuel but also by the nature of the test employed.

EXPERIMENTAL

The test fuels were commercial Jet A fuels which conformed to ASTM Aviation Turbine Fuel Specification D1655-82 [11]. Selected fuel properties are given in Table 1. Fuel samples were thermally stressed with a JFTOT apparatus, which had been modified as described earlier [5] to provide for on-line sampling of the stressed fuel. Test samples (1100 mL) were prefiltered through two Gelman type A/E glass microfiber filters before introduction of the additive. All additives were used at 24 mg/L except the metal deactivator, which was added at 5.8 mg/L, unless stated otherwise. After blending in the additive, the test fuel was sparged with dry air for 15 minutes. Five-inch 304 stainless steel JFTOT heater tubes were employed during runs conducted for 300 minutes. To avoid excessively stressing the fuel in the event that the JFTOT test filter became plugged with filterable insolubles, fuel flow rates were maintained at or above 2.5 mL per minute by bypassing the test filter.

Total carbon contents of the heater tube deposits were measured by combustion to carbon dioxide with a Perkin Elmer model 240 elemental analyzer. After calibration of the analyzer with known compounds, blank carbon values were obtained from unused heater tube sections and subtracted from all deposit measurements.

Oxygen contents in samples of stressed fuel from the JFTOT apparatus were determined as described earlier [5]. Hydroperoxides were determined iodometrically in accordance with ASTM D3703 [12], with the exception that potentiometric detection was employed using a platinum ring electrode with an automatic titrator.

TABLE 1. PROPERTIES OF JET A TEST FUELS

Property	Fuel 8237	Fuel 8711	method
Acidity, total, mg KOH/g	<0.01	<0.01	D 663
Sulfur, mercaptan, wt. %	0.0009	0.0009	D 3227
Sulfur, total wt. %	0.0325	0.0399	D 2622
Aromatics, vol. %	16.6	18.8	D 1319
Distillation temp., °F (°C)			D 86
10% recovered, temp.	364 (184)	363 (184)	
50% recovered, temp.	424 (218)	412 (211)	
90% recovered, temp.	494 (257)	477 (247)	
Final boiling point, °F (°C)	529 (276)	507 (264)	
Distillation residue, %	1.5	2.0	
Distillation loss, %	1.5	0.5	
Gravity, °API (sp gr) at 60°F	41.9 (0.816)	43.7 (0.811)	D 1298
Thermal stability at 260°C			D 3241
Filter pressure drop, inches Hg	0	0	
Tube deposit rating	<2	<2	
Copper, PPM	<0.001	0.004	ICAP

RESULTS AND DISCUSSION

The effects of the additives in fuel 8237 on the amounts of heater tube deposits were determined from the quantities of total carbon found on each tube by combustion. The results from combustion analyses from replicate JFTOT experiments are shown in Fig. 1. When the averages of the total carbon from the two replicate heater tubes are compared, it is apparent that all the additives reduced the amounts of tube deposits at 260°C with respect to the neat fuel. As the stress temperature was increased, FOA-310 and metal deactivator (MDA) continued to reduce the amounts of heater tube deposits, while the effectiveness of the other additives diminished. FOA-310 contains an aliphatic tertiary amine in combination with the metal deactivator and FOA-3 contains the same amine as its major constituent. Therefore, the aliphatic tertiary amine in FOA-3 was not particularly effective in suppressing deposit formation but in combination with the metal deactivator in FOA-310, it did bring about significant reductions. This indicates that the effectiveness of the FOA-310 was attributable to the presence of the metal deactivator. In comparison with the neat fuel, the hindered phenol (ionol) was essentially innocuous. Thus, this antioxidant which has demonstrated inhibition of oxidation at low temperatures was not functioning as such in the temperature range used in these tests. The phenylenediamine (PDA) often increased the amounts of tube deposits at 270°C and above, as did FOA-3 at 270°C.

The measurements of hydroperoxide concentrations in JFTOT effluent, shown in Fig. 2, indicate that fuel 8237 had a low initial hydroperoxide concentration which increased as it was stressed up to a temperature of approximately 270°C. Above this temperature, it has been shown [5] that the hydroperoxides undergo thermal decomposition and their concentration decreases.

Although heater tube deposits were significantly reduced in the presence of FOA-310, levels of hydroperoxides found at temperatures above

260°C were similar to the neat fuel. When the two components of FOA-310 were tested separately, both the metal deactivator and the FOA-3 significantly reduced hydroperoxides from levels reached in the neat fuel. The tertiary amine, as a single functional additive in FOA-3, exhibited moderate activity except it was effective in reducing hydroperoxide concentration. This latter may result from the interaction of the hydroperoxide and FOA-3 to form an amine oxide. The phenylenediamine was the most effective additive in suppressing hydroperoxide accumulation, with a maximum peroxide number of only 0.3 meq/kg measured at 280°C.

Measurements of oxygen content in fuel stressed with JFTOT heater tube temperatures ranging from 21 to 310°C, (Table 2) revealed that oxygen consumption was generally in accordance with the observed peroxidation levels. For instance, ionol exerted little effect but PDA, FOA-310 and MDA reduced oxygen consumption. On the other hand, FOA-3 exhibited no reduction in oxygen usage in contrast to the reduction observed for hydroperoxide formation.

TABLE 2. OXYGEN CONSUMPTION BY FUEL 8237 DURING JFTOT STRESSING

	Percent of Initial Oxygen Consumed					
Tube Temp.,C.	Neat	IONOL	PDA	FOA-3	FOA-310	MDA
200	1.4	0	0	3.9	0	0
220	-	-	1.1	4.1	-	14.7
225	-	21.3	-	-	0	-
240	27.5	-	2.1	25.1	-	16.9
250	44.2	45.7	-	45.1	31.2	-
260	89.5	73.8	28.8	94.8	41.7	35.8
270	88.6	98.8	38.1	-	82.8	-
280	98.2	100.0	85.5	100.0	100.0	94.5
310	100.0	100.0	100.0	100.0	100.0	100.0

The formation of suspended particulates was monitored by measurement of the pressure differential developed across a standard JFTOT test filter. The metal deactivator and the FOA-310 were very effective in suppressing filterable insolubles. The effectiveness of the other additives to reduce filterable insolubles decreased with increasing temperature, in accordance with the other measured properties. At higher temperatures, the hindered phenol had no significant effect, while the FOA-3 tended to increase filterable insolubles somewhat. The most rapid filter plugging generally occurred in the presence of the phenylenediamine, in spite of reducing the rate of oxidation and limiting hydroperoxide formation. When such an increase in insolubles had been previously observed in the presence of phenylenediamines, [13], it had been attributed to thermal degradation of the PDA itself at 200-230°C. In this study, increases in tube deposits with the PDA did not occur until 310°C, whereas filterable insolubles increased dramatically above 270°C. This indicates that either the reaction of the PDA with a hydroperoxide is a prerequisite to the formation of filterable insolubles or, that thermal decomposition of the PDA below 310°C results in the formation of filterable insolubles.

The effectiveness of the MDA in reducing heater tube deposits in the JFTOT was consistent with the sensitivity of the JFTOT to metal deactivator reported [14] with aluminum and stainless steel tubes. In order to define the relationship of MDA effectiveness to concentration, a series of JFTOT experiments were conducted with MDA concentrations ranging from 11.6 to 1.5 mg/L at 260, 280 and 310°C in fuel 8711. The reductions in tube deposit volumes were measured by the dielectric measuring device (DMD), which was applicable to the thicker coatings produced in these 5 hour experiments. It has been shown [15] that deposit volumes by DMD correlate well with total carbon by combustion and could be used to compare levels of tube deposition. The maximum effectiveness of the MDA to reduce deposits from fuel 8711 was attained after the addition of 1.5 mg MDA/L (Table 3) at 260° and slightly more at higher temperatures. Further additions of MDA provided no significant further reductions in tube deposits. Addition of the MDA to fuel 8711, which peroxidized to a maximum of 0.7 meq/kg at 280°C, afforded no significant reductions in accumulated hydroperoxides.

Additions of MDA to a 50% by volume blend of Jet A fuel 8711 with a Naval Distillate also produced a strong inhibitory effect on tube deposition, although slightly more MDA was required. The neat Jet A had low initial levels of peroxides but the initial hydroperoxide concentration in the blend was relatively high since the Naval Distillate had an initial peroxide number of 2.6 meq/kg. The effectiveness of the MDA in suppressing tube deposition was therefore not compromised by the presence of fuel peroxides. As with the neat Jet A fuel, the MDA afforded no significant reductions in hydroperoxides of the blend under the various stress tests.

TABLE 3. QUANTIFICATION OF HEATER TUBE DEPOSITS BY DMD MEASUREMENTS

MDA, Addition mg/L	Deposit Volume, cu.cm. x 10^{-7}			%Reduction in Volume by MDA		
	260°C	280°C	310°C	260°C	280°C	310°C
<u>8711 Jet A</u>						
0	1006	2883	5107			
1.5	124	607	1541	87.7	78.9	69.8
2.9	141	1264	855	86.0	56.2	83.3
5.8	132	511	942	86.9	82.3	81.6
11.6	130	458	805	87.1	84.1	84.2
<u>8711 Jet A + 50% ND</u>						
0	1452	1743				
0.5	978	1509			32.6	13.4
1.5		888				49.1
2.9	318	568			78.1	67.4
5.8	365	505			74.9	71.0
11.6	388	621			73.3	64.4

CONCLUSIONS

An overall summary of additive influences on the measured properties of fuels stressed in the JFTOT is given in Table 4. A very significant reduction (70-85%) in deposits was realized when the metal deactivator was present, either alone or in combination with a tertiary aliphatic amine antioxidant in FOA-310. All the additives exhibited inhibitory effects on insolubles formation and peroxides at lower temperatures, but only those with the metal deactivator remained effective as the temperature increased. The mechanism by which the metal deactivator functions effectively at elevated temperatures is not clear at this time. However, the similar behavior of MDA in fuels with different peroxide levels suggests that one mechanism by which it acts involves the heterogeneous interactions between the fuel and the metal surface of the heater tube rather than as an antagonist for oxidation reactions. However, it would seem that this advantage would be lost as the tube surface becomes coated with an organic deposit and further benefits could then be a result of reactions of the MDA with the fuel and fuel-soluble constituents. Since the copper contents of the jet fuels was very low, complexation of soluble copper was not responsible for the effectiveness of the MDA. The determination of the copper content of the Naval Distillate has yet to be completed, so that copper deactivation cannot be ruled out for the blended fuel.

The tertiary aliphatic amine, FOA-3, was not effective in reducing insolubles at high temperatures, although peroxide levels were suppressed throughout. The phenylenediamine was very effective in reducing peroxidation, but this reduction was accompanied by significant increases in insolubles. The findings do not allow for any distinction to be made as to whether the insolubles were due to thermal decomposition of the phenylenediamine itself or PDA reaction products.

TABLE 4. SUMMARY OF ADDITIVE EFFECTS ON FUEL PROPERTIES AFTER JFTOT STRESSING

Additive	Heater Tube Deposits	Filterable Insolubles	Peroxidation	Oxygen Consumption
IONOL	o	o	o	o
PDA	+	++	--	--
FOA-3	-	+	-	o
FOA-310	--	--	o	-
MDA	--	--	-	-

o: no or minimal effect, +/-: significant increase/decrease, ++/--: large increase/decrease

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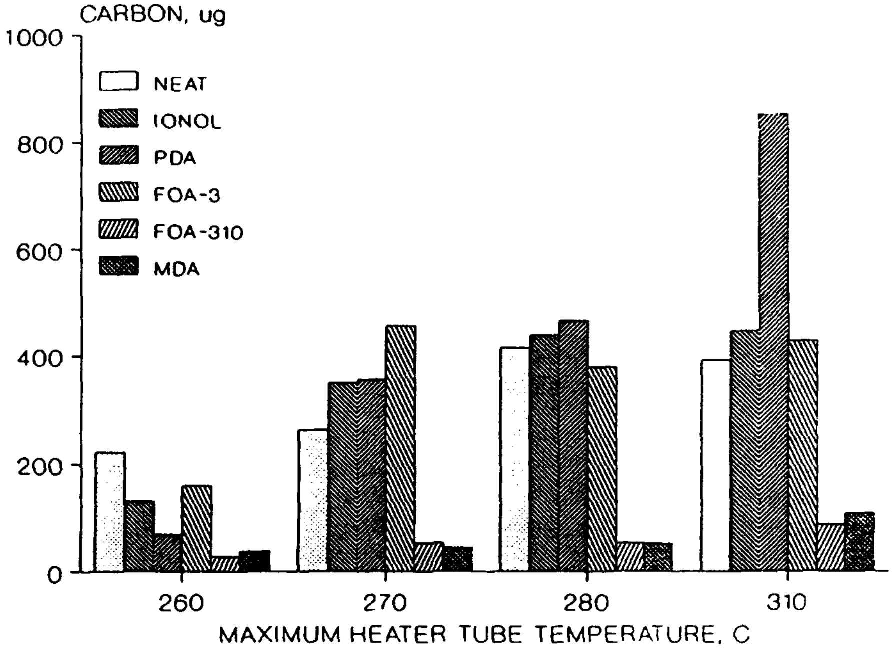

Figure 1. Influences of additives on JFTOT heater tube deposits expressed as total carbon.

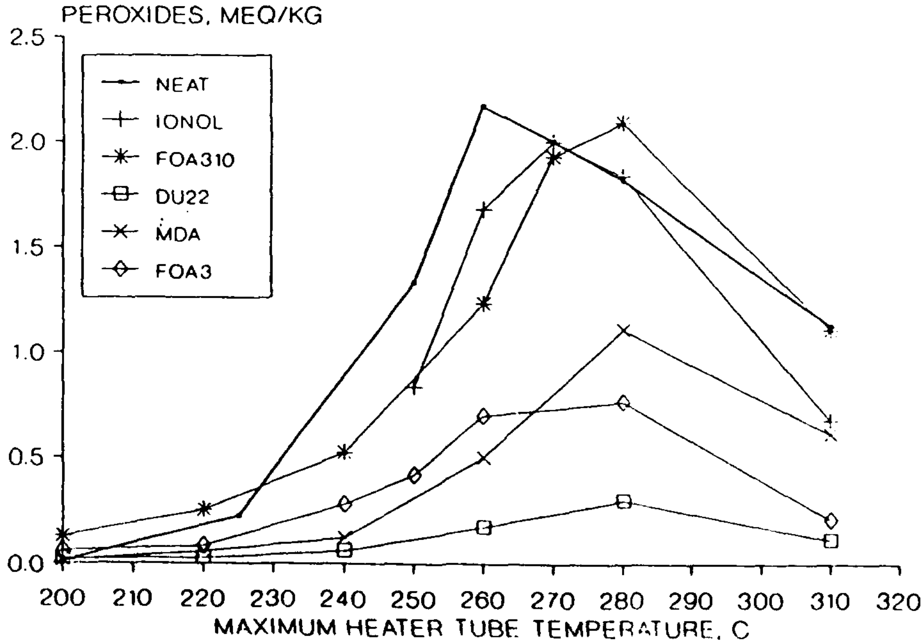

Figure 2. Peroxide concentrations reached in the JFTOT after stressing Jet A fuel 8237 containing stabilizer additives.

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FURTHER STUDIES OF THE EFFECTS OF POLAR COMPOUNDS ON THE THERMAL STABILITY OF JET FUEL

[#46]

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ABSTRACT

The influence of polar compounds on the high temperature degradation mechanism of jet fuel has been studied using a number of experimental techniques. The deposition characteristics of the fuel were assessed by the Jet Fuel Thermal Oxidation Tester (JFTOT), whilst a flask oxidation test was used to probe the initial stages, that is liquid phase oxidation. The results of these tests have given an indication as to where polar compounds act within the overall degradation mechanism.

The studies employed a dual strategy using both polar compounds and extracts obtained from commercial jet fuels. The model compounds encompassed sulphur, nitrogen and acidic species, whilst the use of ion exchange chromatography provided acidic extracts from commercial jet fuels. The work examined not only the individual effect of each compound class, but also their pairwise interactions.

From these studies, we have developed an improved means of predicting, from compositional information, fuel degradation rates in service.

INTRODUCTION

Jet fuels can degrade and form deposits in the hot components of gas turbine fuel systems. These deposits may impair the operation of the aircraft engine. It has long been recognised that it is the trace fuel species rather than the bulk hydrocarbons which are dominant in determining the stability of a fuel. In this respect, current literature(1) accounts of both thermal and storage stability have shown much interest in trace polar species within the fuel.

In an earlier paper(2) on this topic, we have reported work using fuel polar extracts, acidic and sulphur containing species, produced via chromatographic separation techniques. The roles of such species in thermal degradation were determined in small scale test rigs, a flask oxidation test and the JFTOT, in a series of back-doping experiments. This current research divides naturally into two topics. In the first, the emphasis is on small-scale rig testing of model polar compounds from three chemical classes (sulphur containing, nitrogen containing and acidic species), alone and in combination with the aims of investigating whether the compounds have a role in fuel oxidation or deposit production. Secondly, on the basis of this and earlier work(2), we attempt to develop methods of predicting fuel thermal stability.

METHODOLOGY AND AIMS

At Shell Research the topic of fuel thermal stability is researched in three coordinated ways:-

- In large scale rigs realistically simulating critical engine components, so enabling predictions of fuel performance in a realistic environment.
- Critical examination of the JFTOT specification test, assessing its ability to unequivocally predict fuel performance in reality.
- Fundamental mechanistic studies to provide the necessary chemical background for the other studies: An ultimate goal of this research is to make predictions of fuel performance in realistic conditions, given the appropriate analytical detail of a fuel's constituents.

Of its very nature, the work with polar species falls into the final category. The fundamental mechanistic studies make use of two rigs; the Shell flask oxidation test and the JFTOT. In a simplified fuel degradation scheme (Figure 1), there are two principle steps; the initial stage is liquid phase oxidation of the fuel via a free-radical chain mechanism, characterised using the Shell flask oxidation test. The second stage of the mechanism is the formation of insolubles (i.e. the lacquer formed on the engine components), resulting from the oxidation products reacting with trace polar species within the fuel. In this respect, the JFTOT will measure the overall deposition propensity of a fuel, i.e. the net outcome of the first and second stages. Within the context of this two stage mechanism, our first aim was to determine whether a particular polar species played a significant role in the oxidation step and/or the formation of insolubles. Then, given the results from our initial work which suggested that interactions between compounds were at least as significant as individual compound activity, we extended our programme to probe interactions between the three classes of polar compounds. The final aim, as noted above, was to develop a method of predicting fuel thermal stability within a realistic rig environment.

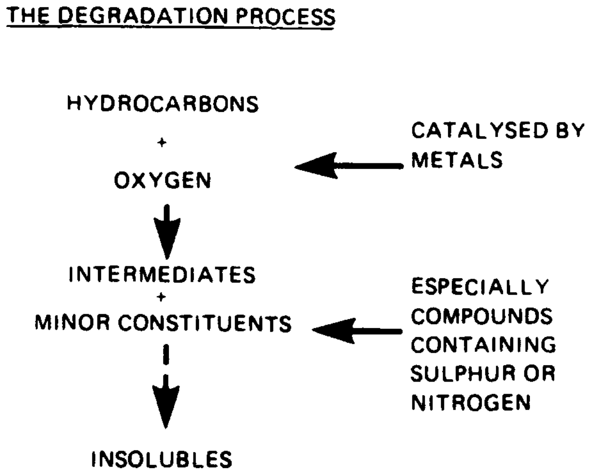

FIG. 1 – Simplified scheme of the thermal degradation of kerosine

EXPERIMENTAL

OXIDATION CHARACTERISTICS - The oxidation behaviour of test fuels was determined in the flask oxidation test, which allows on-line measurement of oxidation rates at elevated temperatures (160°C). A full experimental description has-been given in earlier publications(2,3). The test allows investigation of the initial stage of degradation, liquid phase oxidation, which may be represented as a free radical chain mechanism of the form:-

Initiation

$$RH + O_2 \rightarrow \text{Radicals} \qquad R_i^{fuel}$$

Propagation

$$R\cdot + O_2 \rightarrow RO_2\cdot$$

$$RO_2\cdot + R'H \rightarrow ROOH + R'\cdot \qquad k_p$$

Inhibition

$$RO_2\cdot + IH \rightarrow ROOH + I\cdot \qquad k_{IH}$$

Autoinitiation

$$ROOH \rightarrow RO\cdot + HO\cdot \qquad ek_d$$

Stabilisation

$$ROOH \rightarrow \text{non radical products} \qquad (1-e)k_d$$

Assuming the above kinetic scheme, then the oxidation rate of the fuel, v, is given by

$$v = \frac{(\ell + 1)R_i^{fuel}}{1 - 2e(\ell + 1)} \qquad \ldots(1)$$

In reaching this expression we have tacitly assumed that there are enough natural radical inhibitors (IH) to ensure a steady-state inhibited oxidation. This will be the case for sweetened fuels, however, hydrotreated fuels with little antioxidancy may not produce a steady state oxidation, instead the oxidation rate will increase until all antioxidants (natural or added) are consumed, thereafter rapid autoxidation of the fuel ensues. Thus, in order to facilitate more straightforward measurements, and the use of equation (1), all test fuels were chosen to yield inhibited oxidation. It is then possible to investigate the oxidation mechanism by perturbing the system; for example, the intrinsic radical initiation rate of a fuel, R_i^{fuel}, can be determined by the injection of a known concentration of a radical initiator, R_i^{fuel} is then given by

$$R_i^{fuel} = v_o \ (\Delta R_i/\Delta v)$$

where v_o is the original oxidation rate, Δv is the perturbation to the oxidation rate and ΔR_i is the contribution to the radical initiation from the radical initiator.

In this current programme, we have sought only to follow the changes in oxidation rate, following the addition of various polar species.

DEPOSITION CHARACTERISTICS - The JFTOT (Jet Fuel Thermal Oxidation Tester) assesses the tendency of fuels to lacquer a heated aluminium tube. Whilst the instrument's prime use is that of specification testing(4), its role in the current research is that of a convenient small-scale tester for the fuel deposition process. In our previous work, the standard ASTM JFTOT procedure was refined to determine the amount of carbon deposited on the test section in a single severe test (350°C)(2,5). The carbon is quantified by burning off the tube in a carbon analyser which measures the CO_2 evolved using infra-red spectroscopy. The technique allows a fuel's deposition propensity to be assessed in a non-subjective fashion in a single test determination. Insofar as separate analytical studies of JFTOT lacquers have shown them to be ≈ 80%w carbon, with little dependence on fuel composition, we believe carbon deposit determinations are a good measure of the total lacquer formed.

Rigorous preparation and experimental procedures detailed elsewhere(2,6), have reduced background contamination of JFTOT tubes of the order of 5μg carbon. For comparison, deposit measurements will fall in the range 10 - 300 μg. However, notwithstanding these improvements, when working with polar compounds the repeatabilities of the experiments were significantly reduced. These problems were overcome by ensuring that the JFTOT system was flushed with trisolvent* prior to the start of each test to ensure no contaminants were held up within the pipework and, in addition, polar compounds solutions were always prepared fresh.

FUEL PERFORMANCE IN A REALISTIC ENVIRONMENT - Shell Research's principal technique for determining the stability of fuel in a realistic environment is the Single-Tube Heat-Transfer Rig(7). This simulates an aircraft fuel system and specifically examines a fuel's tendency to foul oil-coolers. As fuel passes through a simulated oil-cooler its stability is assessed by the rate of loss of heat-transfer efficiency between the heat-exchanger and the fuel, caused by the lacquer build-up on the metal wall -so insulating it from the cooling effect of the fuel. Our realisation that STHTR performance was related to fuel sulphur content has led to the current studies to predict fuel performance in the rig from the concentrations of other polar species.

TEST FUELS AND COMPONENTS - Details of the test fuels are given in Table 1. For JFTOT deposition testing with polar doping materials, two hydrotreated fuels A and B, which were selected because of their low polar content, 0.0081% and 0.0026%w S respectively. The aim was to maximise the contributions seen from the added polar species and minimise adventitious interactions within the fuel.

Flask oxidation studies employed fuels A, B, and C which were chosen because they demonstrate inhibited oxidation.

Model polar species were purchased direct from fine chemical suppliers and used without further purification.

Total acid fractions were derived from one litre samples of fuel using ion-exchange chromatography.

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* Trisolvent is an equivolume blend of toluene, ispropyl alcohol and acetone.

Table 1

Properties of test fuels

Property	Fuel			
	A	B	C	D
Acidity, total, mgKOH/g	0.003	0.005	0.001	0.001
Aromatics, %v	9.8	15.2	16.5	17.4
Olefins, %v	0.5	<0.1	0.5	0.3
Sulphur, total, %w	0.0081	0.0026	0.11	0.13
Sulphur, Mercaptan, %w	-	-	0.0005	0.0002
Distillation				
10% recovered, °C	173	175	166	164
20% recovered, °C	180	186	175	170
50% recovered, °C	197	203	198	190
90% recovered, °C	224	235	238	228.5
F.B.P., °C	236	257	256	259
Density @ 15°C, kg/l	0.7920	0.7987	0.8020	0.7878
Freezing point, °C	-48.5	-49.0	-47.5	-51
Smoke point, mm	26.9	26.0	23.0	26.0
Thermal stability				
JFTOT pressure rise, mmHg	0	0	0	0
Tube colour code	0	<2	1	1
Breakpoint °C	310	305	295	285
Existent gum, mg/100 ml	0	0	0	1.0
Additives				
Antioxidant, mg/l	22.0	20.0	0	0
Antistatic, mg/l	0.3	1.0	2.3	N.D.
Metals				
Copper, µg/l	<2	<2	2	<2
Iron, µg/l	<5	<5	-	-

RESULTS AND DISCUSSION

OXIDATION AND DEPOSITION CHARACTERISTICS

(a) Nitrogen compounds

Whilst nitrogen species are recognised as being deleterious to thermal and storage stability, previous studies(8,9) have employed somewhat unrealistic doping concentrations, e.g. 100 ppm N in order to achieve a measurable result, whereas fuels seen by Shell Research encompass the range 1 - 3 ppm N. Consequently preliminary JFTOT work was performed to examine JFTOT carbon deposition as a function of nitrogen doping rate within Fuel A, and thus choose a concentration which provides a measurable level of deposition, albeit at a more realistic doping level. Two compounds were employed (indole and 5 ethyl 2 methyl pyridine) with the results illustrated in Figure 2. Both compounds show markedly different sensitivity to concentration, indole having a much greater deposition propensity; 200µg of carbon were deposited at a 80ppm N dope rate, compared with 50µg carbon for the same nitrogen concentration as 5 ethyl 2 methyl pyridine. These differing responses are significant since their originators represent the two major classes of nitrogen compounds within jet fuel. Indole is based on the pyrole structure, having mildly acidic properties; whereas 5 ethyl 2 methyl pyridine is based on the pyridine molecule, with basic properties. Follow-up JFTOT studies ranked seven model nitrogen compounds at the chosen dope rate of 40 ppm N. These results (Table 2) confirmed the divergence of response of the two different chemical groups, all pyridines showing essentially the same moderate level of deposition, whereas both pyrole types (2,5 dimethyl pyrole and indole) showed a higher level of deposition.

Table 2

Summarised JFTOT carbon deposit data and flask oxidation results for model nitrogen compounds doped into Jet A-1 fuels

Nitrogen compound doped at 40 ppm N	JFTOT carbon deposit (μg) (FUEL A)	Flask oxidation Result (FUEL C)
Base Fuel	10	-
Indole	201	no response
2,5 Dimethyl pyrole	103	mild antioxidant
Quinoline	44	pro-oxidant
2,4 Dimethyl pyridine	48	pro-oxidant
3,5 Dimethyl pyridine	41	pro-oxidant
2,4,6 Trimethyl pyridine	45	pro-oxidant
5 Ethyl 2 methyl pyridine	50	pro-oxidant

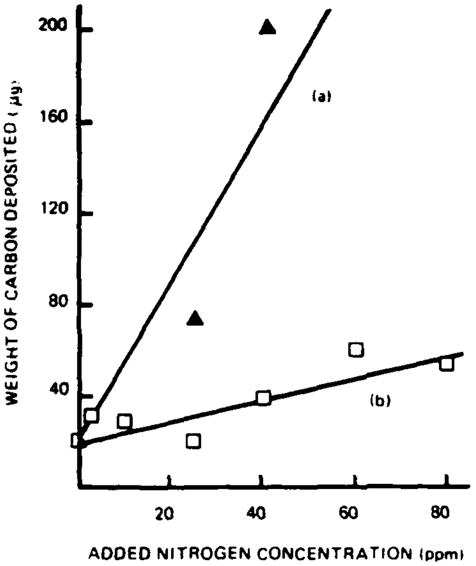

FIG. 2 – The effect of fuel nitrogen concentration on carbon deposition in the JFTOT, using model nitrogen compounds doped into a hydrotreated Jet A–1 (Fuel A): (a) indole, (b) 5 ethyl 2 methyl pyridine

Examining the oxidation behaviour of these species (Table 2), it is immediately apparent that the deposition and oxidation results do not necessarily produce the same order of compound rankings. Thus, 2,5 dimethyl pyrole doped into Fuel C is seen to act as an antioxidant in the flask test, even at the 3ppm level, producing a marked discontinuity in the oxidation trace (Figure 3), thereafter subsequent injections of the compound had no further effect on fuel oxidation. This would imply that this pyrole acts as a free radical inhibitor, reducing the chain length, ℓ (in equation 1), to its minimum value on the first injection. This behaviour of the pyrole is understandable in view of the fact that its structure is not dissimilar from that of a hindered phenol antioxidant. This result contrasts with that of a pyridine (2,4,6 trimethyl pyridine, Figure 4) which had a marked pro-oxidant action in the flask test, further injections having an additive effect. The explanation of this pro-oxidancy is conjecture, more detailed experimentation within the flask test would be required to confirm the exact role of pyridines within the oxidation mechanism.

In summary the results show that the rankings of the compounds by their oxidation and deposition behaviour need not necessarily agree. Thus, whilst the pyrole can act as an antioxidant, the JFTOT indicates it is strongly pro-deposition. The results for the pyridines are more in accord, they have a pro-oxidant action which could account in whole or part for their pro-deposition behaviour.

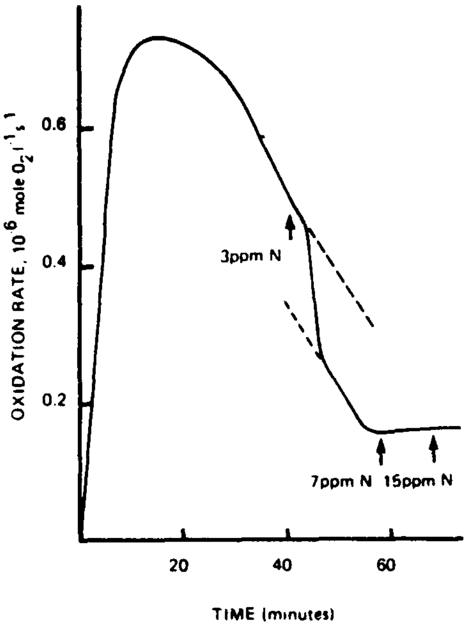

FIG. 3 – The oxidation trace of a sweetened Jet A–1 (Fuel C) with consecutive injections of nitrogen as 2,5 dimethyl pyrrole

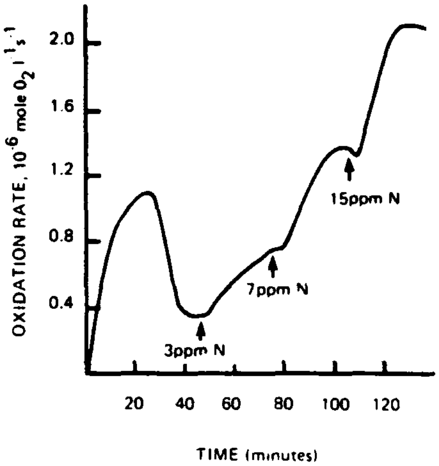

FIG. 4 – The oxidation trace of a sweetened Jet A–1 (Fuel C) with consecutive injections of nitrogen as 2,4,6 trimethyl pyridine

(b) Acidic compounds.

The chosen model compounds may be divided into three groups; strong acids, weak acids and phenols. To rank the deposition tendencies of these species in the JFTOT, a common doping rate of 100mg/l was chosen. This concentration level is reasonable in terms of the amounts of total acids extracted (30 - 300 mg/l) from fuels via ion-exchange chromatography (see later).

The summarised results for oxidation and deposition behaviour (Table 3) show clear distinctions among the three classes, and some level of agreement between the two types of measurement. Phenols were antioxidant and showed little tendency to cause deposition; the weak acids were antioxidant and were moderately pro-deposition; the strong acids were pro-oxidant and strongly pro-deposition.

Table 3

Summarised JFTOT carbon deposit data and flask oxidation results for model acid compounds doped into a Jet A-1 fuel

Acid compound doped at 100 mg/l	JFTOT carbon deposit (μg) (FUEL A)	Flask oxidation Result (FUEL A)
Base fuel	10	-
2,6 Dimethyl phenol	14	mild antioxidant
3,5 Dimethyl phenol	15	N.D.*
Hexanoic acid	27	N.D.
4-Methyl pentanoic acid	30	N.D.
Octanoic acid	31	N.D.
Hexahydro benzoic acid	19	antioxidant
Cyclohexyl acetic	15	N.D.
Benzoic acid	33	N.D.
Ethane sulphonic acid	225	pro-oxidant
p-toluene sulphonic acid	103	N.D.

* Not determined

Examining each class in finer detail, the antioxidancy of 2,6 dimethyl phenol is illustrated by its effect on the oxidation trace of Fuel A (Figure 5). Injection of the phenol at 100 mg/l results in an 8% reduction in oxidation rate, a further injection at 300 mg/l results in a 9% reduction. This behaviour is explained by recourse to the radical oxidation mechanism (see experimental section), since phenols and, in particular, hindered phenols can act as radical inhibitors, thus reducing the chain length, ℓ , in equation 1. The chain length cannot be reduced beyond a certain minimum value thus explaining the reduced efficacy of the second phenol injection. However in spite of this antioxidancy it is also observed that the phenols produce a very low level of deposition over that from the base fuel. Since phenols have been implicated in deposit production(10) within the context of storage stability via oxidative coupling reactions, this behaviour is by no means inconsistent.

The antioxidancy of the weak acid, cyclohexyl carboxylic acid is illustrated in Figure 6. It should be emphasised that this is not arrived at via the same mechanism as the phenol. Weak acids are capable of catalysing the destruction of hydroperoxides (an oxidation intermediate) to non-radical products, thus reducing a major source of radicals; in terms of equation 1 the term e is reduced. It would seem plausible that the deposition tendency of weak acids is attributed to catalysis of the second stage of the degradation mechanism(11) (see Figure 1), in much the same way as in the storage stability context.

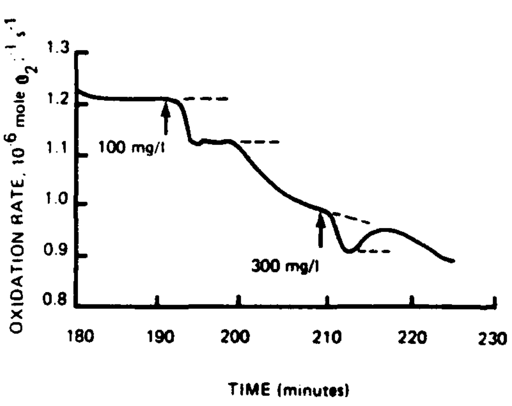

FIG. 5 – The oxidation trace of a hydrotreated Jet A–1 (Fuel A) with consecutive injections of 2,6 Dimethyl phenol

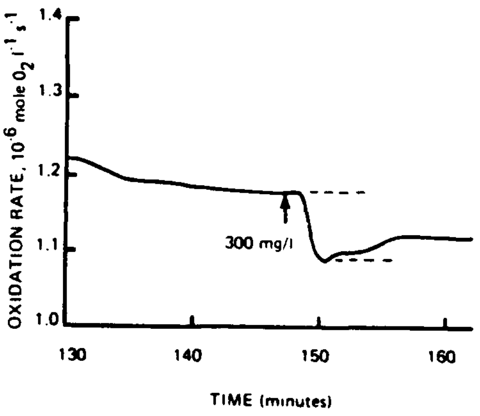

FIG. 6 – The oxidation trace of a hydrotreated Jet A–1 (Fuel A) with injection of a model acid, Cyclo hexyl carboxylic acid

The strong acid, ethane sulphonic, showed a strong pro-oxidant action within the flask test. The explanation of this behaviour is less clear-cut than the other two classes, one possibility is that the acid itself may be a source of radicals.

(c) Sulphur compounds.

Table 4 summarises the oxidation and deposition characteristics of the chosen model sulphur compounds. These encompass three structural types: thiophenes, monosulphides and disulphides. Flask oxidation testing of two sulphur compounds (n-hexyl sulphide and phenyl disulphide) doped into Fuel D indicate that they impart a gradual inhibitory action (antioxidancy) developing over 30 minutes (Figure 7). Two plausible explanations of this response are offered in the literature. Firstly, Koelwijn and Berger(12) have shown that sulphenic acids (a product of sulphide oxidation) are active radical scavengers. Other workers(13) have implicated SO_2 in the acid catalysed destruction of hydroperoxides to non-radical products. More extensive flask oxidation testing would be required to justify either mechanism.

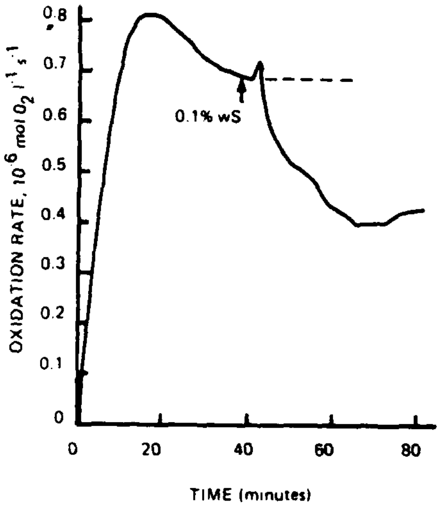

FIG. 7 – The oxidation trace of a sweetened Jet A–1 (Fuel D) with injection of Sulphur as diphenyl disulphide

Table 4

Summarised JFTOT carbon deposit data and flask oxidation results for model sulphur compounds doped into Jet A-1 fuels

Sulphur compound doped at 0.1 %wS	JFTOT carbon deposit (µg) (FUEL B)	Flask oxidation Result (FUEL D)
Base Fuel	37	-
2 Ethylthiophene	81	N.D *
Benzothiophene	68	N.D
n-hexyl sulphide	70	Antioxidant
n-hexyl disulphide	188	Antioxidant
Benzyl disulphide	134	N.D.
Phenyl disulphide	154	N.D.

* Not determined

Within the JFTOT all compounds were ranked at a common doping rate of 0.1%w S in Fuel B, a realistic level for a sweetened fuel. All compounds promoted deposition (Table 4). Any antioxidancy (as described above) would clearly be irrelevant in view of the short fuel residence time within this tester (13 seconds). Now, as we know, oxidation drives fuel thermal degradation, therefore the sulphur compounds must be forming deposits by reacting with oxidation products/intermediates, e.g. hydroperoxides, that is, sulphur compounds act in the second stage of the simplified degradation mechanism (Figure 1). The deposition activities of these sulphur compounds are broadly in line with their chemistries; the disulphides are the most active and the ring bound sulphur (thiophenes) the least active.

INTERACTIONS BETWEEN THE COMPOUND CLASSES - Our earlier work has indicated the importance of interactions between polar compounds in promoting deposition. These ideas have been pursued in this current study by assessing the deposition within the JFTOT of three classes of pairwise interactions:

- nitrogen/acid
- nitrogen/sulphur
- Acid/sulphur

All these doping experiments were performed with the hydrotreated fuel (Fuel A). The results are displayed in Tables 5 - 7, together with the notional amount of deposit predicted by straightforward summation of the individual contributions of each pair. A comparison of these theoretical values with the actual carbon deposit weights provides a measure of any degree of enhancement resulting from interactions. These figures are displayed in the final column of the tables as percentages.

(a) Nitrogen/Acid

All model nitrogen compounds acted antagonistically with the one model acid (hexanoic) to yield deposits greater than the sum of the two constituents (Table 5). Just as the deposition activity of the nitrogen compounds differed between the two chemical classes, the degree of antagonism followed a similar trend. Thus a high level of interaction (50%) is seen for the pyrole species whereas the pyridines displayed a lower level (6 - 24%). This antagonistic behaviour of the pyroles can be accounted for in terms of acid catalysis of coupling and substitution reactions (i.e. deposit precursors). In the case of pyridines, since they act to increase oxidation, more oxidation products will be available to be acid catalysed in the production of deposits. An alternative explanation would be the production of acid-pyridine salts.

Table 5

JFTOT carbon deposit data for the interaction of one model acid, hexanoic acid, with the model nitrogen compounds

Nitrogen compound doped at 40 ppm N	JFTOT carbon deposit (μg)			
	Nitrogen Alone	Nitrogen + Acid Expt.*	Nitrogen + Acid Theory*	% Increase over theory
None (Base Fuel)#	10	27	-	-
Indole	201	331	218	51.8
2,5 dimethyl pyrole	103	180	120	50.0
Quinoline	44	66	61	8.2
2,4 Dimethyl pyridine	48	69	65	6.2
3,5 Dimethyl pyridine	41	72	58	24.1
2,4,6 Trimethyl pyridine	45	76	62	22.6
5 Ethyl 2 methyl pyridine	58	ND$	75	ND

* Hexanoic acid doped to 100 ppm
\# Fuel A
$ Not Determined

(b) Nitrogen/Sulphur

With the exception of one pyridine (2,4,6 trimethyl pyridine) there is no significant antagonism between these two compound classes; the majority of results (Table 6) would even indicate a synergistic interaction (i.e. experimentally determined deposits are less than expected). This result is in broad agreement with an earlier investigation by Amos and two separate degradation mechanisms are occurring independently of each other, (i) oxidation product + nitrogen compounds -> deposits and (ii) oxidation products + sulphur compounds -> deposits.

At this juncture, it is worth pointing out that the JFTOT has limitations when assessing compound interactions. Firstly, interactions can occur within the fuel reservoir resulting in deposits on the pre-filter. The net consequence is a loss of polar material reaching the test section. Secondly the current method of assessing tube deposit weight ignores any enhanced deposition which may occur on the test-filter downstream of the test section. For example, the testing of 2,5 dimethyl pyrole with phenyl Knight(14), who rated polar doped fuels using an accelerated storage test and the JFTOT with TDR rating. Antagonistic interaction was seen in the accelerated storage test, but not within the JFTOT. The implication is that disulphide gave rise to a large deposit on the test filter, requiring it to be bypassed 15 minutes into the test. Thus the derived test section deposit weight 86μg is an underestimate and the -32.2% decrease in expected weight is not a true reflection of any interaction.

Table 6

JFTOT carbon deposit data for the interaction of one model sulphur compound, phenyl disulphide, with the model nitrogen compounds.

Nitrogen compound doped at 40 ppm N	JFTOT carbon deposit (μg)			
	Nitrogen Alone	Nitrogen + Sulphur Expt.	Nitrogen + Sulphur Theory*	% Increase over theory
None (Base Fuel)#	10	59	-	-
Indole	201	218	250	-12.8
2,5 dimethyl pyrole	103	86	152	-32.2
Quinoline	44	101	93	8.6
2,4 Dimethyl pyridine	48	72	97	-25.8
3,5 Dimethyl pyridine	41	81	90	-10.0
2,4,6 Trimethyl pyridine	45	127	94	26.0
5 Ethyl 2 methyl pyridine	58	91	107	-9.3

* Phenyl disulphide doped to 0.1 %wS
\# Fuel A

(c) Acid/Sulphur

Table 7 would indicate that both phenols and weak acids are capable of interacting antagonistically with a sulphur compounds, in particular, phenyl disulphide. The results confirm our earlier work(2) with fuel acid extracts. The synergistic interactions seen with the strong acids is again attributed to shortcomings of using the JFTOT. Considerable material was seen to build up on the reservoir pre-filter due to interactions between the species in the cold.

Table 7

JFTOT carbon deposit data for the interaction of one model sulphur compound, phenyl disulphide, with the model acid compounds.

Acid compound doped at 100 mg/l	JFTOT carbon deposit (μg)			
	Acid Alone	Acid + Sulphur Expt	Acid + Sulphur Theory*	% Increase over theory
None (Base Fuel)#	10	59	-	
2,6 Dimethyl phenol	14	78	63	23.8
3,5 Dimethyl phenol	15	71	64	10.9
Hexanoic acid	27	109	76	43.4
4-methyl pentanoic acid	30	129	79	63.2
Octanoic acid	31	84	80	5.0
Hexahydro benzoic acid	19	94	68	38.2
Cyclohexyl acetic acid	15	113	64	76.6
Benzoic acid	33	ND$	82	ND
Ethane sulphonic acid	225	107	274	-60.9
p-toluene sulphonic acid	103	134	152	-11.8

* Phenyl disulphide doped to 0.1 %wS
\# Fuel A
$ Not Determined

RIG PREDICTIONS FROM POLAR COMPOUND CONCENTRATIONS - The principal Shell Research rig for simulating fuel degradation in a realistic environment, the STHTR(7), has been described in the experimental section. A major drawback of this, and similar rigs, is that to simulate problems which may occur only after thousands of hours of operation, very large fuel samples (1800 litres) are required. It is clearly necessary to be able to predict fuel thermal stability in engine components via small-scale accelerated tests. This task notionally falls to the specification test, the JFTOT, but in the past we have considered three alternative small-scale predictors:

1. JFTOT breakpoint (Bp): defined as the temperature at which a defined level of degradation occurs
2. Radical initiation rate (R_i) (via a blown oxidation test)
3. Fuel sulphur content (S)

Our past studies(2) of the deleterious effects of trace polar species on fuel stability led us to consider the use of polar compound concentrations, and in particular, fuel sulphur content, as indices of thermal stability. However, following our more recent studies of acid species, we have considered a new predictor, fuel total acid content (TAC). We have defined the total acid content of a fuel as the acid fraction yield (in mg/l) from ion-exchange chromatography of a 1 litre sample. The fraction obtained in this way encompasses all acid types from the strong sulphonic species through the weaker carboxylic acids to the phenols.

A statistical analysis of this new predictor has encompassed all the major fuel processing types, i.e. sweetened, hydrotreated and hydrocracked kerosines. The thermal stabilities of these fuels were measured in the STHTR and the data were correlated with the following analytical properties:-

1. Total acid content (TAC) by IEC
2. Fuel sulphur content
3. A combined parameter of sulphur and acid content

Figures 8(a) and 8(b) illustrate correlations, for a subset of the data, i.e. the straight run fuels. Both acid content and sulphur content are seen as good predictors of thermal stability. However, the graphs show that acid content is the better of the two,with fewer points lying away from the regression line and the 95% confidence lines being much tighter. The

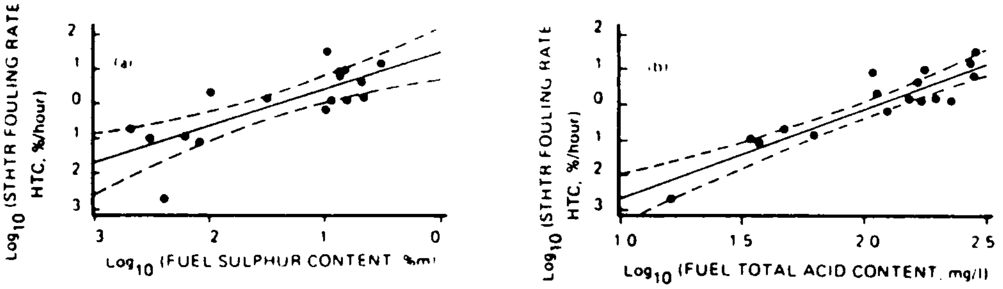

FIG. 8 – The correlations between fouling rates in an oil cooler and (a) fuel sulphur content, (b) fuel total acid content by IEC, using a dataset containing sweetened and hydrotreated fuel components only

Table 8

Results of statistical analyses of correlations between STHTR, fuel sulphur content and total acid content for a group of 17 fuels, sweetened and hydrotreated types only

DEPENDENT VARIABLE	INDEPENDENT VARIABLE	MEAN SQUARE ERROR	CORRELATION CONFIDENCE, %	F VALUE	INTERCEPT ± 1 STANDARD ERROR	GRADIENT ± 1 STANDARD ERROR
$\log_{10}$(HTC)	$\log_{10}$(S)	0.46	99.97	21.44	1.4 ± 43%	1.1 ± 22%
$\log_{10}$(HTC)	$\log_{10}$(Acid)	0.20	99.99	67.98	-5.2 ± 12%	2.5 ± 12%
$\log_{10}$(HTC)	$\log_{10}(S^a Acid^b)$	0.22	99.99	31.75	-5.0 ± 31%	0.03 ± 1050% (S) 2.5 ± 24% (Acid)

statistical and regression parameters (Table 8) confirm these observations, e.g. errors in the gradients are 22% for the sulphur correlation and 12% for the acid correlation. However, considering the entire dataset (all fuel types), the corresponding graphs and statistics (Figures 9(a) and (b), Table 9), reveal that the correlation with sulphur content is not nearly as good when the hydrocracked fuels are included, yielding a 33% error in the regression gradient. In contrast, the correlations with total acids show only a minimal increase in scatter, the error in the regression gradient

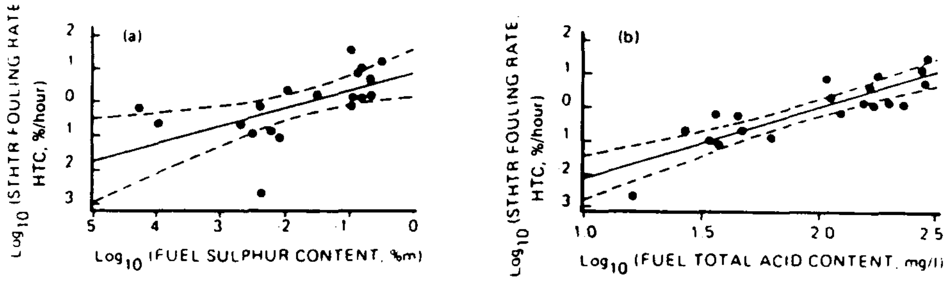

FIG. 9 – The correlation between fouling rates in an oil cooler and (a) fuel sulphur content, (b) fuel total acid content by IEC, using a dataset containing sweetened, hydrotreated and hydrocracked fuel components

Table 9

Results of statistical analyses of correlations between STHTR, and other measures of thermal stability for a group of 20 fuels, including sweetened, hydrotreated and hydrocracked types.

DEPENDENT VARIABLE	INDEPENDENT VARIABLE	MEAN SQUARE ERROR	CORRELATION CONFIDENCE, %	F VALUE	INTERCEPT ± 1 STANDARD ERROR	GRADIENT ± 1 STANDARD ERROR
$\log_{10}$(HTC)	$\log_{10}(R_1)$	0.78	93.86	3.98	-0.22 ± 94%	0.63 ± 50%
$\log_{10}$(HTC)	$\log_{10}$(BP)	0.68	98.61	7.43	32.0 ± 37%	-13.0 ± 37%
$\log_{10}$(HTC)	$\log_{10}$(S)	0.63	99.31	9.30	0.79 ± 43%	0.51 ± 33%
$\log_{10}$(HTC)	$\log_{10}$(Acid)	0.26	99.99	49.2	-4.2 ± 14%	2.1 ± 14%
$\log_{10}$(HTC)	$\log_{10}(S^a Acid^b)$	0.24	99.99	26.88	-5.7 ± 21%	-0.24 ± 71% (S) 2.7 ± 18% (Acid)

increasing from 12 to 14%. Thus it is seen that when compared to fuel sulphur content (and the other parameters within Table 9):

- TAC is a superior predictor of thermal stability
- TAC is more universally applicable

Both sets of statistics (Tables 8 and 9) show that there is no virtue in considering a combined analytical parameter of the form $S^a Acid^b$, because the parameter would be no better than using TAC alone. In addition there is a large error associated with the index a. However the values a and b are significant in that they show that there is a very strong dependence of fuel instability on TAC (b = ca. 2.5) when compared to fuel sulphur content (a = ca. 0). Thus from a manufacturing viewpoint there is more merit in reducing a fuel's acid content than reducing the sulphur content to improve product quality.

Mechanistically, one can interpret an index b of 2.5 as indicating that two acid molecules are involved in the rate determining step of deposit formation, or that one acid molecule catalyses the degradation of another. This would be in accord with Hazlett's work which indicated that strong and weak acids catalysed the degradation of fuel in storage(11). Other work(10) by the same author indicated that phenols produce deposits via oxidative coupling. Thus all three acid fractions are seen as important.

Additionally, we have demonstrated that there is a significant correlation between fuel acid and fuel sulphur content and therefore it could well be argued that sulphur content is no more than a marker for fuel acid content. However, our polar compound doping studies have shown that these compounds are deleterious in their own right. Nevertheless, the superior statistics of the TAC parameter together with the relative values of the indices a and b would suggest that TAC is a more fundamental predictor.

Future work is geared towards an understanding of the correlation by resolving the relative importance of the three acid fractions.

CONCLUSIONS

The Shell flask oxidation test provides a convenient technique to discern how polar compounds perturb free radical oxidation kinetics during thermal degradation. Similarly, despite certain limitations of the JFTOT, carbon deposit determinations within this device have proved to be a useful small scale technique to assess and rank fuel deposition tendencies. Our approach of using both these small scale testers in parallel studies has given a clearer picture on where polar compounds fit into the overall degradation scheme, particularly whether their involvement is in radical oxidation, deposition or both.

Using model compounds, we have confirmed the interaction in deposit production seen between acid and sulphur species, and have demonstrated the existence of interactions between nitrogen and acid species. The levels of some interactions would suggest they are as important as individual compound activities when determining the mechanisms of fuel thermal instability.

A new small-scale predictor of thermal stability, TAC, the total acid content of a fuel derived from ion-exchange chromatography. It has proved to be the best small-scale predictor to date of fuel performance in the Shell oil-cooler rig (STHTR).

ACKNOWLEDGEMENTS

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THE ROLE OF A METAL DEACTIVATOR IN IMPROVING THE THERMAL STABILITY OF AVIATION KEROSINES

[#47]

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ABSTRACT

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

INTRODUCTION

The use of aviation fuel as an engine and airframe systems heat sink, together with the fact that certain components of an aircraft fuel system are located in regions of high ambient temperature, may well result in the fuel thermally degrading and forming deposits. Such deposits within critical engine components, e.g. heat exchangers and fuel controller surfaces and clearances, will ultimately impair the efficient and safe operation of the engine and, in addition, result in a need for the premature overhaul of components.

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* Sold under the proprietary name of DuPont DMD No. 2

The causes behind the thermal instability of fuel are best explained in the form of a two stage mechanism. In the initial stage, heat promotes the liquid phase oxidation of the fuel via a free radical oxidation mechanism. Thereafter, intermediates from this oxidation react with trace fuel components, notably polar compounds (e.g. nitrogen and sulphur containing species), to produce insoluble lacquers and deposits within the fuel system. Thus it is seen that any technique to inhibit the first or second stage of reaction will be beneficial to thermal stability. In this respect, the initial liquid phase oxidation is strongly catalysed by trace metal species within the fuel. These species may enter the fuel from a variety of sources, as constituents of the original crude, as a result of refinery catalyst carry-over and via pipelines and storage tanks. Good quality control and housekeeping will minimise trace metal contamination, but an alternative or joint course of action would be the use of fuel additives. The principal aviation fuel specifications (DERD 2494 and ASTM D1655) permit the use of up to 5.7 mg/l (active) of Dupont MDA* to improve fuel thermal stability. This additive is claimed to act by chelating dissolved catalytic metals such as copper or iron, thereby reducing (deactivating) their catalytic influence. This paper describes research which not only investigates the effect of MDA in its claimed role as a metal chelator, but in addition and more significantly, assesses the role of MDA in realistic engine fuel system environments and within the specification test.

EXPERIMENTAL

The experimental techniques employed in these current studies may be divided into three classes:-

- Realistic large scale simulations of engine components
- Specification testing - the JFTOT
- Fundamental mechanistic studies

Since all the techniques have been fully described elsewhere, only brief descriptions are offered.

(i) Realistic simulations - The two rigs cited in this work are the single-tube heat-transfer rig (STHTR) (1),# used to assess fuel fouling of oil-coolers and the injector feed-arm rig (IFAR) (2), which measures burner-stem fouling.

Within the STHTR (1), the fuel undergoes three stages of heating to simulate heating from those sources encountered in an aircraft fuel system:-

- Fuel tank heating (aerodynamic heating, fuel transfer/recirculation)
- Heating from hydraulics/avionics/environmental system heat exchangers
- Engine oil-cooler (i.e. the test heat-exchanger)

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* N,N'-disalicylidene 1,2 - propane diamine

\# Numbers in parentheses refer to the literature citations at the end of this paper

Dimensions and flows are realistic, but the test is accelerated by using higher temperatures (190 to 240°C fuel outlet temperature) to ensure a measurable deposit within the test heat-exchanger. Degradation is monitored via the reduction in heat-transfer coefficient of the test element. These fouling rates are then presented, in an Arrhenius fashion versus, rig temperature to permit the ranking of fuels. A complete fuel characterisation requires an 1800 litre sample.

The IFAR (2) employs four full scale burner stems and requires 50,000 litres of fuel per test. The build-up of deposited carbon and the resulting increase in stem inner wall temperature allow the fuel degradation to be measured. In common with the oil-cooler rig, conditions are accelerated, in this case via a high (i.e. 165°C) fuel inlet temperature to the feed-arms. The requisite feed-arm wall temperatures (ca. 300°C) are achieved using a fluidised sandbath at 540°C to simulate the hot air downstream of the HP compressor.

(ii) Specification testing - The stability of fuels within the JFTOT is determined by their propensity to lacquer a heated specimen tube and for their decomposition products to block a filter. For specification purposes, the hottest temperature on the tube is controlled to 260°C for 2.5 hours. To pass the test, the tube lacquer colour must not be darker than a specified limit and the filter pressure drop should not exceed 25mm Hg. This results in a go/no-go specification test. However, for research purposes, the concept of a Breakpoint Temperature enables the JFTOT to rank fuels, the Breakpoint being the highest tube temperature at which both lacquer colour and pressure drop criteria are still fulfilled. At Shell Research, fuels may also be ranked and assessed by determining the weight of carbon deposited on the tube from a single severe test (350°C tube temperature) (3). This technique removes the subjective nature of the lacquer colour assessment and allows single test determinations. A single test requires a sample size of 600cc.

(iii) Fundamental mechanistic studies - The Shell Research Flask Oxidation test (4) is used to investigate the liquid phase oxidation kinetics of a fuel, i.e. the initial stages of fuel thermal degradation. The technique comprises a blown oxidation test run at elevated temperatures and requires a sample size of 400cc.

TEST FUELS - Details of test fuels in the following sections will be found in Table 1.

Table 1

Properties of test fuels

Property		Fuel A	B	C	D	E	F	G	H	I	J
Acidity, total	mgKOH/g	0.0015	0.003	0.002	0.002	0.006	0.004	0.001	0.001	0.001	[illegible]
Aromatics	%v	19.5	20.0	19.0	18.0	19.9	21.1	17.4	19.2	17.5	[illegible]
Olefins	%v	0.8	<0.5	0.2	0.5	0.1	1.45	0.3	0.3	0.5	0.5
Sulphur, total	%w	0.11	0.17	0.03	0.07	0.016	0.008	0.13	0.03	0.20	[illegible]
Sulphur, Mercaptan	%w	0.0001	0.0003	0.0001	0.0005	0.0004	0.0005	[illegible]	0.0003	[illegible]	[illegible]
Distillation											
10% recovered,	°C	182	173	174	159	179	185	164	172	165	177
20% recovered	°C	186	185	182	177	187	191	170	181	172	175
50% recovered,	°C	201	207	204	200	209	204	190	203	194.5	198
90% recovered	°C	225	235	238	236	245	230	228.5	230.5	239	228
F.B.P.	°C	261	252	256	254	267	244	259	259	263	254
Density @ 15°C,	kg/l	0.8035	0.8055	0.8030	0.8030	0.8089	0.8048	0.7873	0.8129	0.7930	0.8020
Freezing point	°C	-50.0	-48.0	-48.0	-48.5	-49.0	-48.0	-51	-54	-48.5	-47.5
Smoke point,	mm	26.0	22.0	23.0	23.0	23.0	23.0	26.0	23.0	25.0	22.0
Thermal stability											
JFTOT pressure rise,	mmHg	0	0	0	0	0	0	0	0	1	0
Tube colour code		0	1	1	1	0	0	1	1	1	1
Existent gum,	mg/100 ml	1.3	0	0	0	0	0	1.0	<1	<1	0
Additives											
Antioxidant,	mg/l	0	0	0	0	19.1	0	0	0	0	0
Antistatic,	mg/l	0.8	0.8	1.0	0.8	0.47	-	N.D.*	N.D	1.12	2.3
Metals											
Copper,	µg/l	10	20	2	10	<2	<2	<2	<2	<5	2
Iron,	µg/l	-	-	10	5	<5	<5	N.D.	<5	2	-

N.D. Not determined

RESULTS AND DISCUSSION

MDA AS A METAL CHELATOR - In order to prove the mode of action of MDA as a metal chelator within the context of fuel thermal degradation, there is a requirement for an experimental system to measure the oxidation kinetics of a fuel. The Shell Research Flask Oxidation Test fulfils this role, insofar as it probes the radical oxidation kinetics of kerosines at temperatures similar to those found within an engine environment. The test allows measurement of the liquid phase oxidation rate of the fuel and thence the radical initiation rate (R_i) via a detailed knowledge of the radical chain mechanism; the latter rate is for the reaction:

$$\text{RH (fuel)} + O_2 \xrightarrow[\text{Rate } R_i]{\text{Catalytic metals}} R\cdot\ ,\ RO_2\cdot\ ,\ \text{etc}$$

In the context of MDA studies, the radical initiation rate is significant as this reaction step is metal catalysed. The total oxidation rate is related to the radical initiation rate via the expression:

$$v = \frac{(\ell + 1)R_i}{1 - 2e(\ell + 1)}$$

where R_i is the radical initiation rate, ℓ the kinetic chain length, and e the branching ratio for hydroperoxide intermediate destruction.

Using the Flask Oxidation Test, initial experiments with a sweetened fuel (B) which contained 20ppb of dissolved copper showed a 76% reduction in oxidation rate and a 78% reduction in initiation rate when excess (0.3 mg/l) MDA was added, proving that MDA was acting as a deactivator of the copper, and demonstrating the direct correspondence of oxidation and radical initiation rates. The studies proceeded by doping the same fuel to a total copper content of 80ppb and measuring its oxidation rate as a function of added MDA concentration. Figure 1 illustrates the results from this 'titration'. As progressive amounts of MDA are added, there is an increase in the concentration of copper chelated and thus a decrease in the active copper catalysing the production of radicals. The net result is a decline in oxidation rate as MDA is added to the fuel.

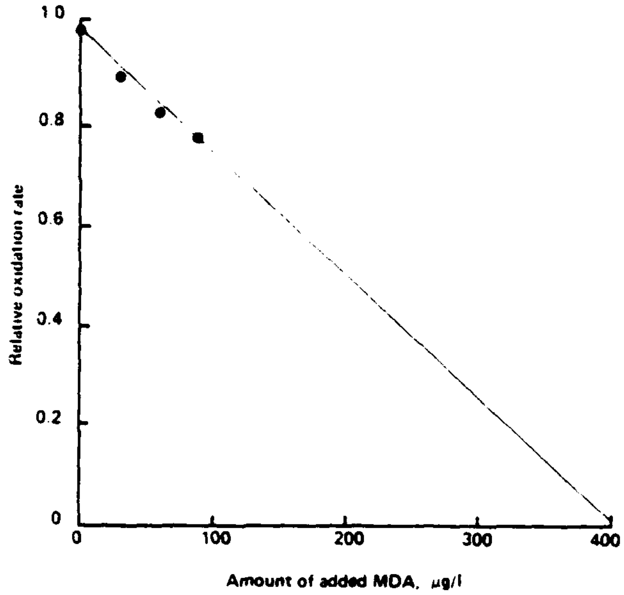

FIG. 1 – The response of fuel oxidation rate at 160°C to Metal Deactivator Additive concentration. Test fuel: Sweetened Fuel C doped to 80 ppb total copper

Extrapolating to zero rate when all the copper would be deactivated (with the assumption that copper catalysis accounts for all the radical initiation), the intercept (400 ppb MDA) indicates a chelation ratio of 5 : 1 w/w MDA : Cu or 1.1 : 1 mol/mol, which within experimental error, agrees with the 1.2 : 1 ratio claimed by DuPont.

It has been suggested that in addition to its chelation role, MDA may also act as an antioxidant via radical inhibition. However, in these experiments, only tentative evidence has been observed in the flask test and then only at the 10 mg/l concentration level, i.e. about twice the current specification maximum.

Thus, in summary, the Flask Oxidation Test has shown that MDA is a powerful metal deactivator acting in almost unity chelation ratio. Consequently, for fuels which contain no dissolved catalytic metals (e.g. hydroprocessed and some sweetened streams), we would expect -and indeed have found -no effect of MDA in the flask test, i.e. no predicted beneficial effect on thermal stability.

MDA IN A REALISTIC ENVIRONMENT - The Shell Research Single-Tube Heat-Transfer rig (STHTR) (1) is a realistic simulation of an engine fuel system designed to measure fuel degradation and fouling within an oil-cooler. In experiments to investigate metal catalysis of fuel degradation, there is a direct correspondence between the flask test and the STHTR, illustrated for Fuel C in Figure 2. Using the rig, experiments were performed to elucidate the effect of MDA on the fouling propensity of a suite of fuels. Fouling rates were measured for each fuel alone and doped with a low concentration of MDA (0.3mg/l), sufficient to chelate 50 ppb of copper. In essence because the sweetened fuels (A, B, C + 10ppb copper and D) within the suite all contained varying amounts of trace catalytic metal, they all showed varying benefits of MDA within the STHTR, as seen in Figure 3. Of great significance was the fact that Fuel B had its fouling rate reduced by 77%, i.e. an identical amount to the benefit seen in the flask test. Thus it is seen that at these low MDA concentrations where there is a one to one correspondence of MDA benefit in the flask test and the STHTR, the benefits in both cases can be ascribed to metal chelation. However as would be expected, the hydrotreated fuels showed no benefit from the additive due to their lack of catalytic metals.

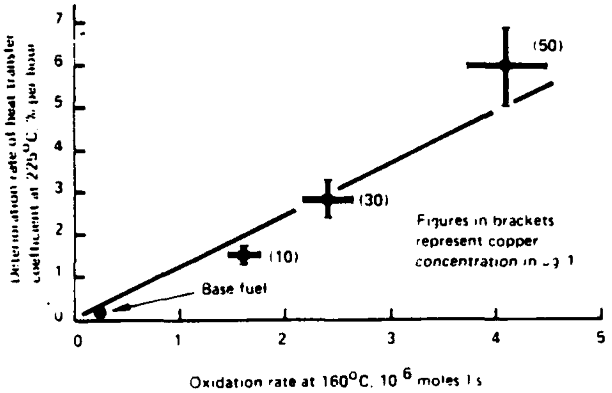

FIG 2 Effect of added copper on Fuel C performance in the STHTR and in flask oxidation tests

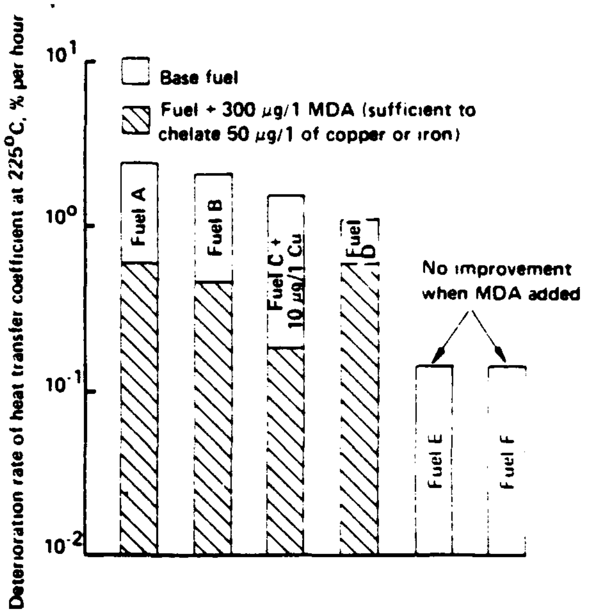

FIG. 3 – The beneficial effect of MDA in the STHTR. Fuels A-D: Sweetened, Fuels E & F: Hydroprocessed

MDA WITHIN THE SPECIFICATION TEST - Given these findings, parallel studies were performed within the JFTOT specification test, using the same MDA doping rate. As expected, the sweetened fuels which contain trace metal species, all gave an increase in the JFTOT breakpoint by 30°C or more. However, of great surprise was the increase in breakpoint of a hydrotreated (i.e. metal free) fuel (F) by 50°C to over 340°C. It is impossible for such an increase to have been caused by metal chelation and thus it was realised that MDA possesses an extra, and very powerful, action within the JFTOT over and above its action as a metal chelator. The remaining experiments reported in this paper were designed to elucidate this mechanism and the regimes over which it might operate.

MDA AS A METAL PASSIVATOR - The above differences observed with MDA in a realistic environment as opposed to the specification test, (where a benefit was observed for fuels even with no metals present) prompted further research using low metals content fuels. The use of Fuel G , a sweetened fuel with no dissolved catalytic metals allowed the elimination of all effects due to the metal chelating ability of MDA. This fuel was tested in the STHTR with increasing concentrations of MDA, i.e. 0, 0.3 and 5.7 mg/l MDA. The results, plotted in Arrhenius-type form in Figure 4, show that there is no discernible difference between the base fuel and the fuel doped to a low MDA concentration (0.3 mg/l) and this is completely in accord with the earlier STHTR experimentation. However, at 5.7 mg/l MDA there was a uniform five-fold benefit in the rig across all the temperatures. This response is attributed to passivation of the STHTR metal test section and, by inference, this same action is presumed to occur for the hydrotreated fuel (F) in the JFTOT, albeit at a markedly lower concentration of the additive. Thus, in the STHTR passivation would appear to be a function of MDA concentration as it is only found at high (>1 mg/l) concentrations. However, in the JFTOT, the passivation effect is evident even at 0.3 mg/l. Table 2 shows in a qualitative fashion the role of MDA (chelation/passivation) within each rig at different MDA concentrations. To quantify this discrepancy between rigs we have conducted flask, JFTOT and STHTR tests using a high (10 mg/l) MDA concentration in a sweetened fuel (H) containing 2 ppb Cu. The JFTOT performance was determined by measuring the weight of carbon deposited at on aluminium tubes 350°C and the STHTR data were acquired at a 225°C fuel outlet condition. The results (scaled relative to the base fuel, Figure 5) show that:

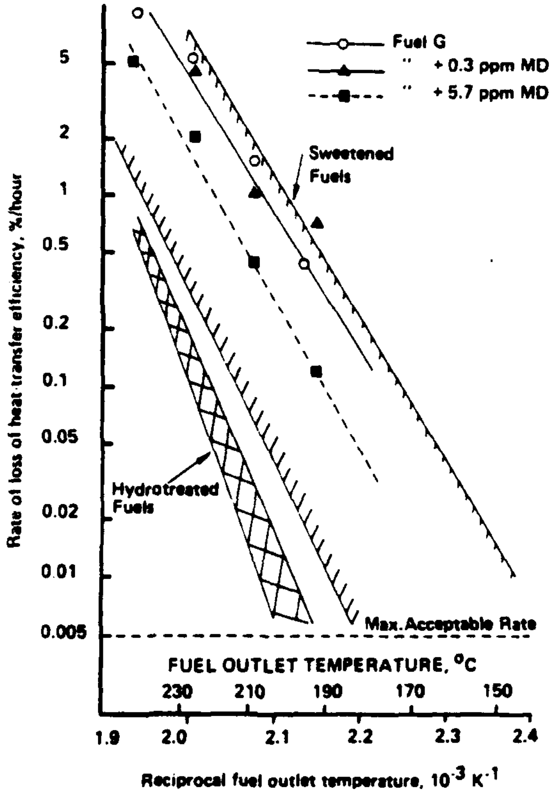

FIG. 4 – The lacquering rate of a test fuel in the STHTR as a function of test temperature. Data displayed in an Arrhenius-type form.

- In the flask test there was only an 8% benefit from MDA. This confirms the absence of any significant quantities of catalytic metals for MDA to deactivate
- In the STHTR there was a 40% reduction in fouling
- In the JFTOT fouling decreased by 74%

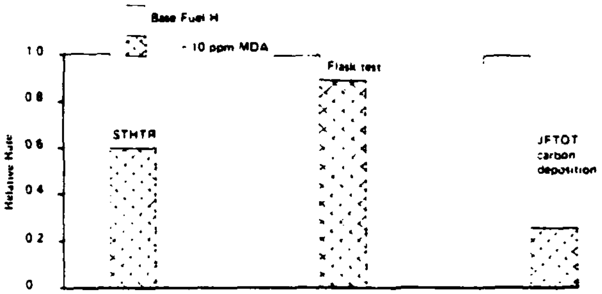

FIG 5 The influence of MDA on the behaviour of Sweetened Fuel H. STHTR operated at 225°C condition. Flask test at 160°C. JFTOT at 350°C to determine carbon deposit weight

Table 2

The role of MDA within fuel test rigs.

Rig	MDA concentration 0.3 mg/l	 5.7 mg/l
Flask Test	Metal Chelation	Metal Chelation
STHTR	Metal Chelation	Metal Chelation + Metal Passivation
JFTOT	Metal Chelation + Metal Passivation	Metal Chelation + Metal Passivation

N.B. Where no catalytic metals are present in the fuel only the effect of metal passivation will be present.

Moreover, in the JFTOT 10 mg/l MDA improved Fuel H's Breakpoint from 285°C to > 330°C; a value far better than that of any hydrotreated stream yet tested by Shell Research.

From these observations we therefore conclude that:

(i) MDA can reduce the severity of surface fouling in certain circumstances via a passivation-like mechanism
(ii) The JFTOT overresponds to the passivating action of MDA

THE LINK BETWEEN METAL PASSIVATION AND MDA OVERRESPONSE IN THE JFTOT - Having demonstrated that MDA possesses an action over and above metal chelation, the investigations were then directed towards an explanation of the different STHTR and JFTOT responses to passivation and, in particular, the overresponsiveness of the JFTOT.

A possible explanation for JFTOT overresponse to MDA has been suggested by results obtained in the Shell Research IFAR (2). Carbon deposition has been measured within simulated burner stems. The fouling is seen to occur in a number of distinct phases (illustrated in Figure 6). Initially, there is an induction period, characterised by slow deposition, as a monolayer of lacquer forms on the clean metal surface. Thereafter deposition accelerates to a near uniform rate for approximately 40 hours. Finally, the fouling rate gradually decays. For the base fuel (H) the induction period was approximately 10 hours; doped with 5.7 mg/l MDA, this period increased substantially to some 30 hours. It should be noted, however, that after the conclusion of the induction period the MDA had no further effect on the deposition rate, i.e. the uniform deposition rate after induction is identical for the base and the additive doped fuel, this consistent with this fuel containing no significant levels of catalytic metals. Consequently, this increase in induction period is attributed to the passivation by MDA of the clean surface of the model feed arms, whereas once a fouled surface has been generated, passivation ceases to be a factor.

These same broad features, of an initial slow deposition to produce a monolayer of deposit (induction period) followed by a faster deposition process on a lacquered surface, have now been observed in other rigs. Figure 7 illustrates the increase in deposition (monitored as increasing heat transfer coefficient) within the STHTR over a period of 60 hours using Fuel I. After ca. 20 hours there is a pronounced increase in deposition indicating the existence of the two distinct deposition regimes.

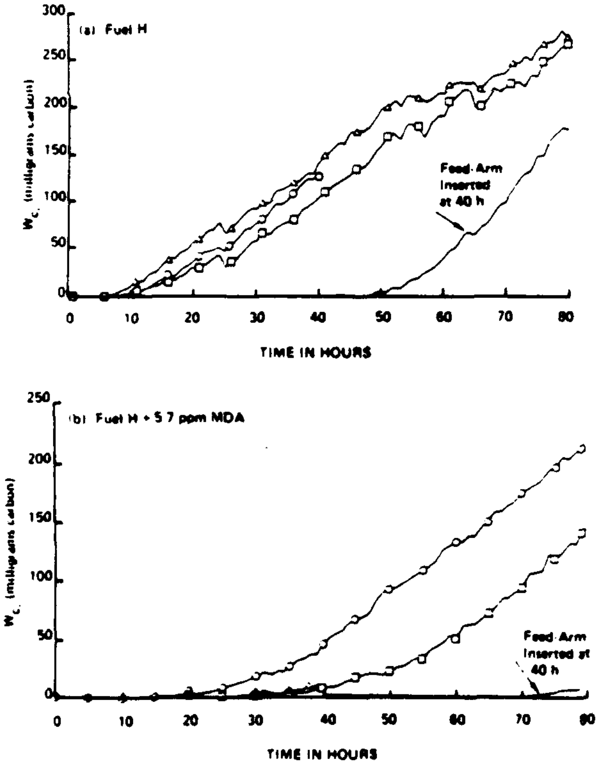

FIG 6 – Evolution of carbon deposition with test duration in the IFAR (a) Merox fuel (b) Merox fuel + 5 7 ppm MDA.
(Fuel inlet temp. 165°C Feed arm wall temp. 300°C)

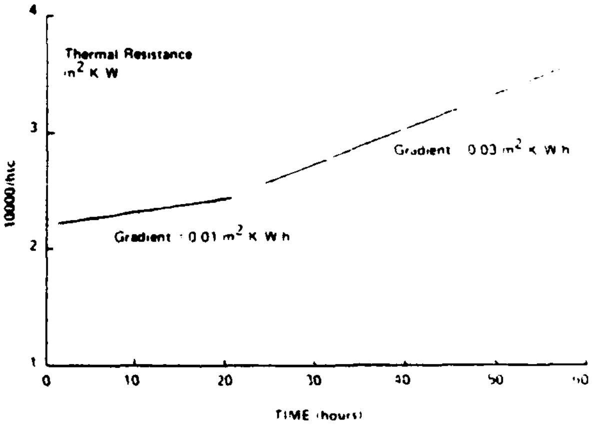

FIG. 7 – The effect of test duration on fouling rate in the presence of 5.7 ppm MDA – STHTR used at the 225°C condition with Fuel I

It is postulated that within the short time frame of a JFTOT test (2.5 hours) deposition will always remain within the first, slow deposition, regime (the induction period), where any passivation effect of MDA will be most noticeable. Unfortunately such a response would be most accentuated when measuring breakpoints as, by definition, these correspond to trace lacquer formation.

Experimental support for the above hypothesis has now been obtained by monitoring JFTOT carbon deposition on stainless steel specimens at 350°C as a function of test duration (Figure 8) (5). The graph illustrates plots for three concentrations of MDA:- (i) Base fuel (J); (ii) A low level of MDA, 0.06 mg/l -the minimum required to chelate any metals present; (iii) A high level of MDA, 5.7 mg/l (the specification limit), i.e. the additive in excess. The data from the separate plots are best interpreted in the form:-

$$\text{Deposit weight} = At^n$$

(where t = test duration, A and n are constants). Values of $n > 1$ indicate an acceleration of deposition with time. For both the base fuel, (i), and the minimum level of MDA (ii), identical curvatures are seen, namely $n = 1.7$. The absolute levels of deposition are different, naturally, reflecting the consequences of catalytic metal activity, i.e. for one the metals are active, for the other they are chelated. However, in complete contrast, at the 5.7 mg/l MDA level, (iii), there is a pronounced change in curvature to $n = 1.1$. This change is taken as an indication of metal passivation.

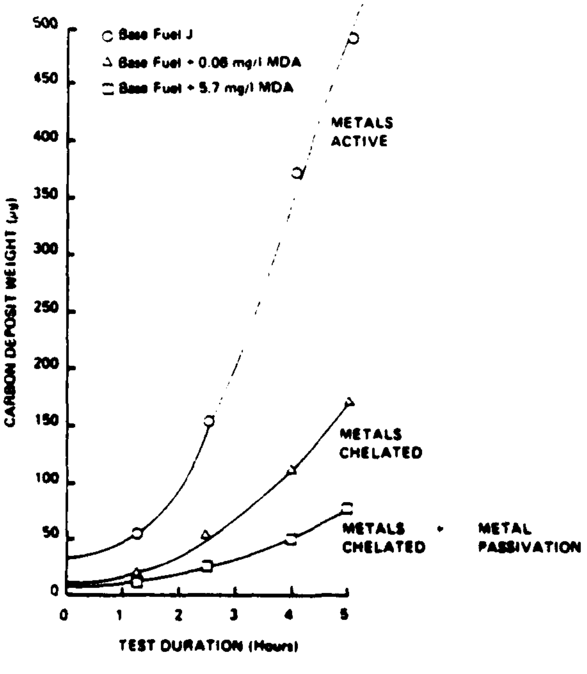

FIG. 8 – Carbon deposition versus test duration profiles for the JFTOT as a function of MDA concentration using Fuel J.

CONCLUSIONS

It has been demonstrated via a flask oxidation test that DuPont MDA acts to chelate and deactivate dissolved catalytic metals. This action also occurs in realistic rigs and confirms that MDA is an effective agent with which to overcome the deleterious effects resulting from metals (e.g. copper) contamination. The additive is also a surface passivator capable of delaying, but not preventing, the deposition of decomposition products on virgin metal surfaces. The JFTOT specification test, due to its short duration, responds particularly strongly to this passivating action such that even fuels containing no dissolved metals show a major benefit. However, as evident in Figure 5, the level of benefit from MDA in the JFTOT is unlikely to be reflected in service. Consequently, it is advisable to limit the use of MDA to those fuels whose thermal stabilities have deteriorated due to metals contamination. Certainly, as metals contamination should not occur during manufacture, the routine use of MDA within refineries to obtain ostensible improvements in JFTOT thermal stability, which may not be manifest in service, should be actively discouraged. To summarise:

- MDA is an effective deactivator of dissolved catalytic metals and provides a real benefit to fuel performance when such metals are present.
- MDA also acts as a surface passivator and is particularly effective in this role on clean metal surfaces in short duration testing such as in the JFTOT.
- The JFTOT overresponds to the benefits of MDA such that poor sweetened fuels doped with MDA appear to be better than the best hydrotreated fuels.

Consequently

- We recommend that MDA should only be used when fuels are known to be off-specification due to metals contamination: indiscriminate use to secure enhanced JFTOT performance should be proscribed.

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JET FUEL INSTABILITY: ORGANO-SULFUR HYDROPEROXIDE INTERACTIONS

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ABSTRACT

The role of organosulfur compounds and hydroperoxides on the oxidative stability of middle distillate fuels is not well understood. Differences in fuel composition, reaction surface, hydroperoxide concentration, dissolved oxygen and reaction temperature all contribute to the variation in observed results. In an effort to clarify this situation, we have examined the t-butyl hydroperoxide liquid phase oxidation of hexyl sulfide, dodecyl thiol, hexyl disulfide, substituted thiophenes, and thiophenol in benzene and a model fuel, tetradecane. The relationship between organo-sulfur compounds and the peroxidation of JP-5 have been studied under conditions of accelerated storage.

INTRODUCTION

The formation of solid deposits in middle distillate fuels has been a continuing problem in the utilization of these fuels. Deposits can plug nozzles, filters and coat heat exchanger surfaces. Deposit formation in fuels is triggered by autoxidation reactions. Although slight thermal degradation is known to occur in nonoxidizing atmospheres, the presence of oxygen or active oxygen species such as hydroperoxides will greatly accelerate oxidative degradation of fuels as well as significantly lower the temperature at which undesirable products are formed. The stability of middle distillate fuels is consequently dependent upon the nature of potential autoxidation pathways which can occur. Heteroatoms and ash have been found to comprise up to 40 percent of such deposits [1]. The sulfur content of these deposits has been found to vary from 0.3 to 9 percent [2-5]. Sulfur (0.4%, maximum allowable) is the most abundant heteroatom present in jet fuel. The source of sulfur in these deposits has been attributed to the participation of thiols (mercaptans), sulfides and disulfides [6]. In jet fuels that have been deoxygenated, sulfides and disulfides have been found to lead to increased solid formation [7]. By contrast, it has been demonstrated that sulfur compounds in lubricating oils act as antioxidants by decomposing peroxides [8].

The rates of reactions in autoxidation schemes are dependent on hydrocarbon structure, heteroatom concentration and speciation, oxygen concentration, and temperature [9-10]. Catalysts and free radical inhibitors can materially alter both the rate of oxidation and the product mix [10]. If sufficient oxygen is present, the hydroperoxide concentration will reach a high concentration. If the available oxygen is low, but the temperature raised, the hydroperoxide concentration will be limited by free radical decomposition. Under these conditions, fuel degradation can be associated both with hydroperoxide formation and decomposition. The detailed mechanism of hydroperoxide decomposition is complicated since free radicals are sensitive to the slight changes in their chemical environment.

This paper is concerned with the reaction between a primary autoxidation product, a hydroperoxide, and organosulfur compounds of the type known to be present in middle distillate fuels. Specifically, we examine the tert-butyl hydroperoxide oxidation of hexyl sulfide, dodecyl thiol, substituted thiophenes, and hexyl disulfide in both deaerated benzene and a model fuel, tetradecane, at 120°C. In addition, the relationship between organo-sulfur compounds and peroxidation of JP-5 was examined using model dopants added to JP-5 jet fuel and stressed under 65°C accelerated storage conditions. Samples were analyzed on a weekly basis for peroxides and sulfur compound concentration.

EXPERIMENTAL

Reagents. tert-Butyl hydroperoxide, tBHP, (90%), hexyl sulfide, dodecyl thiol, thiophene, benzothiophene, thiophenol and hexyl disulfide were obtained from Aldrich Chemical Co. They were distilled in vacuo to 99.9% purity. The solvents benzene (Aldrich Gold Label) and tetradecane (Fisher certified) were refluxed and distilled from calcium hydride. JP-5 fuel was a stable jet fuel supplied by a U.S. west coast refiner without antioxidant. It was filtered before use, but otherwise used as received.

Method. The reactions were carried out in sealed borosilicate glass tubes. The reagents (typically 3-9x10^{-4} mol of tBHP and 6x10^{-4} mol of sulfur compound in 0.6 ml of solvent) were weighed into 6 in. long, 1/4-in. o.d. Pyrex tubes closed at one end and fitted at the other with a stainless steel valve via a Swagelok (Teflon ferrules) fitting. The tube was attached to a vacuum system, cooled to 77K and subjected to several freeze-pump-thaw cycles. The tube was then subsequently flame-sealed below the valve. The ullage volume (0.30 ml) was kept constant for all runs. The deaerated samples were warmed to room temperature and immersed in a Cole-Parmer fluidized sand bath. The temperature was controlled by a Leeds and Northrup Electromax III temperature controller. The total pressure during each run was estimated to be less than 1 atm for the tetradecane solvent and 5.1 atm for the runs in benzene solvent. After the reaction period the sealed tube was quenched to 77K and opened.

Samples were heated for time periods of 15, 30, 60, 120 and 180 min except for those runs with the more reactive thiols (60 min maximum). A search of the literature gives a few examples of catalytic behavior with glass systems [11-12]. However, when a glass tube was partially filled with crushed Pyrex, thus increasing the surface area, the results at 120°C for the reaction time periods were not substantially altered.

The samples were analyzed by combined GC/MS (EI mode). The GC/MS unit consisted of a Hewlett-Packard Model 5710 GC, a H-P Model 5982A mass spectrometer, and a Ribermag SADR GC/MS data system. Also, a Finnigan Model 700 ITD coupled to a 5890A Hewlett-Packard GC and the Finnigan Data Reduction Program was employed. An all glass GC inlet system was used in conjunction with a 0.31 mm x 50 m SP-2100 fused silica capillary column for both MS systems.

A material balance was assessed for each compound. The major peaks of the chromatogram account for approximately 81 to 99% of the original compounds. The 81% was observed only for tBHP in runs with hexyl sulfide at long reaction times. These runs also formed many partially oxidized products. The very small peaks account for another 5 to 10%. The product distribution was repeatable to 2 to 3% for each component.

Accelerated Storage. The method has been described in detail elsewhere [13], but in brief tests were carried out in brown borosilicate glass bottles, 500 ml total capacity, capped with teflon liners, containing 300 ml of fuel per bottle. Stress tests were conducted at 65°C for eight weeks. Samples were analyzed weekly for peroxide concentration by a modified ASTM D3702-85. A Mettler DL20 automatic titrator was employed thus eliminating the need for a starch indicator. Sulfur concentration was monitored weekly with a Tracor 565 gas chromatograph equipped with a 0.31 mm x 50 m SP-2100 fused silica capillary column and a sulfur specific 700A Hall electrolytic conductivity detector. Samples were analysed in triplicate with an external standard.

RESULTS AND DISCUSSION

tBHP products. The mechanism of autoinitiated tBHP decomposition can be depicted by the following equations:

Self Initiation

$$\text{tBHP} \xrightarrow{120^{o}\text{C}} (\text{CH}_3)_3\text{CO}^{\cdot} + {}^{\cdot}\text{OH} \qquad \text{1)}$$

Propagation

$$(\text{CH}_3)_3\text{CO}^{\cdot} \xrightarrow{\text{beta scission}} (\text{CH}_3)_2\text{CO} + {}^{\cdot}\text{CH}_3 \qquad \text{2)}$$

$$(\text{CH}_3)_3\text{CO}^{\cdot} + \text{X-H} \xrightarrow[\text{abstraction}]{\text{hydrogen}} (\text{CH}_3)_3\text{COH} + {}^{\cdot}\text{X} \qquad \text{3)}$$

$$(\text{CH}_3)_3\text{CO} + (\text{CH}_3)_3\text{COOH} \xrightarrow[\text{abstraction}]{\text{hydrogen}} (\text{CH}_3)_3\text{OH} + (\text{CH}_3)_3\text{COO}^{\cdot} \qquad \text{4)}$$

Termination

$$2(\text{CH}_3)_3\text{COO}^{\cdot} \longrightarrow [(\text{CH}_3)_3\text{C}]_2\text{O}_2 + \text{O}_2 \qquad \text{5)}$$

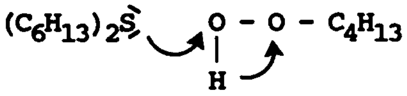
$$2\text{X}^{\cdot} \longrightarrow \text{X}_2 \qquad \text{6)}$$

The major product from tBHP when reacted with various classes of organosulfur compounds was t-butanol, equations 3) and 4), with yields up to 75%. Small amounts of acetone, equation 2) up to 3.5%, were also observed. The greater yield of t-butanol compared to acetone definitely shows that hydrogen abstraction was favored over cleavage under the conditions of this study. The increasing yield of acetone as reaction time increased, however, indicated that at long reaction times beta-scission was a viable competing process to hydrogen abstraction. Other products noted, 1 - 2%, from tBHP included: isobutylene, methane, and di-t-butyl peroxide. Methane resulted from a hydrogen abstraction by the methyl radical, equation 2), di-t-butyl peroxide from equation 5), and isobutylene from an acid catalyzed dehydration of t-butanol.

<u>Sulfide products.</u> The major product observed from the oxidation of hexyl sulfide by tBHP was hexyl sulfoxide. Its yield varied from 74.8% at 15 min to 85.3% at 30 min, gradually decreasing to 80.7% at 180 min of reaction. Other products included: hexyl sulfone, 1.2% at 15 min gradually increasing to 4.0% at 180 min; hexyl disulfide, 0.3% to 0.6%. Minor products included dihexyl thiosulfinate, 0.1%; hexanal, 0.2% at 15 min increasing to 0.3% at 60 min, decreasing to 0.2% at 120 min and disappearing at 180 min; hexene, 0.1% at 15 min, increasing to 0.3% at 120 min and decreasing to 0.2% at 180 min; and hexane, 0.1% at 15 min increasing to 0.4% at 120 min and decreasing to 0.2% at 180 min. Many trace products, yields less than 0.1%, were formed. Most of these products were partially oxidized substances that could not be readily identified by MS. An extensive discussion of the mechanism of formation for the entire product distribution can be found

elsewhere [14].

The hexyl sulfoxide could result from several mechanisms. The most likely mechanism however, would be the reaction of the tBHP itself with the hexyl sulfide followed by a rapid proton transfer and O-O bond rupture, equation 7), [15].



$$(C_6H_{13})_2S \; \underset{\displaystyle H}{\overset{}{O}} - O - C_4H_{13} \qquad 7)$$

Expansion of the sulfur valence shell is probable in the processes involved in this step. Another mechanism could involve the attack of an oxygen centered radical, i.e., peroxy on sulfur followed by a beta scission [16].

The resulting sulfoxide once formed is quite stable. The sulfoxide oxidation product, hexyl sulfone, varied in the present work from an initial 1.2% at 15 min to 4.0% at 180 min of reaction. This slight increase compared to the yield of hexyl sulfoxide at 180 min (80.7%) illustrates the resistance of an alkyl sulfoxide to oxidation by a hydroperoxide. The oxidation of a sulfoxide to a sulfone is believed to proceed by a mechanism similar to that for the sulfoxide formation.

Thiol products. The major product from the oxidation of dodecyl thiol by tBHP was dodecyl disulfide, 74.4% at 15 min increasing to 78.8% at 30 min and then decreasing to 74.1% at 60 min. Other oxidation products included: dodecyl sulfoxide, 2.3% at 15 min decreasing to 2.1% at 60 min; dodecyl sulfone, 0.9% at 15 min increasing to 1.7% at 60 min. Minor reaction products observed were: Dodecyl sulfide, 1.9% at 15 min decreasing to 1.4% at 60 min; dodecanal, 0.6% at 15 min increasing to 1.1% at 60 min; dodecane, 0.1% at 15 min increasing to 0.4% at 60 min; and trace (less than 0.1%) amounts of dodecyl thiosulfinate. In addition, small amounts of dodecyl sulfonic acid were observed. To determine this product, the solution was derivatized to the methyl ester and determined by solid probe MS.

The mechanism of thiol oxidation has been the subject of discussion for many years [17]. We support the thesis that the t-butoxy or peroxy radical generated from tBHP abstracts the thiol hydrogen , equation 8). Rapid dimerization, equation 9), then follows generating the major product dodecyl disulfide.

$$C_{12}H_{25}SH \; + \; t\text{-}C_4H_9O^{\cdot} \longrightarrow C_{12}H_{25}S^{\cdot} \; + \; t\text{-butanol} \qquad 8)$$

$$2\ C_{12}H_{25}S^{\cdot} \longrightarrow C_{12}H_{25}\text{-}S\text{-}S\text{-}C_{12}H_{25} \qquad 9)$$

Thiol in tetradecane. The reaction was similar both in benzene and tetradecane, but minor differences were found. The product slate, other than solvent products, was identical. Differences included slightly lowered yield of t-butanol in tetradecane, 72.1% vs 76.7% in benzene, while the yield of acetone 8.6% was increased from that observed in benzene. The major product dodecyl disulfide was formed in greater yield, 80.6% compared to 74.1% in benzene. Dodecyl sulfonic acid was also noted in this solvent. Products observed from tetradecane solvent participation were tetradecanones and tetradecanols. These were minor products and are reported as totals of all isomers, because the isomers elute in an overlapping pattern. Tetradecanones for a 60 min stress were 0.3% and the tetradecanols were found to be 0.6%. By contrast, no oxygenated products of the benzene solvent were observed.

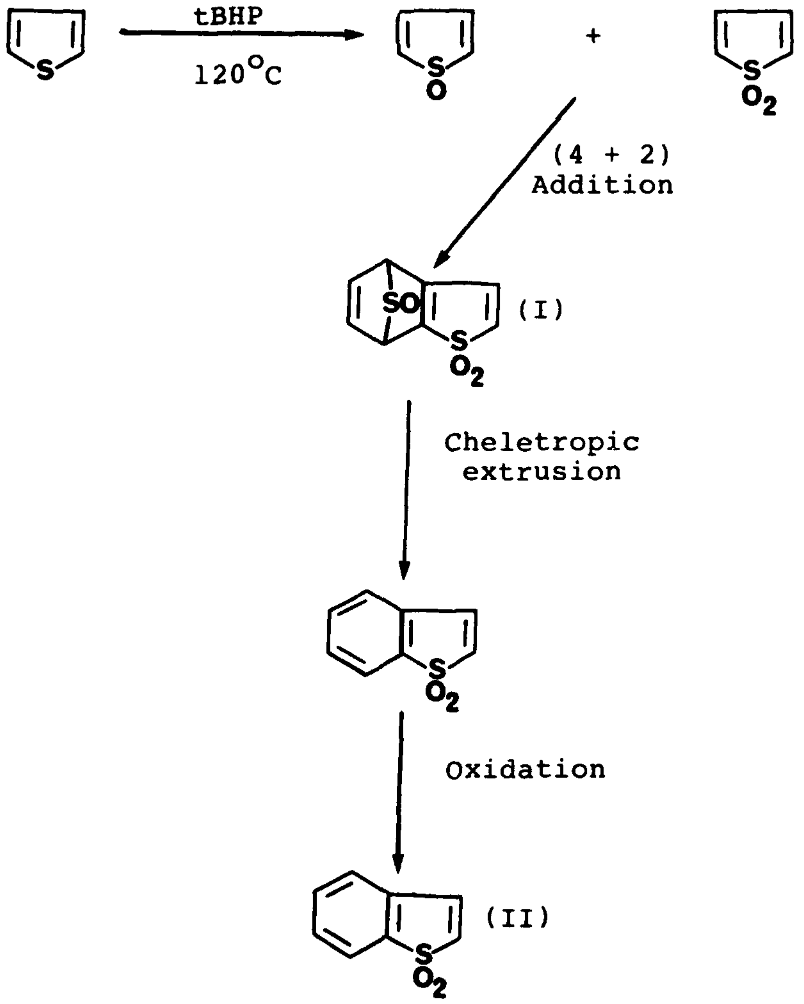
Thiophene products. Thiophene compounds investigated were thiophene, tetrahydrothiophene, 2,5-dimethyl thiophene and benzothiophene. Reactions with tBHP were conducted in benzene solvent. The reaction for thiophene with tBHP is illustrated in equations 10) - 12).

The oxidation of tetrahydrothiophene by tBHP gave the sulfoxide as the major product; at 15 min the yield was 13.8% increasing to 26.8% at 180 min. A mechanism similar to equation 7) would be predicted for the sulfoxide formation. From tBHP, t-butanol increased from 34.1% at 15 min to 68.6% at 180 min, acetone increased from 1.3% to 2.3% at 180 min. Other products included: tetrahydrothiophene sulfone, methane, isobutylene, and di-t-butyl peroxide. Thus this cyclic sulfide gave a product slate similar to an aliphatic sulfide although the yields were much lower.

Thiophene and its methylated analog do not yield simple, easy to identify products. In fact, no GC identifiable products were formed in any of the runs. Rather, an intractable water soluble solid results at all reaction times. Detailing the reaction mechanism for the thiophenes is further complicated in that the solid product itself is not thermally stable [16]. Products identified in the solid from both thiophene and 2,5-dimethyl thiophene included traces of the sulfoxide, the sulfone, and the water soluble Diels-Alder condensation products, 4:7:8:9-tetrahydro-4:7-sulphinyl thionaphthene 1:1-dioxide (I), and thionaphthene 1:1 dioxide (II), along with the 2,5-dimethyl analogs. Both products were identified by solid probe MS. Confirmation of both structures was by synthesis of the compounds and a comparison of their MS spectra [18]. The 2,5-dimethyl thiophene was more reactive than the thiophene as measured by thiophene disappearance.

The literature contains little information on thiophene oxidation especially in a radical environment [19-21]. The thiophene ring system can survive moderate oxidizing conditions. However, if the ring is attacked, it generally breaks down to oxalic or other substituted carboxylic acids with the sulfur being converted to sulfuric acid [22]. With tBHP, no evidence of ring opening was observed.

Benzothiophene was the least reactive, as measured by reactant disappearance, sulfur compound studied. At the end of a 180 min stress period >97% of the benzothiophene remained unreacted. In the presence of tBHP, benzothiophene yields minor amounts of the sulfone product and a trace of the sulfoxide product.



10)

11)

12)

<u>Thiol, olefin products</u>. The reaction of thiols with active olefins, such as styrene and indene was investigated with both oxygen and tBHP. For the styrene reaction with molecular oxygen and thiophenol the major product observed was the addition product, 1-phenyl-(2-phenylthiyl) ethane; at 15 min its yield was 41.3% increasing to 71.2% at 30 min and decreasing to 68.3% at 60 min. Other products included: the 1-phenyl-(1-phenylthiyl) ethane isomer, 1,4-diphenyl butane, 1-phenyl-(2-phenylethyl) sulfoxide, 1,4-diphenyl-(2-phenylthiyl) butane, and phenyl thiosulfonate. Trace products (< 0.1%) included: 1-phenyl-(2-phenylethyl) sulfone, styrene

oxide, phenyl methyl sulfide and 2-ethyl toluene. For a 15 min stress with tBHP, the product slate was the same for both oxygen and tBHP, but the yields of individual components varied significantly. The major product, 1-phenyl-(2-phenylthiyl) ethane increased to 62.4% and the sulfoxide product was more than doubled at 3.9% in the presence of the stronger oxidant, tBHP.

The product slate for the indene reaction with oxygen included both addition and oxidation products. The major addition product observed was 2-phenylthiyl indan; at 15 min its yield was 39.4% increasing to 58.2% at 30 min and decreasing to 55.8% at 60 min. Another addition product was phenyl disulfide. Oxidation products included: 2-phenylthiyl-1-indanol and indanone, 1-phenylthiyl-2-indanol and indanone, and phenyl thiosulfonate. Minor products included: 1- and 2-indanols and indanones, 2-phenylsulphinyl -1-indanols, 1-phenylsulphinyl-2-indanols, 2-phenylsulphonyl-1-indanol, and 1-phenyl sulphonyl-2-indanol. The major product showed a significant increase in yield when the reaction was carried out with tBHP, 48.3% at 15 min. In these tBHP runs, t-butanol was the major product from the hydroperoxide.

The reactions with either molecular oxygen or tBHP and a thiol can be described by the following mechanism steps. The thiyl radical once formed

$$\text{RSH} \begin{array}{lll} + O_2 & \longrightarrow RS^{\cdot} & + HO_2^{\cdot} \qquad 13) \\ \text{or} & & \text{or} \\ + t\text{-}C_4H_9O^{\cdot} & \longrightarrow RS^{\cdot} & + t\text{-}C_4H_9OH \qquad 14) \end{array}$$

Where R = alkyl or aryl

can then react with an active olefin. For styrene, the reaction sequence with thiophenol can be described by the following equations.

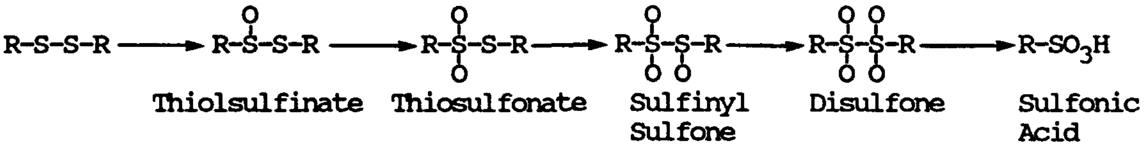
$$\phi S^{\cdot} + H_2C{=}CH\phi \begin{array}{l} \longrightarrow H_2C\text{-}CH(\phi)(S\phi) \qquad 15) \\ \qquad \text{or} \\ \longrightarrow \phi SCH_2\text{-}CH\phi \qquad 16) \end{array}$$

$$\phi SCH_2\text{-}CH\phi \xrightarrow{\text{hydrogen abstraction}} \phi SCH_2\text{-}CH_2\phi \qquad 17)$$

Equation 16) was the preferred pathway since it resulted in the more thermodynamically stable radical. For styrene the major product, 1-phenyl-

(2-phenylthiyl) ethane, then resulted from hydrogen abstraction, equation 17). The other radical generated, equation 15), leads to one of the observed minor products, 1-phenyl-(1-phenylthiyl) ethane. For the reaction with indene, only the 2-phenylthiyl indan reaction product was observed from steps 15) and 16).

Disulfide products. Oxidation of disulfides leads ultimately to sulfonic acids, but several of the oxidation intermediates can be obtained. In the present work in the presence of the mild tBHP oxidant at 120°C the major products observed are the intermediate oxidation products with only a minor amount of sulfonic acid produced. For hexyl disulfide, two major oxidized products were observed, the hexyl thiolsulfonate and the hexyl disulfone. Minors amounts of the hexyl thiol, hexyl sulfoxide and hexyl sulfone were observed. tBHP products included the major product t-butanol, along with acetone, and isobutylene. The observed disulfide oxidation products can be interpreted by the following mechanism.



$$R{-}S{-}S{-}R \longrightarrow R{-}\overset{O}{S}{-}S{-}R \longrightarrow R{-}\underset{O}{\overset{O}{S}}{-}S{-}R \longrightarrow R{-}\underset{O}{\overset{O}{S}}{-}\underset{O}{S}{-}R \longrightarrow R{-}\underset{O}{\overset{O}{S}}{-}\underset{O}{\overset{O}{S}}{-}R \longrightarrow R{-}SO_3H$$

Accelerated Storage. The above results indicated that some sulfur compounds might be inhibitors for controlling hydroperoxide formation in jet fuels. Therefore, samples of an aviation turbine fuel that undergoes extensive peroxidation were doped with different classes of organo-sulfur compounds at 0.03% added sulfur and analyzed for hydroperoxide formation during a 65°C/eight week stress period. The organo-sulfur compounds employed as dopants included: n-nonyl thiol, n-butyl sulfoxide, n-butyl sulfone, 2-butyl thiophene, and benzothiophene. Figure 1 shows the results for both the undoped control and the n-nonyl thiol doped JP-5 fuel. This dopant was dramatic in its control of hydroperoxide formation. It eliminated measurable hydroperoxides. Figure 2 shows the effect of added sulfur in the form of n-butyl sulfoxide. This dopant also exhibited control over peroxidation. The results for n-butyl sulfone, Figure 3, are different. A slight enhancing action on peroxidation was noted. n-Butyl thiophene, Figure 4, and benzothiophene, exhibited no controlling action. In fact, a negative syngerism was operating to increase peroxidation above control levels.

The results of the accelerated storage tests can be intrepreted based on model studies. Thiols as reported in this paper are readily oxidized, forming small amounts of sulfonic acids. Sulfoxides are somewhat resistant to oxidation at 120°C, while sulfones are stable at temperatures well above 120°C. These observations could account for the behavior noted with these dopants under accelerated storage conditions. Model studies have indicated that the thiophenes are the most oxidation resistant organo-sulfur compounds under the relatively mild conditions of this investigation. Alkyl substituted thiophenes and benzothiophene were the most unreactive sulfur compounds studied. At stress times of 180 min at 120^{o}C, >97% of benzothiophene remained unreacted. Results for the thiophene dopant studies show that they do not control the formation of hydroperoxides. Since they are so oxidation resistant, the hydroperoxide concentration increases are uncontrolled.

SUMMARY

The observed deterioration of fuels can manifest itself in many ways, including the formation of insoluble deposits both in storage and in an engine fuel system or nozzle. Reactive species in petroleum fuels which may be involved in the deterioration are alkyl sulfides, thiols, aromatic thiols, disulfides, thiophenes and hydroperoxides. Trace quantities of compounds such as sulfonic acids have also been implicated in deposit formation. This paper specifically examined the hydroperoxide or oxygen induced oxidation of hexyl sulfide, dodecyl thiol, thiophenol, hexyl disulfide, substituted thiophenes, and the co-oxidation of thiophenol with the active olefins,styrene and indene, in both deaerated benzene and tetradecane solvents at 120C. The product mix was studied over various reaction times of 15 min to 180 min. For each organo-sulfur compound, a common slate of products was observed for all reaction time periods. The yield of individual components, however, varied significantly with reaction time. The major product derived from the tBHP was t-butanol. Other observed tBHP products included methane, acetone and isobutylene. The major product from the hexyl sulfide oxidation was hexyl sulfoxide. Other sulfur containing products were hexyl sulfone, hexyl disulfide and hexyl thiosulfinate. The major product from dodecyl thiol was dodecyl disulfide. Oxidized products included dodecyl sulfoxide, dodecyl sulfide and dodecyl sulfone. Hexyl disulfide gave primarily oxidation products, hexyl thiolsulfonate, and hexyl disulfone. The substituted thiophenes gave sulfoxideS, sulfones and the Diels-Alder product from these reactive species. The Diels-Alder products formed from the thiophenes were observed to be water soluble. From the co-oxidation of thiophenol with styrene, the major product was 1-phenyl-(2-phenylthiyl) ethane. Other products included: 1-phenyl-(1-phenylthiyl) ethane and the oxidized products phenyl- (2-phenylethyl) sulfoxide and phenyl thiosulfonate. For indene, the major addition product observed was 2-phenylthiyl indan. Oxidation products included the 2-phenylthiyl-1-indanol and indanone. These products were derived from the breakdown of hydroperoxide of indane. Minor amounts of the oxidized addition products were also observed.

The results of the accelerated storage studies with sulfur dopants in jet fuel can be intrepreted based on the results and mechanisms observed with model compounds.

Solvent participation was noted by the formation of toluene from benzene and tetradecanones and tetradecanols from tetradecane. No oxygenated products of benzene were observed.

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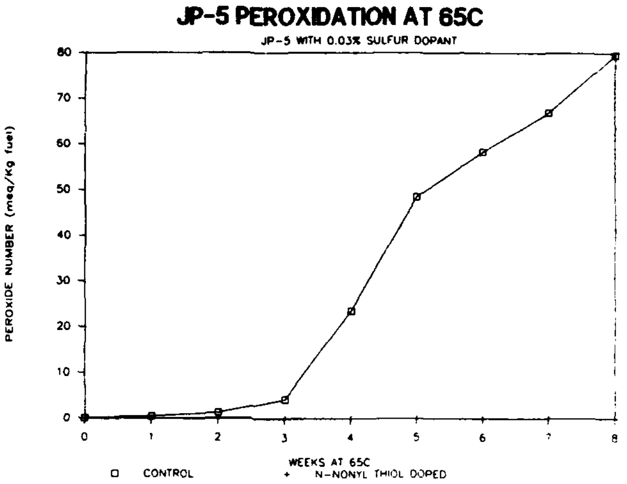

Figure 1

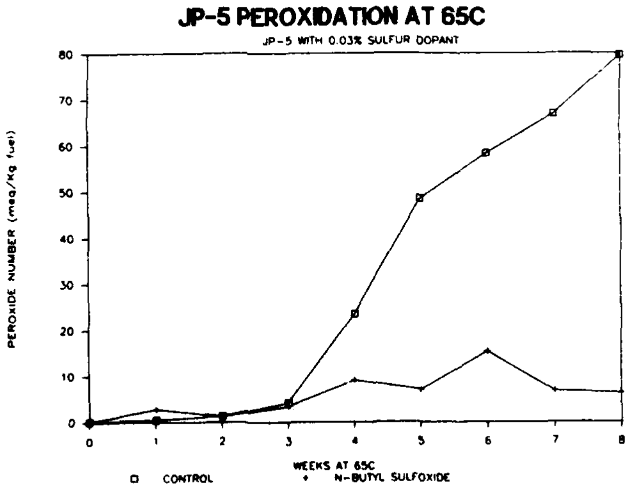

Figure 2

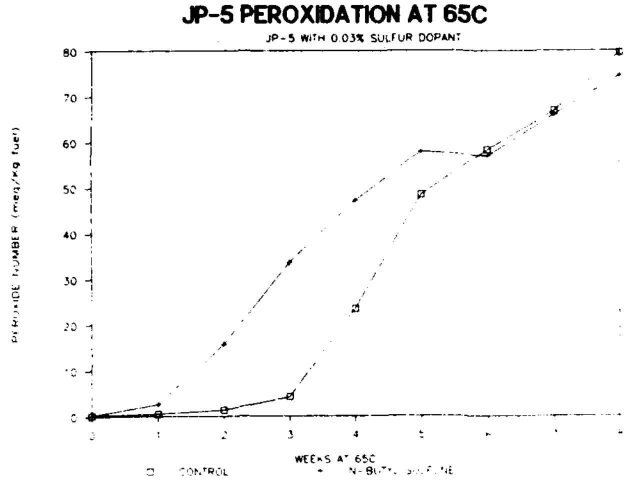

Figure 3

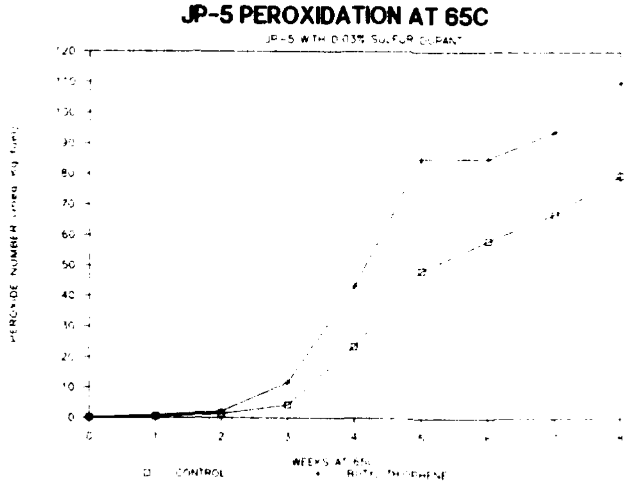

Figure 4

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HYDROPEROXIDE FORMATION AND REACTIVITY IN JET FUELS

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ABSTRACT

Hydroperoxides in jet fuels attack elastomers in aircraft fuel systems resulting in leaks or inoperation of fuel controls. Examination of fuels refined by different processes has indicated that significantly higher peroxide concentrations exist in fuels which have been severely hydrotreated. It is believed that hydogenation is responsible for removing natural inhibitors, including sulfur compounds, to peroxide formation. To test this thesis, the relationship between aryl thiols and peroxidation of jet fuels was examined using model dopant studies under 65°C accelerated storage conditions. Samples were analysed on a weekly basis for peroxides and sulfur compound concentration. Thiophenol demonstrated effectiveness in reducing and/or controlling peroxide concentration for an equivalent ambient storage time of approximately two years.

INTRODUCTION

Hydroperoxides in jet fuels attack elastomers in aircraft fuel systems with consequent leaks or inoperation of fuel controls. Problems have been associated with Jet A, JP-4, and JP-5 jet fuels. The first reported incidents occurred with Jet A in Japan in 1962 when fuel hoses of neoprene or nitrile rubber cracked and leaked (1). In 1976 the U.S. Navy experienced attack on neoprene fuel pump diaphragms on jets operating in the Phillipines (2). More recent problems have been encountered in Thailand with JP-4 when Buna-N O-rings cracked and leaks from fuel pumps occurred (3). All incidents involved fuels which had been hydrotreated and had peroxide levels from 1 to 8 milliequivalents of active oxygen per kilogram of fuel (peroxide number or P.N.).

Examination of fuels refined by different processes has indicated that significantly higher peroxide concentrations develop in fuels which have been severely hydrotreated. The U.S. Navy has continuing concerns with this topic due to increasing hydrogenation for jet fuel processing. In addition, lower grade crudes and future shale-derived fuel production will involve more extensive and higher pressure hydrotreatment. It has been demonstrated that sulfur compounds in lubricating oils act as antioxidants by decomposing peroxides (4). It is believed that hydrogenation is responsible for removing natural inhibitors, including sulfur compounds, to peroxide formation.

Hydroperoxide concentration has been found to be a factor in fuel instability. Fuel degradation is observed to occur under long-term low-temperature storage conditions (storage stability) as well as short-term high-temperature stress (thermal oxidative stability) (5,6,7,8). The latter situation is found during flight conditions, where fuel serves as a coolant on its path to the combustion chamber. Although slight thermal degradation is found to occur in non-oxidizing atmospheres, the presence of oxygen or active species such as hydroperoxides will greatly accelerate oxidative degradation as well as significantly lower the temperature at which undesirable changes in fuel take place. The rates of reactions in autoxidation schemes are dependant on hydrocarbon structure, heteroatom concentration, oxygen concentration, and temperature (9,10,11). If sufficient oxygen is present, the hydroperoxides will reach a high level. If the available oxygen is low, but the temperature raised, the hydroperoxide concentration will be limited by free radical decomposition. Under these conditions, fuel degradation can be associated with both hydroperoxide formation and decomposition.

Several solutions to the problem of fuel peroxidation have been suggested. Antioxidants have been mandated by some authorities, particularly for hydrotreated fuels. Viton elastomers and other materials have been proposed as replacement materials but their low temperature properties make them marginal for aircraft use. Clay filtration has been suggested as a means for field removal of hydroperoxides but this treatment has been found to be too expensive (2). Although hindered phenols have given satisfactory peroxide control, those phenols which are permitted in the jet fuel specifications were developed for gum control in gasoline. Their effectiveness for peroxide control was found to be marginal, depending on structure (12). Rolls-Royce defined the peroxidation potential of a fuel with an accelerated 100°C test for 24 hours (1). Investigations into the relationship of temperature to peroxide concentration in fuel, along with determining the relevance of the 100°C test to ambient storage conditions, indicated that fuels containing antioxidants behaved differently at different temperatures, and in fuels without antioxidant peroxide levels were lower than expected at the lower temperatures (12). A comparison of peroxidation rates in two fuels, one with and one without antioxidant, showed that a fuel without antioxidant produced peroxides at a linear rate while a fuel containing antioxidant produced peroxides in an exponential fashion, indicating a depletion with time of the antioxidant and its ability to control peroxidation (12).

Sulfur is the most abundant heteroatom present in jet fuels (up to 0.4% allowed by specifications). Deposits formed in jet fuel in the presence of oxygen contain a higher percentage of sulfur than that present in the fuel itself (13). The formation of these deposits has been attributed to the participation of sulfides, disulfides, and thiols (mercaptans) (14). In jet fuels that have been deoxygenated, sulfides and disulfides have been found to lead to increased solid formation (15). Examination of the reactions between both alkyl and aromatic thiols with tert-butylhydroperoxide have indicated that aromatic thiols are more reactive than other classes of sulfur compounds with hydroperoxides. The reaction of thiophenol with tBHP was found to produce trace amounts of sulfonic acid while depleting the amount of both reactants in solution (16). It was thus desirable to test the relationship between sulfur compound reactivity and peroxide formation using an aryl thiol as a model dopant under accelerated storage conditions.

This paper discusses the effect on hydroperoxide formation of using an aryl thiol, thiophenol, as a dopant in a Jet A, a shale-derived jet fuel, and two jet fuel blending stocks under 65°C accelerated storage conditions. A 65°C stress test was chosen for the sulfur compound study based on previous time-temperature peroxidation studies completed at NRL (12). The effect on peroxide formation versus added sulfur concentrations is also reported.

EXPERIMENTAL

Fuels and Reagents. The four fuels used in the investigation were a Shale-II JP-5, a Jet-A, a Hydrocracked and a Hydrofined Jet A blending stock. Thiophenol was obtained from Aldrich Chemical Co. and was distilled in vacuo to 99.9% purity.

Method. The stress test was patterned after that used by the laboratories which participated in the recent Coordinating Research Council cooperative studies on peroxidation (17). Tests were carried out in brown borosilicate glass bottles, 500 ml total capacity, capped with teflon liners, containing 300 ml of fuel per bottle. Duplicate samples of the four fuels were prepared, with sulfur in the form of thiophenol weighed into one sample of each fuel. The first series of samples were prepared by adding 0.10% sulfur (weight/volume) from thiophenol, followed by sets with 0.05, 0.03 and 0.01% added sulfur concentrations. Stress tests were conducted for five weeks for the samples containing 0.10 and 0.05% added sulfur. The samples containing 0.03 and 0.01% added sulfur were stressed at 65°C for eight weeks. Samples were analyzed weekly for peroxide concentration by ASTM method D3703-85 from the control and test bottles for each fuel.

A Mettler DL20 automatic titrator was employed for the 0.03 and 0.01% added sulfur tests, eliminating the use of starch solution from the ASTM method. Thiophenol concentrations were monitored weekly with a Tracor 565 gas chromatograph equipped with a sulfur specific 700A Hall electrolytic conductivity detector. Samples were analysed in triplicate against an external standard for thiophenol, which was also analysed in triplicate.

RESULTS AND DISCUSSION

An original added sulfur concentration of 0.10% sulfur (weight/volume) from thiophenol was used. To examine the effect of added sulfur concentration on peroxidation, a second test was run using 0.05% added sulfur from thiophenol. Based on the results of the 0.05% added sulfur test, additional series were run using 0.03 and 0.01% added sulfur from thiophenol. The data for these tests are presented in Tables I, II, III, and IV respectively.

For all of the sulfur concentration tests, the control samples, fuel only, exhibited similar behavior. Differences in actual peroxide numbers between tests can be attributed to slight temperature differences in the ovens that were used, and to the fact that the fuel samples had been in storage for varying times before these tests were started. It was interesting that in the Jet A control samples peroxide formation occurred in a cyclic pattern. This has been observed in other peroxidation studies with Jet A. The two Jet A blending stocks formed peroxides at a greater rate than the Shale JP-5 or the Jet A samples.

The most important aspect of all the tests was that the samples doped with sulfur in the form of thiophenol did not undergo peroxidation as rapidly as the fuel only samples. In fact, thiophenol addition eliminated any ROOH present in starting samples of all four fuels in the 0.05% added sulfur series, and after the first week in the Shale II and Hydrocracked Jet A blending stock samples in the 0.10% test. In the samples doped with 0.10% sulfur, peroxide formation was not observed until the fourth week of the stress test. When the concentration of added sulfur was reduced (halved) peroxide formation began one week earlier in the three fuels which did exhibit peroxidation, indicating a relationship between added sulfur concentration and peroxide formation (or peroxide inhibition). None of the doped samples of the Hydrofined Jet A blending stock showed evidence of peroxide formation throughout the duration of the tests.

In the series doped with 0.03% added sulfur from thiophenol, peroxides were eliminated after one week of 65°C stress in all of the samples except for the Shale II JP-5, which contained a larger starting concentration of peroxides that required two weeks to be reduced to zero as measured by the ASTM method. The Jet A sample began to exhibit peroxidation in the third week of the test, while the Shale II and Hydrocracked Jet A blending stock samples did not show any trace of peroxidation until the fourth week, before disappearing again to re-emerge in the seventh week of the test. Even though peroxidation was not observed until later in this test than in the 0.10 and 0.05% added sulfur samples, the 0.03% added sulfur controlled peroxidation, most noticeably in the Hydrocracked and Hydrofined Jet A blending stock samples, which did not exhibit any peroxidation during the test, in spite of the fact that both of these samples perodized extensively when the thiophenol was absent.

The samples doped with 0.01% added sulfur from thiophenol also demonstrated the ability of added sulfur to control peroxidation. In the Shale II and Hydrocracked Jet A blending stock samples, the starting peroxide concentrations were gradually decreased to zero after three weeks of stress. Peroxidation wasn't evident in the Shale II sample until the sixth week of the test, but began again in the Hydrocracked Jet A blending stock sample in the fifth week of stress. This can be explained by comparing the relative peroxide levels present in the control samples, 0.991 meq active O_2/Kg fuel versus 29.200 meq active O_2/Kg fuel for the Shale II and Hydrocracked blending stock samples, respectively. The 0.01% added sulfur was not enough to control the large amount of peroxide formation after five weeks in the Hydrocracked Jet A blending stock sample. The Jet A samples, both control and doped, exhibited interesting cyclic behavior similar to that in the 0.03% added sulfur study, while the doped Hydrofined Jet A blending stock sample did not undergo peroxidation during the test after the starting peroxide concentration was depleted.

The thiophenol concentrations in the doped samples decreased throughout the tests as measured by the sulfur specific electrolytic conductivity detector on the gas chromatograph. Tables V and VI contain the data for the 0.10 and 0.05% sulfur from thiophenol doped samples, respectively. Samples were analysed in triplicate and compared to an external standard for thiophenol which was also analysed in triplicate. Average values are reported and were used for all calculations. It is interesting to note that the sulfur concentrations decreased more rapidly and to a greater extent in the doped Shale II, Jet A and Hydrocracked blending stock samples, those fuels which did exhibit some peroxidation, than in the Hydrofined blending stock sample which did not exhibit peroxidation during the test. This was true for both concentrations of added sulfur with the exception of the Hydrocracked sample which depleted slower in the 0.05% doped test. The presence of new peaks on the chromatogram indicated the formation of new sulfur-containing compounds, however concentrations were too low to permit identification. It should be noted that in the 0.10% doped samples there were still measurable sulfur concentrations for the duration of the stress test, but for the 0.05% doped samples, the added thiophenol disappeared much faster and was completely depleted between the fourth and fifth weeks of the test for the Shale II and Jet A samples. A direct comparison of the sulfur concentration to peroxidation in the Shale samples can be seen in Figures 1 and 2 for the 0.10 and 0.05% doped samples, respectively. The place on the graphs where the lines intersect indicates the approximate concentration of added sulfur at which peroxidation is no longer controlled. It should be noted that this concentration was approximately 0.4 mg of sulfur for the 0.10% doped sample and 0.2 mg sulfur for the 0.05% doped sample.

The results for the 0.03 and 0.01% added sulfur from thiophenol studies are reported in Tables VII and VIII, respectively. The doped samples in these series exhibited behavior similar to the first two tests. The sulfur concentrations in the two Hydrofined Jet A blending stock samples did not decrease as rapidly or to the same extent as the concentrations in the other fuels. The sulfur concentration in the 0.03% sulfur doped Shale JP-5 sample was depleted by the eighth week of the test while the concentration in the 0.01% doped sample was zero by the third week of the test. In the Hydrocracked Jet A blending stock samples there were low sulfur concentrations throughout the duration of the tests, with the 0.01% doped sample dropping to zero by week five. The 0.03% doped Jet A sample exhibited cyclic peroxide formation and a rapid decrease in sulfur concentration, while the 0.01% doped sample showed an immediate decrease in sulfur concentration during the first week of stress. Figures 3 and 4 provide a direct comparison of the sulfur concentration to the peroxidation of the samples doped with 0.03 and 0.01% added sulfur. According to this data, the concentration at which peroxidation was no longer controlled was about 0.03 mg added sulfur for the 0.03% doped sample. This concentration was reached at the end of six weeks of stress and peroxidation began between the sixth and seventh week of the test. In the sulfur concentration versus peroxidation graph for the shale sample with 0.01% added sulfur, peroxide inhibition stops in the fifth week of stress when the added thiophenol concentration was reduced to zero as measured by the sulfur detector. The comparison of sulfur concentration to peroxidation indicated that control or inhibition of peroxidation was lost at approximately 0.2 +/- 0.1 mg of added sulfur in all fuel samples.

CONCLUSIONS

The effect of adding sulfur in the form of an aromatic thiol, thiophenol, was significant to peroxide formation. Thiophenol has been found to act as an inhibitor or controller of peroxide formation in Jet A, Shale-II derived JP-5, and petroluem derived Jet A blending stocks. Hydrotreated jet fuels exhibited higher peroxide formation and concentration than other fuels. Hydrotreatment reduces the sulfur content of the fuel, which removes those naturally occurring sulfur compounds which possibly act as inhibitors to peroxide formation. There appeared to be a minimum concentration of sulfur as thiophenol above which peroxide formation was inhibited. If this concentration was decreased or consumed, peroxidation began.

Since aromatic thiols are quite reactive in the presence of peroxides, the thiophenol most likely undergoes oxidation by the peroxide species. These reactions could be similar to other observed liquid phase oxidation reactions that take place between thiophenol and t-butyl hydroperoxide.

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Table I

JET FUEL PEROXIDATION AT 65°C WITH ADDED THIOPHENOL 0.10% SULFUR DOPANT

	SHALE-II JP-5		JET A		HYDROCRACKED JET A BLENDING STOCK		HYDROFINED JET A BLENDING STOCK	
WEEK	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED
0	0.25	0.25	0.00	0.00	0.16	0.16	0.00	0.00
1	0.24	0.00	0.19	0.00	0.57	0.00	0.18	0.00
2	0.31	0.00	0.44	0.00	1.16	0.00	0.49	0.00
3	0.37	0.00	0.19	0.00	1.73	0.00	1.10	0.00
4	0.51	1.29	0.40	0.51	5.38	0.26	4.08	0.00
5	0.48	0.97	0.26	0.40	8.47	0.25	10.82	0.00

Table II

JET FUEL PEROXIDATION AT 65°C WITH ADDED THIOPHENOL 0.05% SULFUR DOPANT

	SHALE-II JP-5		JET A		HYDROCRACKED JET A BLENDING STOCK		HYDROFINED JET A BLENDING STOCK	
WEEK	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED
0	0.69	0.00	0.12	0.00	0.24	0.00	0.10	0.00
1	0.70	0.00	0.18	0.00	1.58	0.00	0.60	0.00
2	0.73	0.00	0.16	0.00	6.01	0.00	2.09	0.00
3	0.94	0.45	0.28	0.54	37.66	0.61	12.41	0.00
4	1.11	0.68	0.26	0.22	62.05	0.51	25.27	0.00
5	1.56	0.88	0.29	0.81	59.92	0.25	56.67	0.00

Table III

JET FUEL PEROXIDATION AT 65°C WITH ADDED THIOPHENOL 0.03% SULFUR DOPANT

	SHALE-II JP-5		JET A		HYDROCRACKED JET A BLENDING STOCK		HYDROFINED JET A BLENDING STOCK	
WEEK	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED
0	0.60	0.60	0.01	0.01	0.27	0.27	0.06	0.06
1	0.62	0.14	0.04	0.00	0.96	0.00	0.32	0.00
2	0.72	0.00	0.05	0.00	1.88	0.00	0.78	0.00
3	0.84	0.00	0.00	3.98	4.20	0.00	2.46	0.00
4	0.90	0.01	0.09	0.01	10.04	0.01	5.89	0.00
5	0.93	0.00	0.05	0.50	22.43	0.00	13.26	0.00
6	0.99	0.00	0.00	0.70	49.03	0.00	28.54	0.00
7	1.14	0.03	0.13	1.38	77.88	0.62	60.62	0.00
8	1.29	0.15	0.07	0.88	97.40	0.36	77.44	0.00

Table IV

JET FUEL PEROXIDATION AT 65°C WITH ADDED THIOPHENOL 0.01% SULFUR DOPANT

	SHALE-II JP-5		JET A		HYDROCRACKED JET A BLENDING STOCK		HYDROFINED JET A BLENDING STOCK	
WEEK	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED	CONTROL	DOPED
0	0.51	0.51	0.00	0.00	0.25	0.25	0.06	0.06
1	0.60	0.20	0.10	1.04	1.02	0.73	0.50	0.00
2	0.67	0.17	0.13	0.72	2.37	0.11	1.32	0.00
3	0.81	0.00	0.20	0.89	4.66	0.00	3.63	0.00
4	0.85	0.00	0.17	0.55	13.22	0.00	13.79	0.00
5	0.99	0.00	0.21	0.59	29.20	0.22	29.10	0.00
6	1.08	0.23	0.17	0.42	55.33	0.14	48.57	0.00
7	1.12	0.33	0.19	0.72	89.57	0.19	78.27	0.00
8	1.51	0.46	0.24	0.65	131.13	0.28	124.98	0.00

Table V

SULFUR CONCENTRATION vs. TIME
0.10% SULFUR DOPANT FROM THIOPHENOL

SHALE-II JP-5		JET A		H-CRACKED JET A STOCK		H-FINED JET A STOCK	
WEEK	mg. S/2mL	WEEK	mg. S/2mL	WEEK	mg. S/2mL	WEEK	mg. S/2mL
0	2.20	0	2.08	0	2.12	0	2.10
1	1.16	1	0.98	1	0.92	1	1.78
2	0.51	2	0.81	2	0.74	2	1.47
3	0.43	3	0.63	3	0.67	3	1.58
4	0.26	4	0.47	4	0.48	4	1.43
5	0.24	5	0.41	5	0.47	5	1.38

Table VI

SULFUR CONCENTRATION vs. TIME
0.05% SULFUR DOPANT FROM THIOPHENOL

SHALE-II JP-5		JET A		H-CRACKED JET A STOCK		H-FINED JET A STOCK	
WEEK	mg. S/2mL	WEEK	mg. S/2mL	WEEK	mg. S/mL	WEEK	mg. S/2mL
0	1.00	0	1.00	0	1.00	0	1.00
1	0.76	1	0.25	1	0.86	1	0.37
2	0.23	2	0.33	2	0.63	2	0.76
3	0.15	3	0.16	3	0.78	3	0.33
4	0.02	4	0.15	4	0.38	4	0.21
5	0.00	5	0.00	5	0.49	5	0.16

Table VII

SULFUR CONCENTRATION vs. TIME
0.03% SULFUR DOPANT FROM THIOPHENOL

SHALE-II JP-5		JET A		H-CRACKED JET A STOCK		H-FINED JET A STOCK	
WEEK	mg. S	WEEK	mg. S	WEEK	mg. S	WEEK	mg. S
0	0.61	0	0.60	0	0.60	0	0.60
1	0.13	1	0.17	1	0.17	1	0.31
2	0.05	2	0.03	2	0.12	2	0.20
3	0.06	3	0.01	3	0.01	3	0.21
4	0.05	4	0.01	4	0.05	4	0.19
5	0.05	5	0.01	5	0.03	5	0.18
6	0.03	6	0.01	6	0.05	6	0.13
7	0.03	7	0.01	7	0.01	7	0.10
8	0.00	8	0.01	8	0.00	8	0.10

Table VIII

SULFUR CONCENTRATION vs. TIME
0.01% SULFUR DOPANT FROM THIOPHENOL

SHALE-II JP-5		JET A		H-CRACKED JET A STOCK		H-FINED JET A STOCK	
WEEK	mg. S	WEEK	mg. S	WEEK	mg. S	WEEK	mg. S
0	0.21	0	0.20	0	0.21	0	0.20
1	0.03	1	0.00	1	0.01	1	0.09
2	0.02	2	0.00	2	0.00	2	0.12
3	0.00	3	0.00	3	0.01	3	0.05
4	0.00	4	0.00	4	0.00	4	0.07
5	0.00	5	0.00	5	0.00	5	0.06
6	0.00	6	0.00	6	0.00	6	0.04
7	0.00	7	0.00	7	0.00	7	0.03
8	0.00	8	0.00	8	0.00	8	0.05

Figure 1

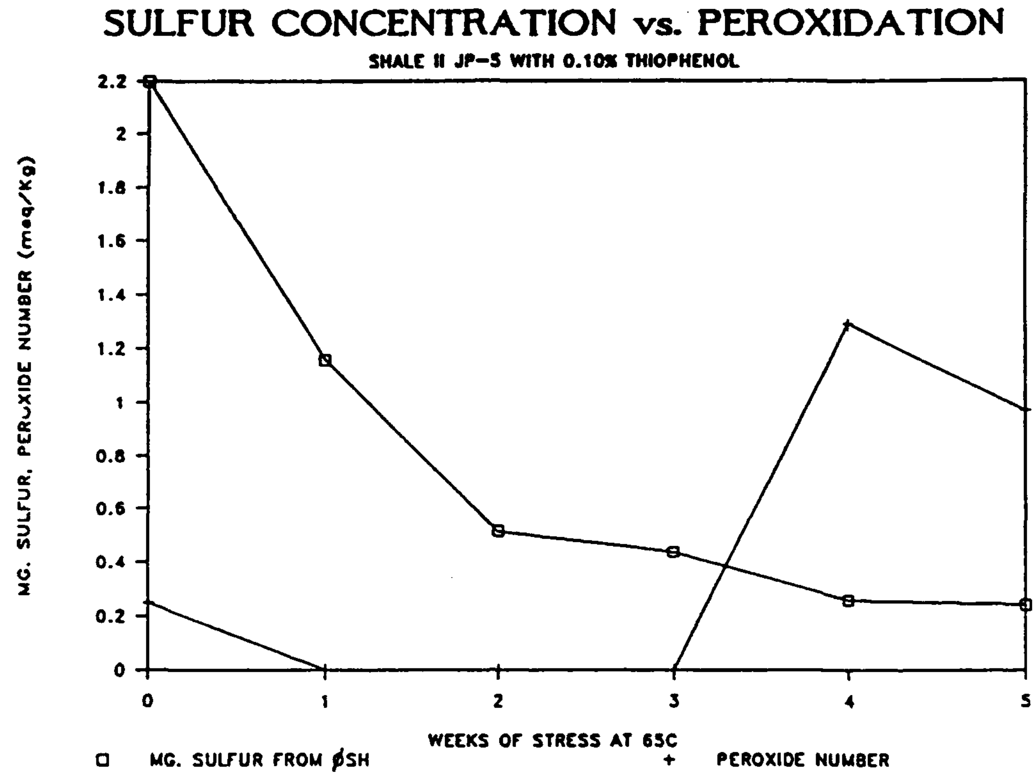


Figure 2

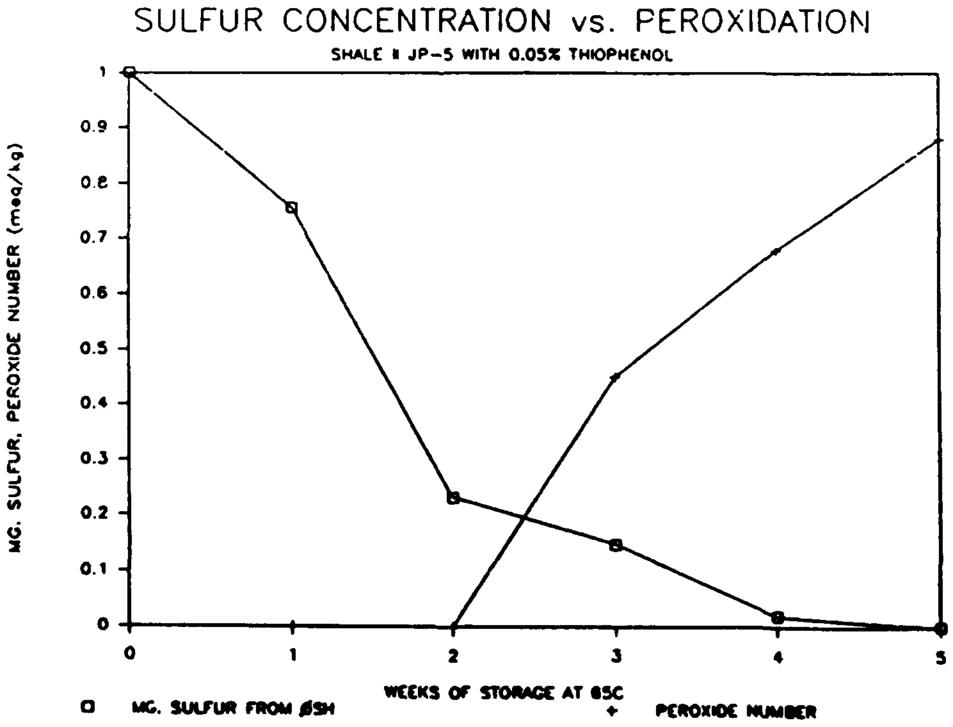
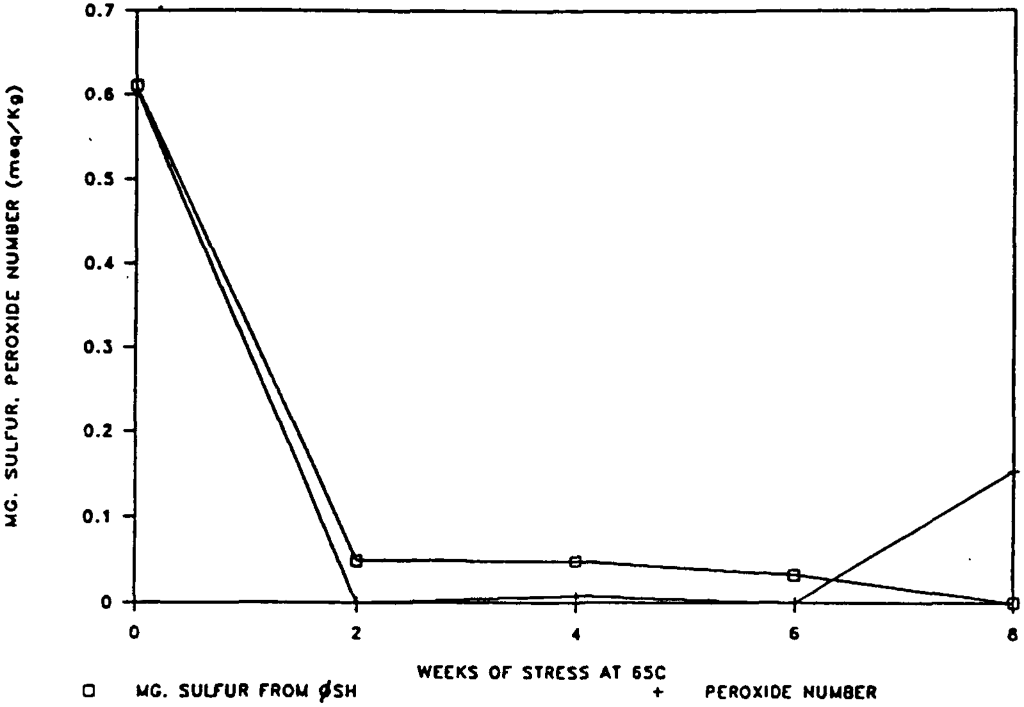


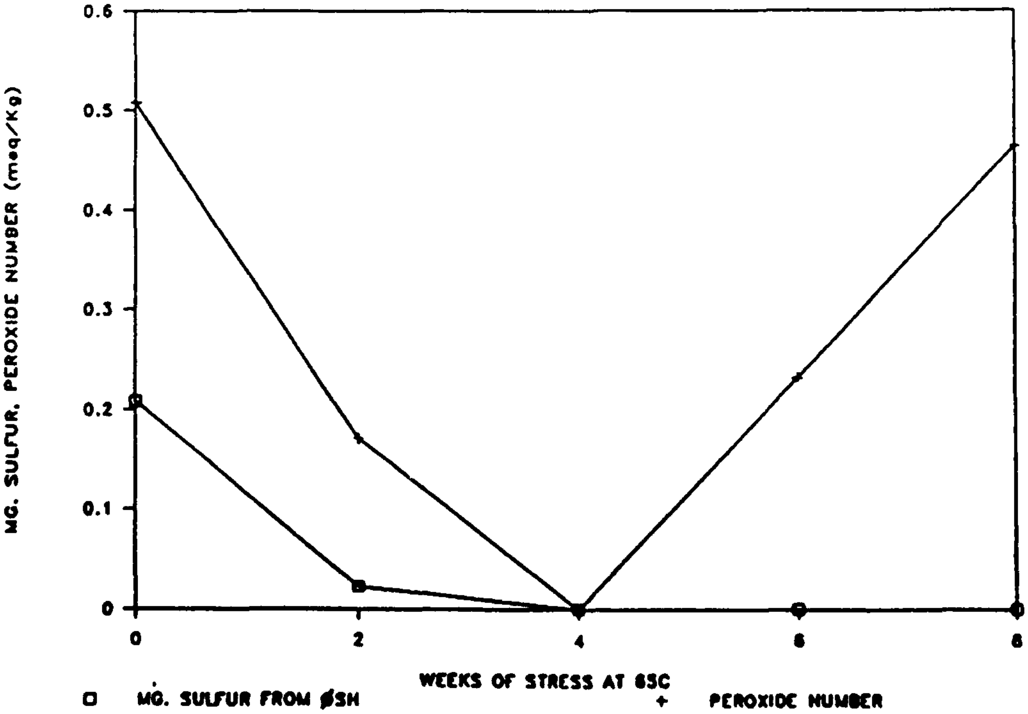
Figure 3



SULFUR CONCENTRATION vs. PEROXIDATION

SHALE II JP-5 WITH 0.03% THIOPHENOL

Figure 4



SULFUR CONCENTRATION vs. PEROXIDATION

SHALE II JP-5 WITH 0.01% THIOPHENOL

THE CHEMISTRY OF ANTIOXIDANT ADDITIVE DEPLETION IN JET FUELS

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ABSTRACT

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

INTRODUCTION

As heavier crude oils are introduced into refineries and the use of higher severity processes is increased, greater problems of solids formation, corrosiveness, color formation, long filtration times, and increasing viscosity are being experienced in jet fuels provided to the military under current specifications. These problems can result in fuel pump failures, filter plugging, and flame-out. Antioxidants (usually hindered phenols) have been generally used to overcome storage instability in these fuels. The objective of this investigation is to determine the compositional changes that occur in severely refined jet-type fuels as antioxidants are depleted. Methods to monitor the antioxidants were developed in an earlier study and the results reported previously [1,2]. The objective of this study is addressed in this report in terms of changes in bulk physical and chemical properties of the fuels and formation of sediments, and in terms of the detailed analyses of the fresh and aged additive-free fuels and their sediments. Similar detailed analytical results on corresponding samples from the fuels containing the antioxidants will be obtained and compared to the additive-free fuel results in a later paper.

Stability of hydrocarbon fuels, including aviation fuels, has been a concern for many years and has been the subject of several reviews including a recent one published in 1983 [3]. Although the chemistry involved in sediment formation in fuels is complex, it is generally accepted that most sediment formation is initiated by oxidation of reactive compounds which are components of the fuel. A chain mechanism involving free radical initiated oxidation of the reactive fuel components by molecular oxygen has been accepted as a fundamental mechanism in sediment formation [4,5]. More recently, a second oxidation mechanism, electron-transfer initiated oxidation, has been suggested as a mechanism for autoxidation of pyrroles and as a significant mechanism in fuel storage instability [6]. Part of the support for the electron-transfer initiated oxidation mechanism for the autoxidation of pyrroles is the observation that radical scavenger antioxidants, such as the hindered phenols used in this study, have little effect on the rate of alkylpyrrole oxidation [6,7]. In another recent study on sediment formation during ambient storage of diesel fuel, two commercially-available stability-improvement additives were found to have little effect on sediment formation and a harmful effect on fuel filterability [8]. Alkylindoles were determined to be important constituents of the fuel sediment. Another recent study proposed two mechanisms in addition to free radical chain oxidation in the formation of gum deposits in jet turbine and diesel fuels [9,10]. In the oxidation of six hydrocarbons, three jet turbine fuels, and three diesel fuels at 130° C without t-butylperoxide (t-Bu_2O_2) as initiator and at 100° C with t-Bu_2O_2, the results were explained by a mechanism of gum formation involving coupling of substrates by peroxides in the absence of oxygen, by a mechanism involving condensation of oxidation products from alkylnaphthalenes, and by a free radical chain mechanism. Other recent studies have investigated the role of nitrogen- and sulfur-containing compounds in the aging of JP-5 and diesel fuels [11], and the adverse effect of coal-derived Lewis bases [12] and mixed effect of organo-sulfur compounds [13] on Jet A turbine fuel storage stability. In related work, laser light scattering was correlated with the extent of deposit formation and with oxygen uptake in storage stability studies of jet fuels doped with individual pyrroles, sulfur-containing compounds, olefins, iron and copper phthalocyanines, and with mixtures of these compounds [14]. Finally, free radical concentration measured by electron-spin resonance spectroscopy was found to correlate only approximately with sediment formation in middle distillate fuels [15]. Thus, although considerable progress has been made toward determination of various mechanisms and reactions involved in sediment formation in jet fuels, further elucidation of mechanisms and reactions and determination of their relative importance in fuels of varied composition are necessary for a better understanding of fuel degradation processes both in the presence and absence of antioxidants and for determining more effective means of preventing fuel degradation.

EXPERIMENTAL SECTION

The fuels selected for this study were fresh samples obtained from two different West Coast (U.S.A.) refinery hydrocracker streams. Both samples had boiling ranges similar to that of JP-5 jet fuel. The two hydrocracker stream samples, designated fuel A and fuel B, and blends of the fuels with hindered phenol antioxidants were aged at 60° and 80 °C by a method similar to ASTM D 4625, "Standard Test Method for Distillate Fuel Storage Stability at 43 °C (110° F)" [16]. The antioxidants, designated antioxidant 1 (99% 2,6-di-tert-butyl-4-methylphenol) and antioxidant 2 (65% 2,4-di-tert-butylphenol, 35% mixed di-tert-butylphenols), were blended individually with the test fuels at concentrations of 12 and 24 ppm. Selected physical and chemical properties of the two fuels were determined and are summarized in Table I. Fuel A was below the military specification for JP-5 fuels in hydrogen content. Both fuels had low nitrogen and sulfur contents. Peroxide number, color, and additive concentration were determined by ASTM Method D 3703-85, "Standard Test Method for Peroxide Number of Aviation Turbine Fuels" [17]; ASTM Method D 1500, "Standard Test Method for ASTM Color of Petroleum Products (ASTM Color Scale)" [18]; and by an electrochemical/liquid chromatographic (EC/LC) method developed in an earlier project [1], respectively.

In the analytical experiments, samples of the fresh fuels and aged samples at early maximum peroxide development and at late storage (high sediment) were selected for examination by GC/MS. The aged samples for fuel A were 16- and 68-week samples stored at 60° C and for fuel B were 2- and 20-week samples stored at 80° C. The fuel samples that had formed sediments were filtered before analysis. Sediment samples from fuel A after 19 weeks at 80° C and 44 weeks at 60° C and from fuel B after 8 and 12 weeks at 80° C were selected for analysis by GC/MS and PMD/MS. The fresh and aged fuels and methylene chloride solutions of the sediments (essentially 100% dissolved) were separated, before and after acylation and esterification [19], on a 100-m X 0.25-mm ID, fused-silica, bonded-phase, methylsilicone column interfaced directly to a Kratos MS-80 mass spectrometer. The GC column film thickness was 0.5 micron. The Carlo Erba Model 4662 GC was programmed as follows: 20° C, 2-min hold; 20° C/min to 70° C; 2° C/min to 325° C, 10-min hold. The split-splitless injector temperature was 300° C, helium carrier gas flow was 1 cc/min, and samples were injected in the splitless mode for 18 s initially. The MS-80 was operated at a scan rate of 0.5 s/decade over a mass range of 27-456 amu, at a static resolution of 1000, an ionizing voltage of 70 eV, and a source temperature of 250° C. The data system was a Kratos DS-55, Data General Nova 4X based system. PMD/MS data were acquired with a Kratos MS-50 mass spectrometer operated at a scan rate of 100 s/decade, a mass range of 70-800 or 55-1000 amu, a static resolution of 28,000, an ionizing voltage of 12 eV, and source temperature of 300° C. The data system was a Kratos DS-55. The probe temperature was controlled from -80° to 350° C with a Masspec Inc. controller using total ion current feedback to regulate the rate of temperature increase. Typically, 80 to 95% of the sediment sample was vaporized under these conditions. Data were processed on a DEC Microvax II computer using software developed in-house [20]. Infrared spectra of the sediments in methylene chloride or carbon tetrachloride were acquired on a Perkin-Elmer Model 283 dual beam, dispersive, infrared spectrometer. Each sediment was also examined by IR after chemical derivatization to convert hydroxyl compounds to trifluoroacetate esters and carboxylic acids to esters of heptafluorobutanol to determine the extent of reaction. The derivatization procedures were particularly useful in the GC/MS analyses for identification of compound types in the sediments.

RESULTS AND DISCUSSION

Bulk Physical and Chemical Properties. Generally, the fuel and fuel-plus-antioxidant aging experiments are characterized by an induction period, followed by a period of rapid peroxide formation, and finally a period of decreasing peroxide content, increasing color, and increasing sediment formation. For those samples containing antioxidant, the antioxidant concentration remained high during the induction period, decreasing sharply as the peroxide content increased.

Figure 1 shows time profiles for peroxide content and total sediment (adherent and filterable) in the aging at 60° C of fuel A neat and after blending with 12 ppm and 24 ppm antioxidant 2. After an induction period of about 4 weeks, the peroxide content of the neat fuel began increasing rapidly, reaching a peak of over 2800 ppm at 32 weeks before decreasing. Sediment began forming slowly as the peroxide number increased; then as the peroxide concentration reached its peak and began decreasing, the quantity of sediment increased rapidly (Figure 1A) The sediment was almost entirely adherent sediment. The amount of filterable sediment remained quite small, with the maximum in filterable sediment occurring at the same time as the maximum peroxide concentration. Thus, as the sediment formed, most of it adhered quickly to the bottom or walls of the storage bottle. Color appeared at about the same time as or shortly before sediment began forming. The color slowly intensified with increasing storage time and increasing sediment formation. The fuel-antioxidant blends exhibited behavior similar to that of the neat fuel, but with a much longer induction period. The blends with antioxidant 2 (Figures 1B and 1C) began to exhibit significant peroxide concentrations after about 24 weeks at 60 °C. The blend with 24 ppm of the antioxidant had a slightly slower peroxide formation than the 12 ppm blend; however, both blends reached their peak peroxide concentration of about 2600 ppm after 52 weeks of aging. At that point, the peroxide content began decreasing and sediment began forming. Antioxidant 1 was more effective than 2 in retarding oxidation and sediment formation. With the 12 ppm antioxidant 1 blends (Figure 2), rapid peroxide formation began after approximately 52 weeks at 60 °C. The peroxide concentration was still increasing, and color formation was just beginning when the experiment was terminated after 68 weeks at 60 °C. Fuel A with 24 ppm of antioxidant 1 was just beginning to form significant peroxides at 68 weeks. Although only limited data were obtained in aging experiments with fuel B at 60 °C, the time profiles for peroxide content (Figure 3) clearly show this fuel to be less stable than fuel A as the peroxide contents of the neat fuel and of the fuel with 12 ppm antioxidant 2 peaked at about 18 and 24 weeks, respectively, compared to 32 and 52 weeks for the corresponding values for fuel A. Also, antioxidant 1 was more effective than antioxidant 2 in delaying peroxide, color, and sediment formation in fuel B as it was with fuel A.

In aging experiments at 80 °C, the formation of peroxides and sediment followed a pattern similar to that at 60 °C, except the induction period was much shorter, and the reactions proceeded much more rapidly. Again, antioxidant 1 was more effective in retarding oxidation and sediment formation than was antioxidant 2. Time profiles for peroxide number, color formation, and sediment formation for fuel A alone and with the two additives are shown in Figure 4. Color values reported as less than a given number by the ASTM method were arbitrarily assigned an intermediate numerical value equidistant between the values prescribed in the method (e.g., a value reported as <0.5 was assigned as 0.25). When aged at 80 °C, fuel B again was less stable than fuel A at the same conditions, but the differences in stability were less pronounced than for the 60 °C data. After 8 weeks at 80 °C, fuel B and the fuel-antioxidant blends were murky in appearance and contained a large quantity of gelatinous filterable sediment. With increasing aging time, the samples had increasing quantities of adherent sediment and much smaller amounts of filterable sediment. The quantity of adherent sediment produced in the neat fuel reached a maximum of about 1.5 grams per 100 ml of fuel at an aging time of 20 weeks, then decreased with longer aging times. The explanation for this decrease in adherent sediment is not certain. Experimental error is a possibility; however, values obtained for duplicate samples would indicate otherwise. A possible explanation is increased solubility of the sediment material in the fuel as the fuel becomes increasingly oxidized.

Analysis of Fresh and Aged Fuels. Efforts to detect oxygenated products in the fuels met with limited success. GC/MS results on acylated and esterified samples of the whole fuels showed very low levels of these derivatives in all samples. Since hydroxyaromatics and carboxylic acids are known to be present in the sediment (as discussed below), this may suggest that they are readily lost from the fuel by insolubility or by reaction to form sediment. In any case, compounds of these classes that are soluble in the fuel may or may not be very representative of those compounds that react to form sediment. In an attempt to detect any aldehydes or ketones in the fuels, the samples were derivatized by methoxyhydroxylamine followed by gas chromatographic analysis with a nitrogen-specific detector. Although neither of these carbonyl classes was detected in the samples of the fresh and early peroxide-maxima fuels, both fuels from the late-storage (high sediment) stage showed traces of carbonyls. However, the levels detected were too low to justify attempts to pursue identification by GC/MS.

Another approach was pursued to determine compounds in the fuel which are precursors to sediment formation. In this approach, the total-ion-current (TIC) chromatograms and individual mass chromatograms of the fresh and aged fuels were examined to detect those compounds that decreased in concentration during the aging process. Most of the fuel components appeared to be stable under the conditions of these experiments. Thus, it was possible to determine some of the more reactive fuel components by their decreasing peak response in the relatively stable field of the other fuel compounds. A summary of the results is given in Table II. The dominant reactive species identified in both fuels are cycloalkylmonoaromatics (alkylindans/tetralins). Lesser numbers of alkylbenzenes and olefins or cycloparaffins were identified as reactive components. Analysis of the sediments by GC/MS and by PMD/HRMS, as discussed below, has identified alkylindans and alkyltetralins as being among the major compound classes present in the sediments. In addition, oxygenated compounds with structures related to indans and tetralins have been identified in the sediments by GC/MS and their elemental formulas verified by PMD/HRMS.

Identification of reactive compounds directly in the fuels is complicated also by the fact that production of significant amounts of sediment may occur with only relatively small changes in overall fuel composition. In this regard, samples of the fresh fuels and the fuels at various stages of aging were separated by HPLC into acid, base, and neutral fractions [21]. The results summarized in Table III show dramatic increases in both acid and base fractions after aging of both fuels. However, even with these large increases, the total of the acid and base fractions remained less than 5% of the total fuel in each case. Thus, changes in concentrations of neutral fuel components after aging could be difficult to determine unless relatively few components are oxidized to polar compounds. Therefore, although the GC/MS results on the fuel samples indicated that alkylindans/tetralins were oxidized more readily than other fuel components, direct analysis of the sediments may provide better information concerning sediment precursors and reaction paths and mechanisms.

Analysis of Sediments. Composite results from GC/MS analyses of the four sediment samples before and after derivatization (acylation and esterification) are summarized in Table IV. The GC/MS peak identifications were made by both retention time and mass spectral matching of authentic samples of the parent and, where available, alkyl-substituted homologs for the compound types shown unless otherwise noted in Table IV. Figure 5 shows example GC/MS total-ion-current chromatograms of plain and derivatized sediment from fuel A (60° C, 44 weeks). These chromatograms are typical of those obtained from the other sediments. The combined acylation-esterification derivatization significantly altered the sample, as seen from comparison of Figures 5A and 5B. Loss of alkylindenes [designated C_0-10H [22] (indene) and C_1-10H (methylindene isomers) in Figure 5A] after derivatization is quite evident, difficult to explain, and will be discussed later. Figure 6 shows an example of a compound identification by GC/MS. The mass spectrum and retention time matched those of the trifluoroacetyl derivative of 1-naphthol. The spectrum was recorded at a retention time of 55 min 6 s in the GC/MS run of the fuel B, 12-week, 80° C, derivatized sediment sample. Comparison of the individual GC/MS analysis data sets indicated that the compositions of the four sediment samples were very similar. Some differences in relative abundances of the compound types present were observed. However, basically the same compound types were observed in each of the four sediment samples. Prominent compound types were alkylindenes, alkyl-1,2-dihydronaphthalenes, alkylnaphthalenes, alkyl-1-tetralones, alkylindenols, and alkyl-1-naphthols. Lesser amounts of alkylindans, alkylphenols, and alkylindanols were detected. In addition alkyl-2,3-benzofurans, and alkyl-o-phthalic anhydrides were identified by GC/MS. No sulfur-containing compounds and little or no nitrogen compounds were detected in the sediment samples. Their absence might have been predicted from the very low elemental sulfur (<9 ppm) and nitrogen (<0.3 ppm) contents of these fuels.

PMD/MS composite results, summarized in part in column 7 of Table IV, indicated that broader ranges of compound types and carbon numbers within each type were present than the GC/MS results showed. However, the predominant types indicated by PMD/MS were consistent with those determined by GC/MS. Additional less abundant, or secondary, distributions of hydrocarbons, and compounds containing one, two, and three oxygen atoms were observed by PMD/MS. These secondary compound distributions were at m/z and Z values consistent with the compounds being dimers of the predominant hydrocarbons and oxygen-containing compounds determined both by GC/MS and PMD/MS.

PMD/MS results for the fuel A, 44-week, 60° C sediment are typical. This sediment was found to consist primarily of hydrocarbons and compounds containing one, two, and three oxygen atoms. No significant amounts of compounds containing nitrogen or sulfur were detected. Hydrocarbons of the type C_nH_{2n+Z} with Z values of -8, -10, and -12 were most prominent. Lesser amounts of hydrocarbons with Z values of -4, -6, and -16 were also detected. The -8H compounds are consistent with alkylindans and alkyltetralins which were identified in the GC/MS analysis of this sediment (see Table IV for structures of most compounds discussed in the PMD/MS results). Ions at m/z 118, 132, 146, and 160 were observed in the high-resolution spectra. In the -10H Z series, compounds which are consistent with indene, dihydronaphthalene, and their alkylated homologs (also identified by GC/MS) were observed. Ions at m/z 116, 130, 144, 158, 172, and 186 were observed, with those at 130 and 144 the most abundant. The Z-series -12H compounds observed are consistent with naphthalene and its alkylated homologs several of which were identified by GC/MS. Ions at m/z 128, 142, 156, 170, and 184 were observed, with methylnaphthalenes (m/z = 142) apparently most abundant. Small amounts of -6H compounds (alkylbenzenes) and traces of -4H, -14H, and -16H compounds were also detected.

High resolution results for fuel B sediments differed in that considerably more hydrocarbon types (with Z values ranging from -16 to -30) were observed than for the sediment from fuel A. However, it should be noted that the most abundant hydrocarbon types observed in each case were the -8H, -10H, and -12H hydrocarbons (alkylindans/tetralins, alkylindenes/dihydronaphthalenes, and alkylnaphthalenes, respectively).

Prominent oxygen-containing compound types observed in fuel A, 44-week sediment were also similar to those observed in fuel B sediment and appear to be (at least in part) oxidation products of the predominant hydrocarbons observed. Single oxygen-containing compounds ($C_nH_{2n+Z}O$) with Z values from -4 through -22 were observed. The most prominent types were -8(O), -10(O), and -12(O). These Z-series types are consistent for the most part with specific compounds identified in the GC/MS studies on this sediment. Compound classes and carbon number ranges for the prominent types are given in Table IV. The high-resolution mass spectral data indicated dioxygen compounds are also present in fuel A sediment in large concentrations. Again, the major O_2 types were in Z-series with Z values of -8, -10, and -12. Very little success was attained in identifying specific O_2 compounds. The GC/MS data suggest the presence of hydroxybenzofurans and carboxylic acids. Lesser amounts of -4(O_2), -6(O_2), -14(O_2), -22(O_2), -24(O_2), and -26(O_2) compound types were observed by PMD/MS. The lack of compounds in Z-series with Z values from -16 through -20 and the appearance of compounds in the -22(O_2) and -24(O_2) Z-series suggest that the latter may be dimers of the prominent -8(O), -10(O), and -12(O) compound types. Dimers and trimers have been observed previously in analyses of diesel fuel [8] and jet fuel [23,10] sediments and oxidized fuels, although they were determined or suspected to be nitrogen compounds in two cases [8,23]. Results for O_3- and O_4- compound types were similar to those for the HC, O, and O_2 types discussed above. In summary, PMD/MS analysis of fuel A sediment formed after 44 weeks of aging at 60° C indicated that O-, O_2-, hydrocarbon, and O_3-compound types were the most abundant types present (listed in decreasing order of abundance).

As with the mass spectral analysis results discussed above, infrared analyses of each sediment and derivatized sediment sample indicated that the four sediments were similar in composition. However, the IR data indicated that fuel A sediments had higher levels of hydroxyl compounds than fuel B sediments. Furthermore, in each case, the dominant IR band observed occurred in the spectral region characteristic of carbonyl functional groups. The broadness of the carbonyl bands indicated multiple types and/or intermolecular bonding. A very broad band typical of hydrogen-bonded hydroxyl groups was also evident in the spectra. The hydroxyl band shape and frequency range were analogous to those observed in carboxylic acid spectra. Thus, the IR data support the tentative identification of carboxylic acids by GC/MS. Comparison of the carbonyl band data for each of the sediment samples indicated that similar levels of about 40 weight percent carbonyl-containing compounds were present in all four sediments. This determination is only approximate and is based on assumptions of equal carbonyl IR response factors of 33L m^{-1} mm^{-1}, average molecular weights of 230, and only one carbonyl group per molecule. The intense carbonyl band coupled with the broad hydroxyl band and relatively less intense bands from carbon-hydrogen vibrations suggests a preponderance of oxygen-containing compounds in the sediment samples.

Although significant uncertainty exists in the qualitative and quantitative interpretation of the IR spectra, the results are reasonably consistent with the GC/MS and PMD/MS results, which also indicate a predominance of oxygen-containing species and similar compositions for the four sediment samples. The main apparent disparity between the IR and MS results is the indication of higher concentrations of hydrocarbons according to the PMD/MS results assuming equal response factors for all compounds. Since assumptions are involved in quantitation of both the IR and MS data, the differences may be more apparent than real.

The IR-MS apparent disparity is consistent, however, with one explanation for the disappearance of methylindenes in the GC/MS run of derivatized fuel A, 44-week, 60° C sediment, while they were observed in the GC/MS run of the same underivatized sample (Figures 5A and 5B). It is possible that the sediment contains some thermally labile compounds (such as alcohols or peroxides) which decompose in the GC split-splitless injector (T = 300° C) to form hydrocarbons (e.g., the methylindenes). If the derivatized compounds are sufficiently more thermally stable, or if they decompose to other products, the disappearance of the methylindenes could be explained. Preliminary experiments with on-column injection of methylene chloride solutions of the fuel A, 19-week, 80° C sediment show much less GC resolution and no significant quantities of indans/tetralins or indenes/dihydronaphthalenes present. This may indicate that considerable decomposition (pyrolysis) of the sediment occurred in the split-splitless injector used in the earlier GC/MS analyses.

Significant hydrocarbon peaks were observed in the PMD/MS of the sediments, where the sediments are vaporized at approximately 10^{-6} torr and encounter temperatures ranging from -80° to 350° C. Ions consistent with the methylindenes and other alkylindenes and/or alkyldihydronaphthalenes were observed at probe temperatures from 50° to 150° C. It is possible that the suspected thermally labile compounds also decompose upon ionization at low-ionizing voltages (approximately 12 eV) producing apparent hydrocarbon molecular ions. If this does not occur, a discrepancy still exists.

Further examination of the sediments by field desorption and/or fast atom bombardment mass spectrometry may allow determination of the presence or absence of thermally labile compounds and/or higher molecular weight polymeric material. In addition, analysis of polar fractions separated from the aged fuels and analysis of sediments formed in the presence of hindered phenol antioxidants may reveal further aspects of sediment formation reactions and mechanisms. Also, results from analyses of fuels and sediments in the aging experiments with antioxidants present, which are planned in the next phase of the study, will be compared with the current results to determine any effects of the additives on sediment composition and fuel degradation reactions. Nevertheless, a number of conclusions can be drawn from the results obtained in this phase of the study.

CONCLUSIONS

The consistent picture from the aging experiments with these two fuels and the fuels with added antioxidants indicates the presence of an initial induction period in which the added antioxidants and/or any naturally occurring antioxidants in the fuel prevent the formation of significant quantities of peroxides. The induction period is followed by a period of rapid depletion of antioxidant and an increase in peroxide content. The final period is characterized by decreasing peroxide content, increasing color formation, and increasing sediment formation. The presence of the antioxidant additives increases the induction period, thereby delaying the onset of peroxide, color, and sediment formation. These observations support the free radical chain oxidation mechanism as a primary mechanism operative in sediment formation for these two fuels. The very low nitrogen content of both fuels precludes the presence of any appreciable pyrrole- or indole-type compounds in either fuel. Thus, the lack of evidence to support an electron-transfer initiated oxidation mechanism, which is proposed for the autoxidation of pyrroles, is completely understandable for these two fuels.

The fuel and sediment analytical results indicate that oxidation of parent and alkyl-substituted indans, tetralins, indenes, dihydronaphthalenes, naphthalenes, and benzenes results in formation of sediments or gums. The presence of dimers is consistent with either the condensation of oxidation products of alkylnaphthalenes or the coupling of substrates by peroxides. The GC/MS, PMD/MS, and IR data supplement and confirm each other to a great extent, with each indicating that the four sediment samples are similar in composition differing mainly in the relative amounts of the compound types determined. The infrared data indicate that fuel A sediments had higher levels of hydroxyl compounds than fuel B sediments. The PMD/MS data indicate a slight trend toward decreased hydrocarbon content (or compounds producing apparent hydrocarbon molecular ions) and increased oxygenated compound content with increased aging time. Whether the hydrocarbons are detected because they are part of the sediment by being absorbed on or occluded in the sediment or because they are decomposition products of sediment molecules, the predominance of similar structures in the hydrocarbon and oxygen-containing compound types detected indicate that sediment produced in these fuels results primarily from oxidation of indans, tetralins, indenes, dihydronaphthalenes, and naphthalenes present in the fuel.

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22. In this notation, C_x indicates x number of carbon atoms in the alkyl substituents. The -10H is the Z-series notation for the homologous series of compounds with formulas C_nH_{2n-10}. In the Z-series notation, the numerical part (-10 in this case) comes from the value of Z in the general formula $C_nH_{2n+Z}N_aO_bS_c$. Z can be considered as a measure of the hydrogen deficiency of a compound type relative to a paraffin (Z = +2). Letters following the numerical part indicate any heteroatoms present except that H

indicates a hydrocarbon (i.e., no heteroatoms present). Numerical subscripts (represented by a, b, and c in the general formula) indicate the number of each heteroatom present in each compound in the homologous series (the numerical subscript is left blank when equal to 1). Finally, the letter "O", representing an oxygen atom, is placed in parentheses when necessary to avoid confusing it with a zero in the numerical part of the notation.

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Table I. Selected Physical and Chemical Properties of Fuels A and B and JP-5 Specifications

	Fuel		JP-5
	A	B	Specifications
Specific gravity @ 60°/60 °F	0.8307	0.8249	0.7883-0.8448
Elemental content			
Carbon,[a] wt pct	87.01	86.27	---
Hydrogen,[a] wt pct	12.96[d]	13.63	13.4 min
Nitrogen,[b] ppm	0.3	0.2	---
Sulfur,[c] ppm	8.1	0.5	4000 max

[a] Perkin-Elmer 240C analyzer.
[b] Antek chemiluminescence technique.
[c] Microcoulometric Method, ASTM D 3120
[d] Off-specification.

Table II. - Summary of reactive components from GC/MS analysis of fuel samples

	Fuel A	Fuel B
Peaks tagged	19	67
Peaks identified	18	45
Alkene or cycloalkane	4	10
Cycloalkylmonoaromatic	9	26
Other aromatic	5	3

TABLE III - Acid, base, and neutral fraction yields of fresh and aged fuels

	Weight percent			
Sample	Acids	Bases	Neutrals	Total
Fuel A, fresh	0.08	0.03	97.22	97.32
Fuel A, aged 28 weeks at 60° C	3.10	0.39	92.46	96.07
Fuel B, fresh	0.21	0.01	100.96	101.18
Fuel B, aged 6 weeks at 80° C	2.78	0.85	98.70	102.33
Fuel B, aged 8 weeks at 80° C	3.35	1.00	97.24	101.59
Fuel B, aged 16 weeks at 80° C	3.66	0.85	98.08	102.59

TABLE IV. Compound types identified in sediments

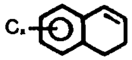
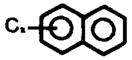
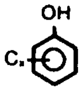
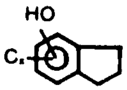
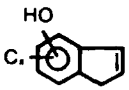
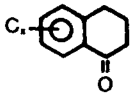
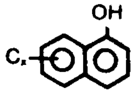
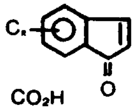
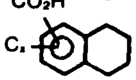
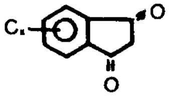
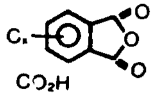
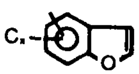
Compound type	Subtype	Empirical formula	Z-series	Structure	Range for carbon numbers in alkyl substituents (x) GC/MS	PMD/MS	Overall abundance in sediments
Hydrocarbon	Alkylindans	C_nH_{2n-8}	-8H		0-4	0-5	low
Hydrocarbon	Alkylindenes	C_nH_{2n-10}	-10H		0-4	0-6	high
Hydrocarbon	Alkyldihydronaphthalenes	C_nH_{2n-10}	-10H		0-2	0-5	high
Hydrocarbon	Alkylnaphthalenes	C_nH_{2n-12}	-12H		0-4	0-5	medium
Hydroxyaromatic	Alkylphenols	$C_nH_{2n-6}^{0}$	-6(0)		0-5	1-8	low
Hydroxyaromatic	Alkylindanols	$C_nH_{2n-8}^{0}$	-8(0)		0-4	0-7	low
Enol or Hydroxyaromatic	Alkylindenols	$C_nH_{2n-10}^{0}$	-10(0)	 	0-4	0-6	high

TABLE IV. Compound types identified in sediments (cont'd)

Compound type	Subtype	Empirical formula	Z-series	Structure	Range for carbon numbers in alkyl substituents (x) GC/MS	Range for carbon numbers in alkyl substituents (x) PMD/MS	Overall abundance in sediments
Ether	Alkylbenzofurans	$C_nH_{2n-10}O$	-10(O)		0-4	0-7	low
Ketone	Alkyl-1-tetralones	$C_nH_{2n-10}O$	-10(O)		0-2	0-5	high
Hydroxyaromatic	Alkyl-1-naphthols	$C_nH_{2n-12}O$	-12(O)		0-4	0-5	high
Ketone	Alkyl-1-indenones	$C_nH_{2n-12}O$	-12(O)		?	1-6	presence suspected but unconfirmed
Carboxylic Acids	Alkyltetrahydro-naphthoic acids	$C_nH_{2n-12}O_2$	$-10(O)_2$		?	0-4	presence suspected but unconfirmed
Dione	Alkyl-1,3-indandiones	$C_nH_{2n-12}O_2$	$-12(O)_2$		?	0-6	presence suspected but unconfirmed
Anhydride	Alkyl-o-phthalic anhydride	$C_nH_{2n-12}O_3$	$-12(O)_3$		0-2	1-7	low
Mixed Ether Acids	Alkylbenzofuran-carboxylic acids	$C_nH_{2n-12}O_3$	$-12(O)_3$		?	0-6	presence suspected but unconfirmed

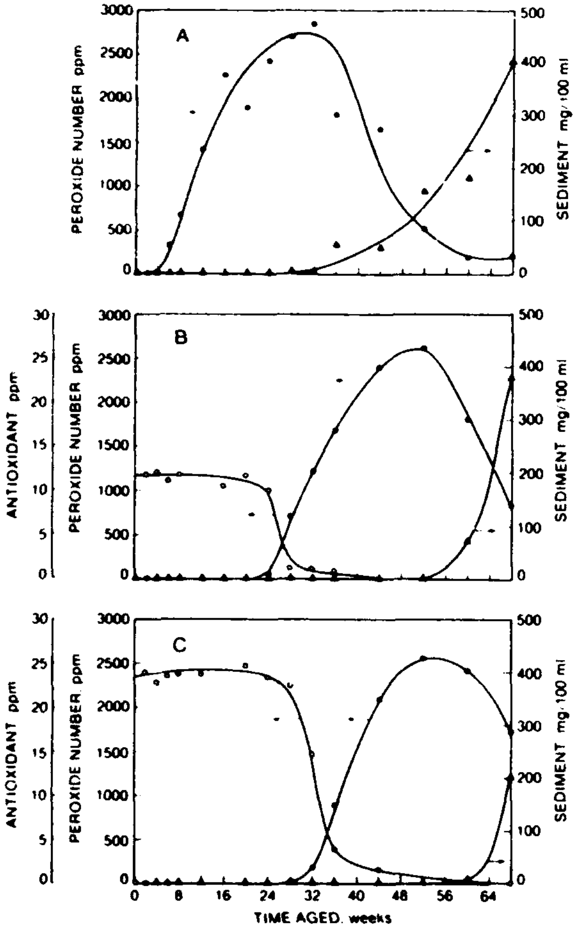


Figure 1. Time profiles of antioxidant level (○), peroxide number(●), and total sediment (filterable and adherent sediment) (▲) in fuel A neat (A), blended with 12 ppm antioxidant 2 (B), and blended with 24 ppm antioxidant 2 (C), aged at 60 C.

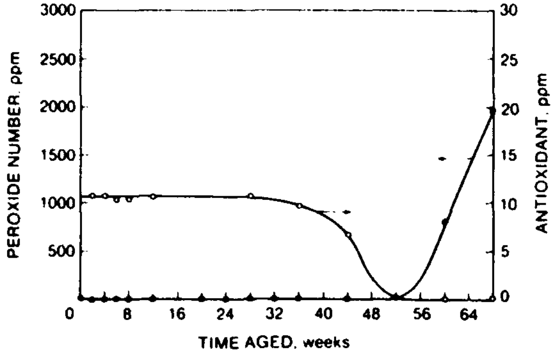


Figure 2. Time profiles of antioxidant level (○) and peroxide number (●) in fuel A blended with 12 ppm antioxidant 1 aged at 60 °C.

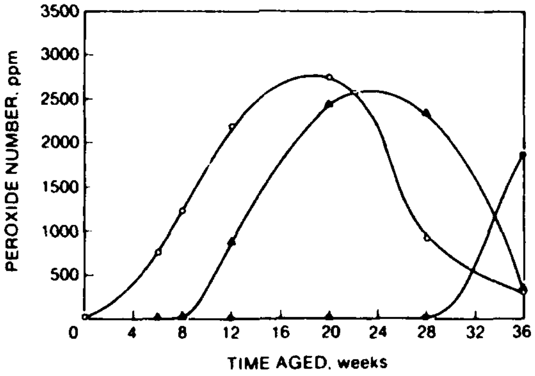


Figure 3. Time profiles of peroxide numbers in fuel B neat (○), blended with 12 ppm antioxidant 1 (●), and blended with 12 ppm antioxidant 2 (▲), aged at 60 °C.

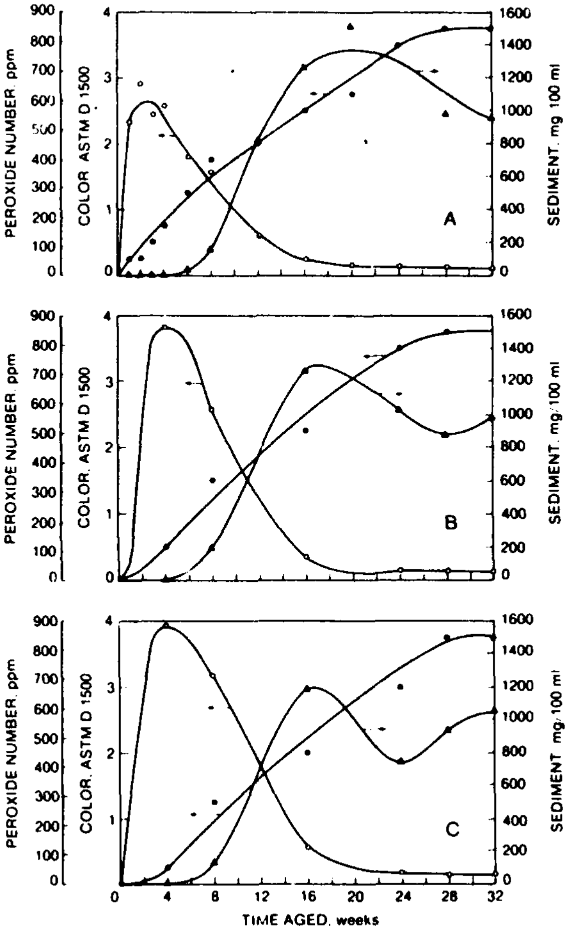


Figure 4. Time profiles of peroxide number (○), color formation (●), and total sediment (▲) in fuel B neat (A), blended with 12 ppm antioxidant 2 (B), and blended with 12 ppm antioxidant 1 (C), aged at 80 °C.

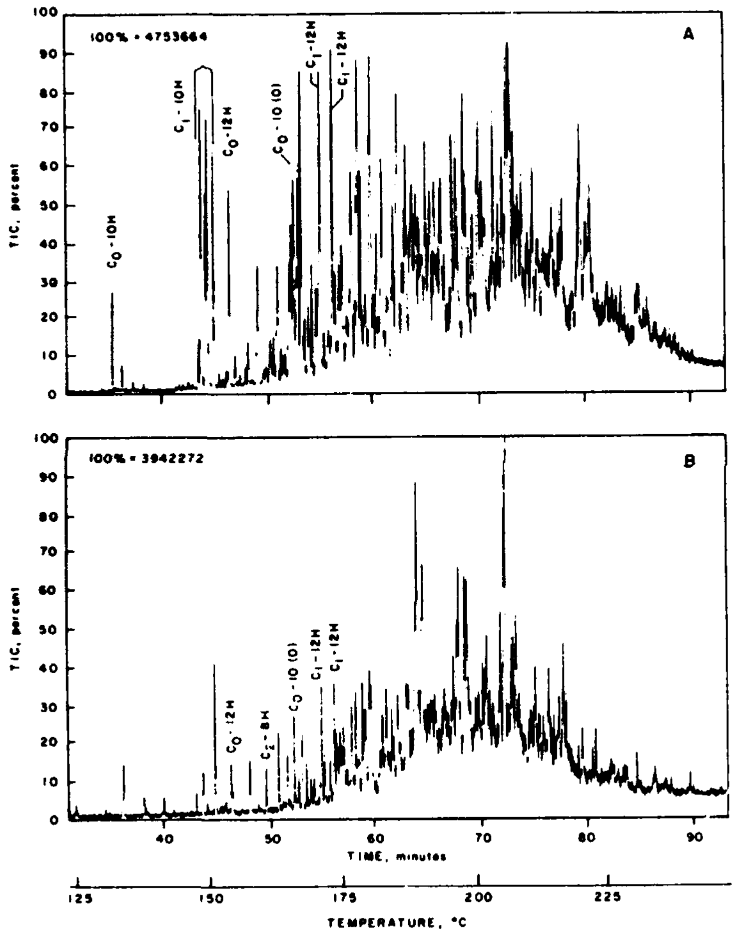


Figure 5. GC/MS total-ion-current (TIC) chromatograms of plain (A) and derivatized (B) sediment from fuel A (60 °C, 44 weeks). See Table IV for identities of labeled peaks.

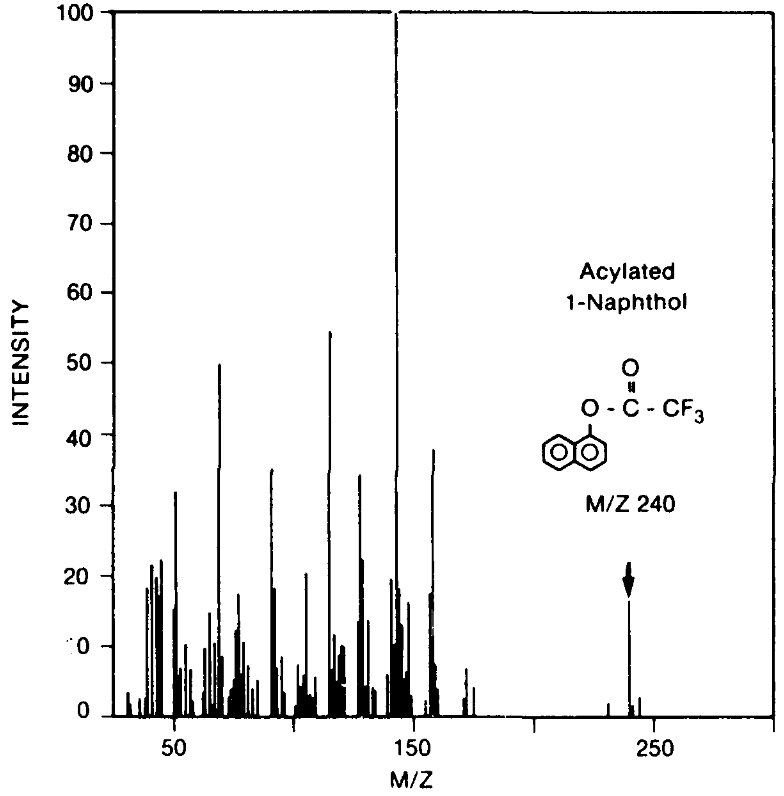


Figure 6. Mass spectrum recorded in scan 2216 at 55 min 6 s in the GC/MS run of fuel B, 12-week, 80 °C, derivatized sediment. Retention time and mass spectrum matched authentic sample of trifluoroacetyl derivative of 1-naphthol.

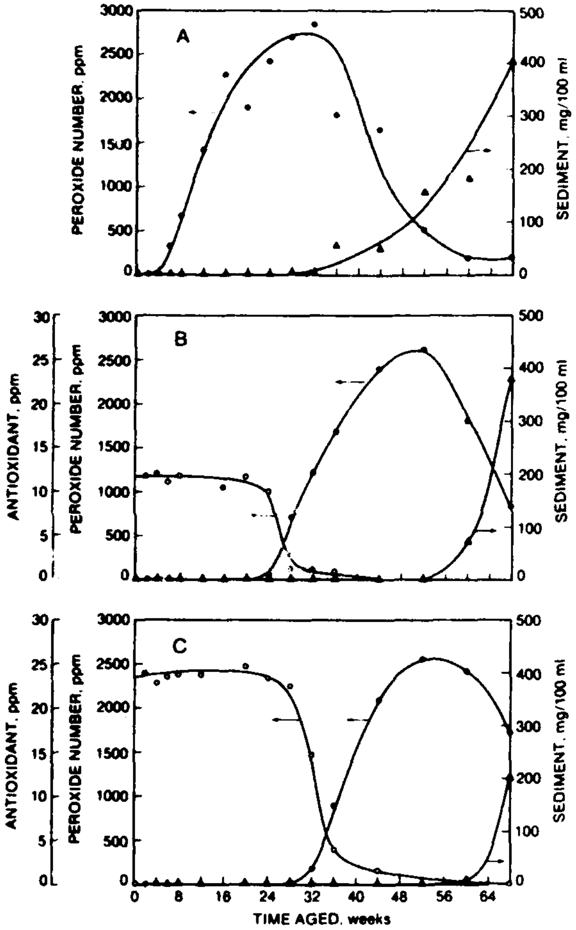


Figure 1. Time profiles of antioxidant level (○), peroxide number(●), and total sediment (filterable and adherent sediment) (▲) in fuel A neat (A), blended with 12 ppm antioxidant 2 (B), and blended with 24 ppm antioxidant 2 (C), aged at 60 °C.

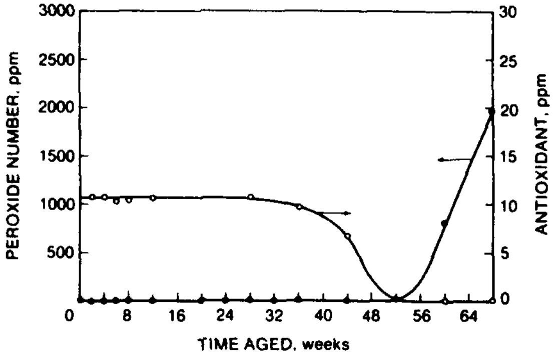


Figure 2. Time profiles of antioxidant level (○) and peroxide number (●) in fuel A blended with 12 ppm antioxidant 1 aged at 60 °C.

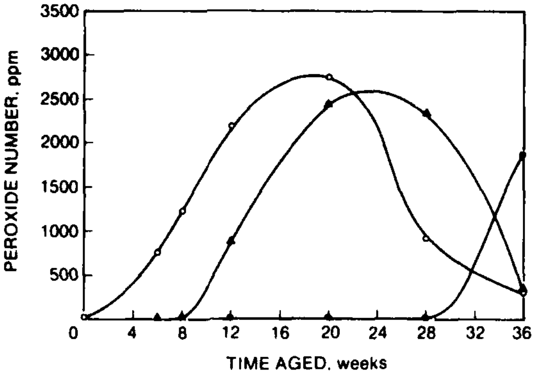


Figure 3. Time profiles of peroxide numbers in fuel B neat ( ), blended with 12 ppm antioxidant 1 (●), and blended with 12 ppm antioxidant 2 (▲), aged at 60 °C.

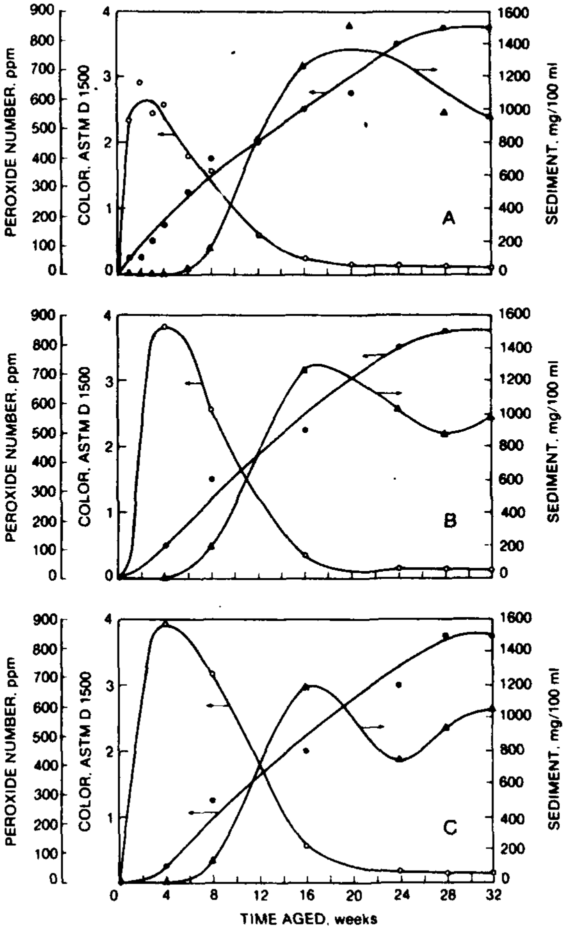


Figure 4. Time profiles of peroxide number (○), color formation (●), and total sediment (▲) in fuel B neat (A), blended with 12 ppm antioxidant 2 (B), and blended with 12 ppm antioxidant 1 (C), aged at 60 °C.

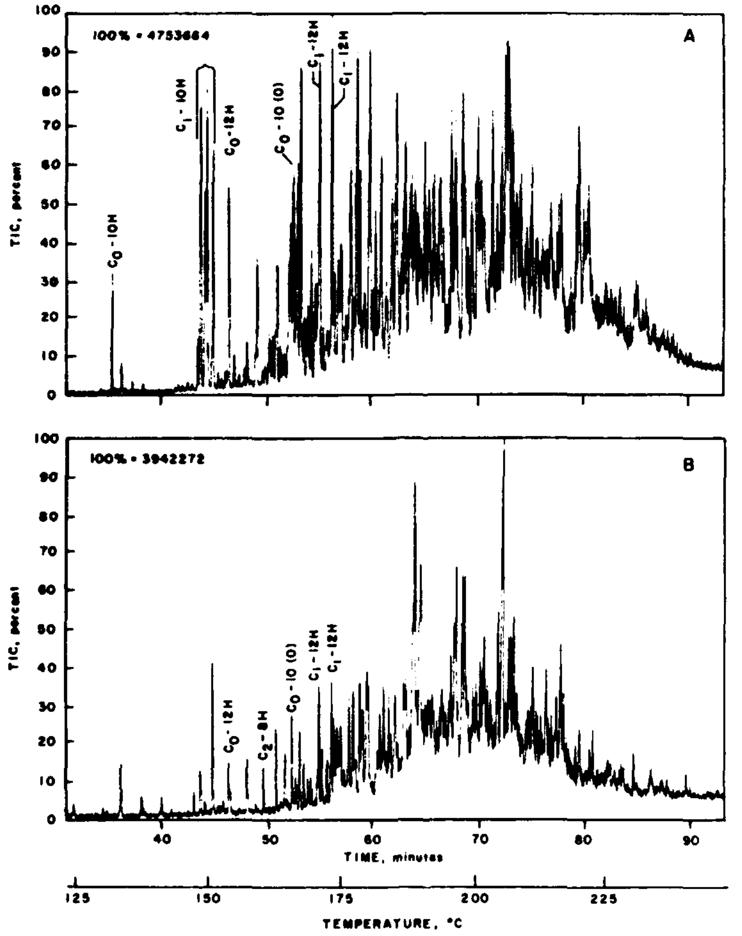


Figure 5. GC/MS total-ion-current (TIC) chromatograms of plain (A) and derivatized (B) sediment from fuel A (60 °C, 44 weeks). See Table IV for identities of labeled peaks.

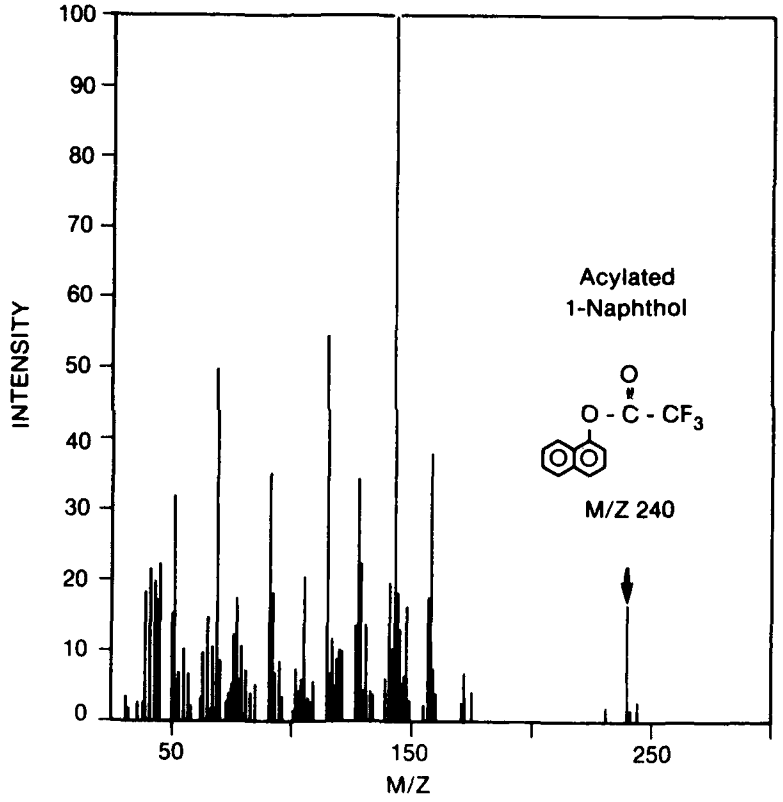


Figure 6. Mass spectrum recorded in scan 2216 at 55 min 6 s in the GC/MS run of fuel B, 12-week, 80 °C, derivatized sediment. Retention time and mass spectrum matched authentic sample of trifluoroacetyl derivative of 1-naphthol.

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EFFECT OF PEROXIDE CONTENT ON THE THERMAL STABILITY OF HYDROCRACKED AVIATION FUEL

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ABSTRACT

Extensive research efforts have been conducted to study the chemistry of both storage and thermal oxidation stability but very little work has been done to relate these two areas. Recent findings however have indicated that there may be a relationship between the two stability temperature regimes based upon the similarity in chemical composition of the gum deposits formed during accelerated storage stability tests and the deposits obtained by thermal stressing in the Jet Fuel Thermal Oxidation Tester (JFTOT).

Accelerated storage stability tests were conducted on two hydrocracked aviation fuels with and without antioxidant. Samples were analyzed for peroxide number, total acid, existent gum and thermal oxidation stability (JFTOT) regularly over a period of 16 weeks. A link was developed relating the increase in peroxide concentration of the fuel during storage with the increase of deposition in the JFTOT.

INTRODUCTION

The U. S. Navy conducts operations worldwide, therefore, there is a need to store aviation fuels at strategic locations for extended periods of time. The period of storage between production and usage varies greatly dependent upon tactical operation, therefore there must be assurance that when the fuels are used they have not deteriorated during that time.

The potential for the fuel to degrade (form peroxides, acids and gums) during storage is quite high due to the increased amount of severe hydroprocessing currently used to refine todays' lower quality feedstocks. Naturally occurring inhibitors are removed during this process, thus increasing the fuel's ability to peroxidize during storage [1]. In addition, severe cracking reactions create branched chain compounds which have proven to be extremely susceptible to oxidation [2].

Since 1976, the U. S. Navy has required the addition of phenolic type antioxidants into aviation fuel to inhibit hydrocarbons from reacting with dissolved oxygen during storage. The antioxidant is added at concentrations between 17.2 ppm (minimum) and 24 ppm (maximum) at the refinery prior to exposure to air [3]. Even though this precaution of using an additive inhibitor as protection against instability during storage currently alleviates the problem, there are still many technical questions to be resolved. First, is the type and level of inhibitor adequate to maintain the fuel's stability? Second, if the inhibitor was to be accidentally omitted or consumed during long periods of storage, what effects would the degraded fuel have on the aircraft?

The effects of antioxidant structure and concentration for inhibiting fuel degradation are well documented. In addition, significant work has been performed relating the effects of fuel degradation, specifically peroxide formation, on elastomers [4,5]. However, no work has been done to determine the effects of degradation on accelerating the fuel deposition within heat exchangers, injectors and pumps. This area becomes of increasing concern as current and future generation aircraft expose the fuel to increased heat stress for extended periods of time, thereby greatly increasing the possibility of fuel fouling.

This paper will discuss the effects on thermal oxidation stability, as measured by the JFTOT, caused by the degradation of severely hydroprocessed fuels, both with and without antioxidant, during accelerated storage.

EXPERIMENTAL DESIGN

To achieve the program objective, two fuels designated as NAPC-45 and NAPC-46 were chosen to be analyzed using standard ASTM specification tests to evaluate the fuel's storage and thermal stability. NAPC-45 was an Alaskan North Slope crude that had been hydrocracked, stripped, and caustic washed. NAPC-46 was a mixture of several different hydroprocessed crude streams and had a strong tendency toward peroxidation which made them appropriate for use in this study.

Fuel samples were stored in teflon-capped, borosilicate bottles in a 60 C (140°F) oven for a period of 16 weeks. The bottles were wrapped with aluminum foil in order to eliminate the effects of light on the oxidation process. Eighty-eight one liter bottles were prepared in this manner. The samples were stored in sufficient quantity to provide for duplicate analysis. The arrangement of samples included 32 liters of each neat fuel (without antioxidant) and 12 liters of each fuel with 12 ppm antioxidant (2,4 di-tert-butyl phenol). A lower concentration of a less effective antioxidant [6] was selected in order that some degree of peroxidation would occur. Duplicate samples of neat fuel were drawn on a weekly basis for a total of 16 weeks. Samples with additive were removed from week 9 to the conclusion of the study. The inhibited samples were stored for a longer time period before removal in order to allow peroxides to form.

The samples were analyzed using the following test methods:

1. ASTM D3703 Peroxide Content of Aviation Fuels, 2. ASTM D3242 Acid Number of Aviation Fuels and 3. ASTM D381 Gum Content of Aviation Fuels by Jet Evaporation. The thermal stability of each fuel was determined by the JFTOT (ASTM D3241). Each sample was run at a maximum tube temperature of 282°C (540°F) (breakpoint temperature for both NAPC-45 and NAPC-46) for 210 minutes. The test duration was extended from the current specification of 150 minutes in order to form enough deposit to perform further analysis. However, time and cost considerations prevented this portion of the program from being completed. The deposit formed on the tubes was rated by a Mark 8A Tube Deposit Rater (TDR). Although this method allowed only a semi-quantitative measurement of deposit formation, it did provide an adequate method to compare the test samples.

RESULTS AND DISCUSSION

NAPC-45 AND NAPC-46 responded to the accelerated storage conditions of 60°C (140°F) following the typical sequence of degradation observed in previous studies (Figure 1). Degradation of JP-5 occurs by auto-oxidation which is a free radical-initiated chain reaction whereby hydrocarbons react with oxygen to yield alkyl hydroperoxides. The decomposition of hydroperoxides produces free radical chain carriers that react to form secondary oxidation products which eventually lead to the formation of insoluble gums [7]. Gums are believed to be the precursors to solid deposits; however, no correlation between the rate of oxidation and amount of deposit actually formed has been observed.

Initial induction periods for each fuel were followed by a build-up of peroxides (Figure 2). As the hydrocarbon radicals and dissolved oxygen within the fuel were exhausted, the peroxide content reached a maximum level and began to taper off. In the fuel samples with antioxidant, the inhibitor did not eliminate the oxidation of fuel hydrocarbons but lengthened the period of induction. Results of this study agreed with work recently completed; that peroxides will remain low to non-existent until the detectable level of antioxidant reaches 0 ppm [8]. As peroxide level began to decrease, an increase of acid was observed (Figure 3) followed by an increase in filterable (Figure 4) and adherent sediment formation.

A decrease in thermal oxidation stability, as measured by the JFTOT, was observed for both NAPC-45 and NAPC-46. Significant increases in the deposition formed on the tubes were noticed as the fuel samples exhibited increased degradation during storage. The results for both fuels followed very similar trends. At low concentrations of peroxides, 0 to 150 ppm, the deposition formed appeared as a dull brown lacquer. This lacquer spanned the JFTOT tube from approximately the 35 mm to the 53 mm position. As the peroxide concentration increased the deposit became whitish in color and began much further upstream on the tube. Upstream is defined as being closer to the fuel inlet position (0 mm) and corresponds to a lower tube temperature.

Observations from the preliminary visual inspection were confirmed by the Mark 8A TDR profiles. In Figure 5, the TDR profiles for NAPC-45 containing low concentrations of peroxides, 4 ppm and 50 ppm, were single narrow peaks. These peaks began at approximately the position of highest tube temperature (38.7 mm) and spanned the tube until the 52 mm position. As the peroxide concentration increased, shown by the 580 ppm and 1850 ppm curves in Figure 5, the TDR profile became much wider with the point of initial deposition shifted to a lower tube temperature. The TDR profiles for NAPC-46, Figure 6, followed the same basic pattern as was observed for NAPC-45. At low peroxide concentrations (14 ppm and 40 ppm), a narrow single peak, which began at approximately the 35 mm tube position (corresponding to a tube temperature of 280°C (536°F), was observed. At increased concentrations, the deposition again began to shift to a lower tube temperature thereby creating a much wider TDR profile.

The total delta TDR is used as a semi-quantitative method of measuring the total amount of deposition that forms on the JFTOT tube. This value is a summation of all the spun TDR ratings made on the tube. For this study the spun ratings were made at 1 mm increments on the tube from the 12 mm to the 56 mm position. For both fuels the total delta TDR showed no correlation with either total acid concentration (ASTM D3242) or total gum formation (ASTM D381). A linear correlation (R squared = .85) however was observed between peroxide concentration and total TDR for NAPC-46 (Figure 7). A similar comparison between total delta TDR and peroxide concentration for NAPC-45 failed to give any correlation.

Further investigation related the total peroxide concentration with the tube position, and therefore, tube temperature, of both initial deposit formation and the deposit of a 15 TDR rating. A TDR of 15 was chosen because previous studies have shown that it most closely corresponded to the ASTM Thermal Oxidation Stability Specification rating of a visual code 3. The results for both fuels tested (Figure 8 and Figure 9) showed that two distinct regimes were present. These regimes were defined as low peroxide (approximately 0 ppm to 150 ppm) and high peroxide (approximately greater than 450 ppm). The transition region between the two regimes however could not be well defined. The effects of peroxide concentration in this area warrant additional work to better determine the boundaries of the high and low peroxide regions.

For NAPC-45, Figure 8, the tube temperature of initial deposition in the low peroxide regime ranged from 278°C (532°F) to 282°C (540°F). In contrast the tube temperature of the initial deposition in the high peroxide region was decreased by approximately 44°C (80°F) to 238°C (460°F). Although the peroxide concentration in this regime varied from 450 ppm to 1800 ppm very little change in tube temperature was observed. The tube temperatures of a 15 TDR rating exhibited some basic trends as were observed for the temperatures of initial deposition. In the low peroxide regime the 15 TDR was formed at tube temperatures ranging from 535°F to 540°F. The tube temperatures to reach the same TDR were almost 28°C (50°F) lower in the high peroxide samples.

The results for NAPC-46, Figure 9, followed the same trends as observed for NAPC-45 although a greater amount of scatter was noticed in the data. The tube temperature for initial deposition in the low peroxide regime ranged from 266°C (510°F) to 280°C (536°F). In contrast the temperatures of initial deposition in the high peroxide concentration regime were approximately 28°C (50°F)) lower than those measured in the low peroxide region. Tube temperatures to reach a 15 TDR rating were 11°C (20°F) to 22°C (40°F) lower in the high peroxide samples than the low peroxide samples.

Therefore both fuels tested exhibited a very significant shift of JFTOT tube deposition upstream (11°C (20°F) to 28°C (50°F) lower tube temperatures) as the peroxide concentration increased into the high peroxide regime. In addition a significant but scattered increase in total deposit, as determined by the total delta TDR, accompanied this shift. The addition of antioxidant only delayed this behavior by increasing the induction period before peroxide formation.

CONCLUSION

Although fuel degradation has been extensively investigated in the areas of both thermal oxidation and storage stability, very little effort has been performed to relate the two areas. This study has demonstrated a potential link between the peroxide concentration formed during storage degradation and the increase in thermal oxidation instability as measured by the JFTOT. For the two fuels tested, it was shown that high peroxide concentrations (greater than approximately 450 ppm) can decrease the tube temperature of JFTOT deposition by 11°C (20°F) to 39°C (70°F). Although these peroxide concentrations were extremely high they could possibly be encountered during long term storage.

The link between peroxide concentration and thermal oxidation stability could become of increasing importance as current and future aircraft expose the fuel to increased temperatures for extended periods of time. The degradation that occurs during extended storage could cause a fuel of acceptable thermal oxidation stability to degrade under the increased thermal environment. Additional work is needed however to fully understand the relationship between the fuel degradation which occurs during storage and the possible decrease in thermal oxidation stability of the fuel in the aircraft.

ACKNOWLEDGMENT

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[8] Brinkman, D.W., Bahn, O., "Storage Stability of JP-5", NIPER, Quarterly Report, April 1-June 30, 1987

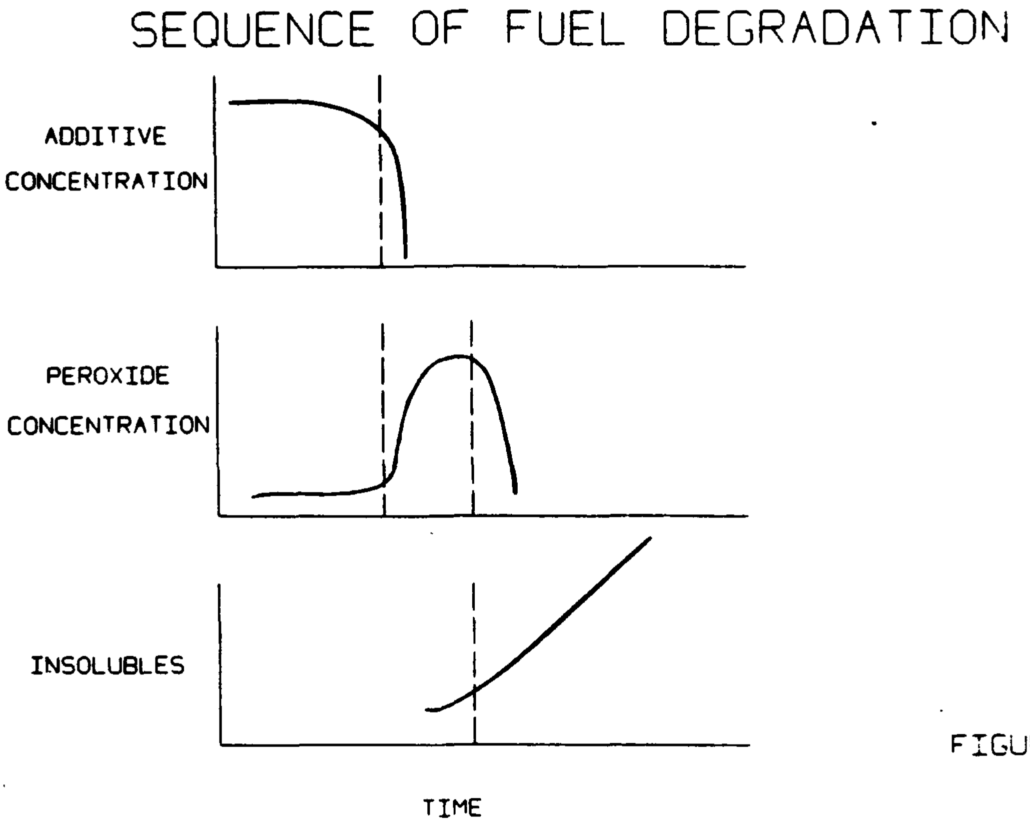

SEQUENCE OF FUEL DEGRADATION

FIGURE 1

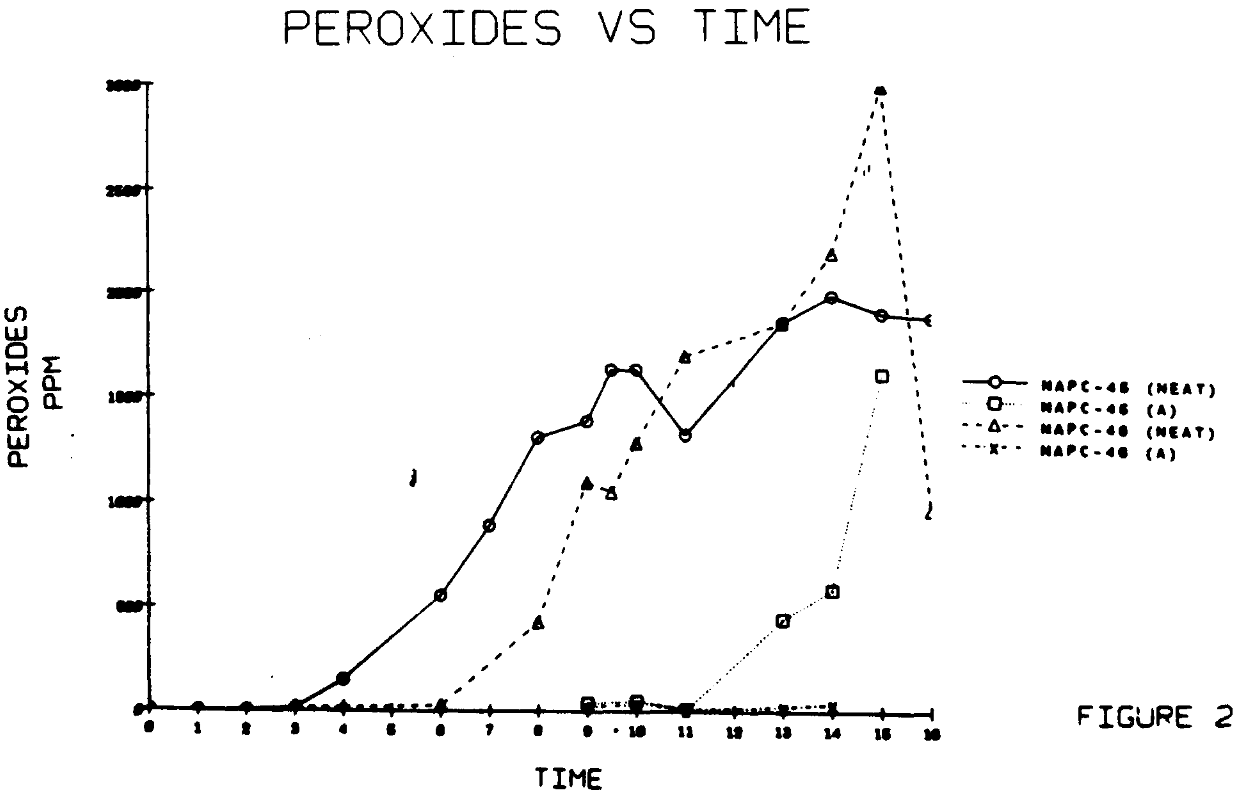

PEROXIDES VS TIME

FIGURE 2

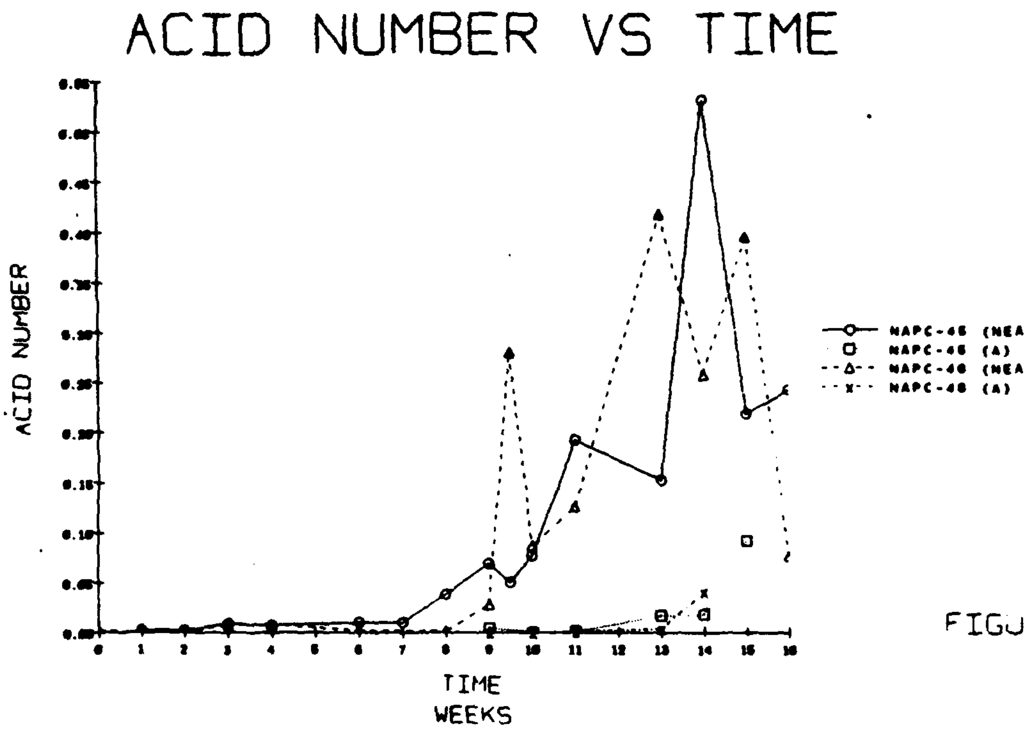


FIGURE 3

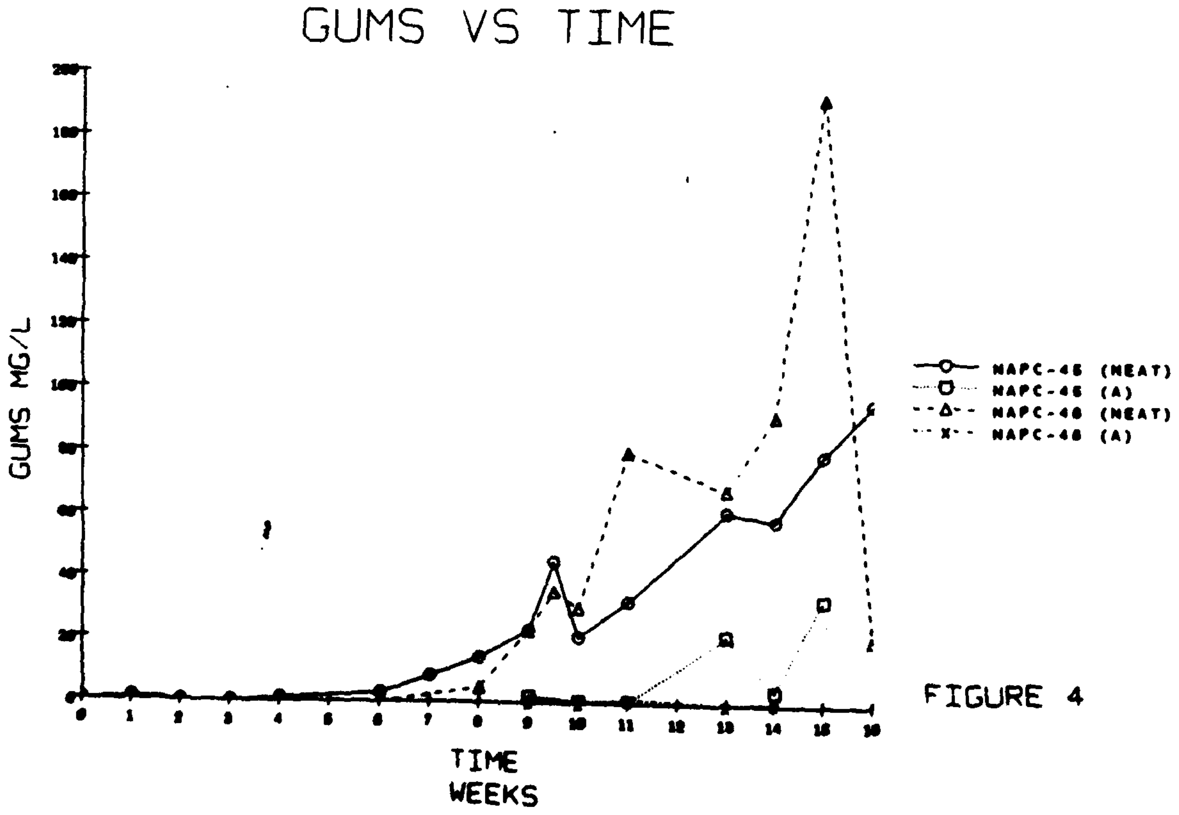


FIGURE 4

TDR PROFILES FOR NAPC-45

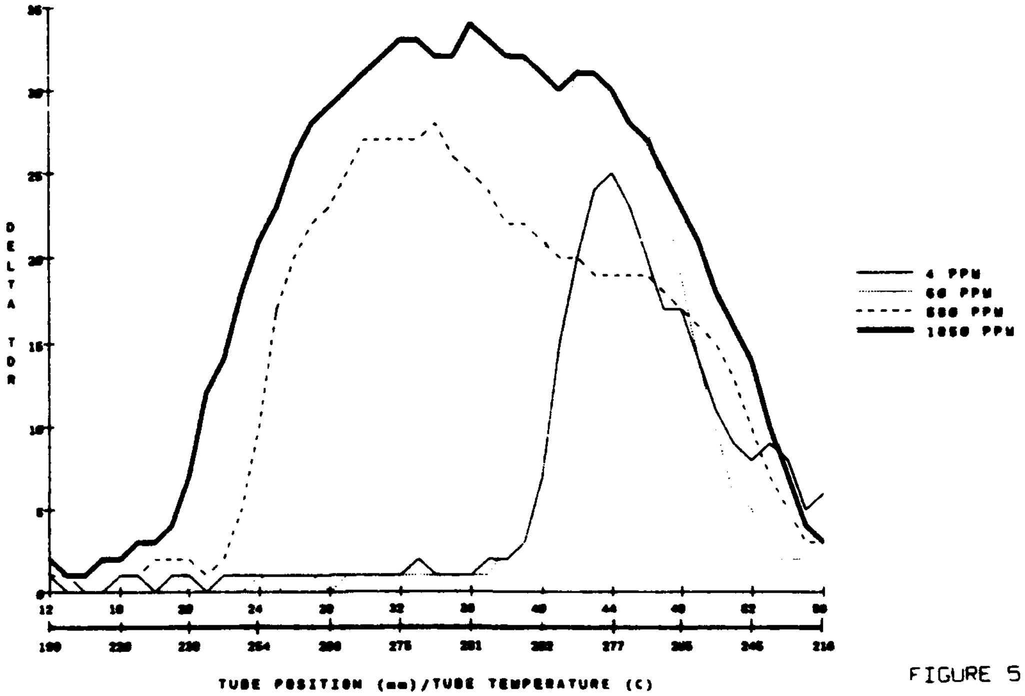


FIGURE 5

TDR PROFILES FOR NAPC-46

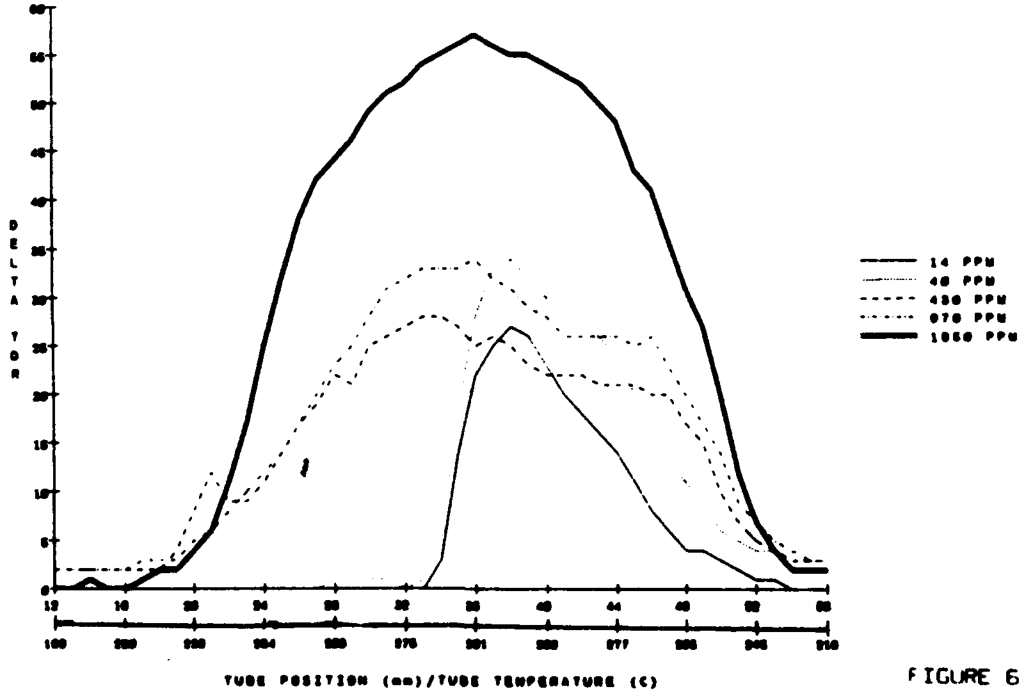


FIGURE 6

PEROXIDE CONTENT VS TOTAL DELTA TDR FOR NAPC-46

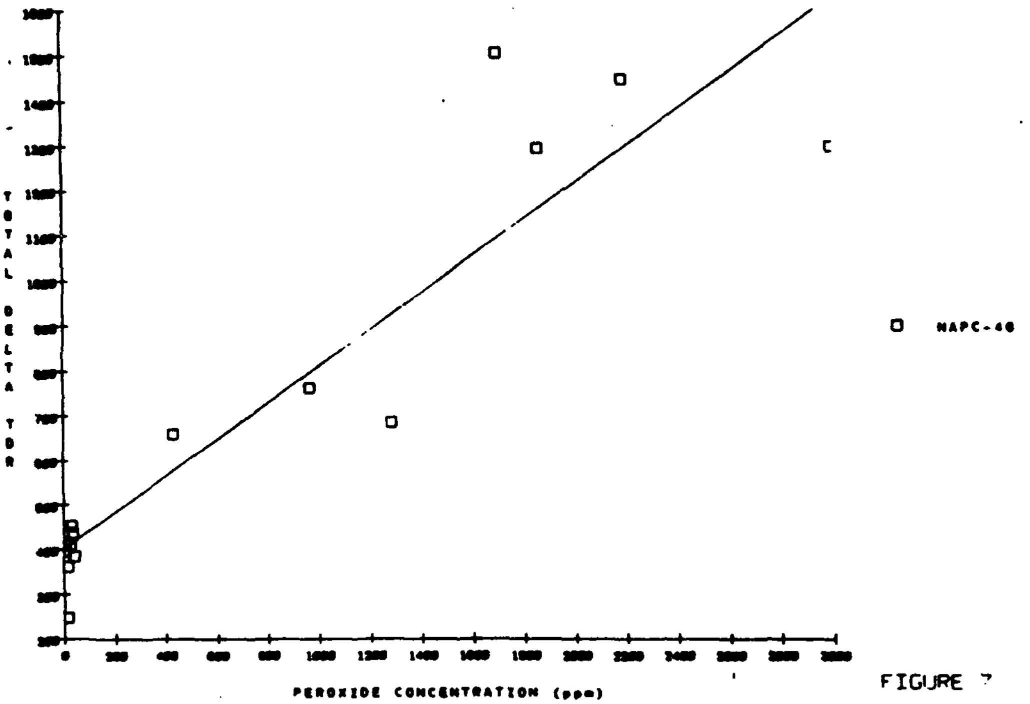


FIGURE 7

PEPOXIDE CONCENTRATION VS TDR OF INITIAL DEPOSITION AND TDR OF 15 FOR NAPC-45

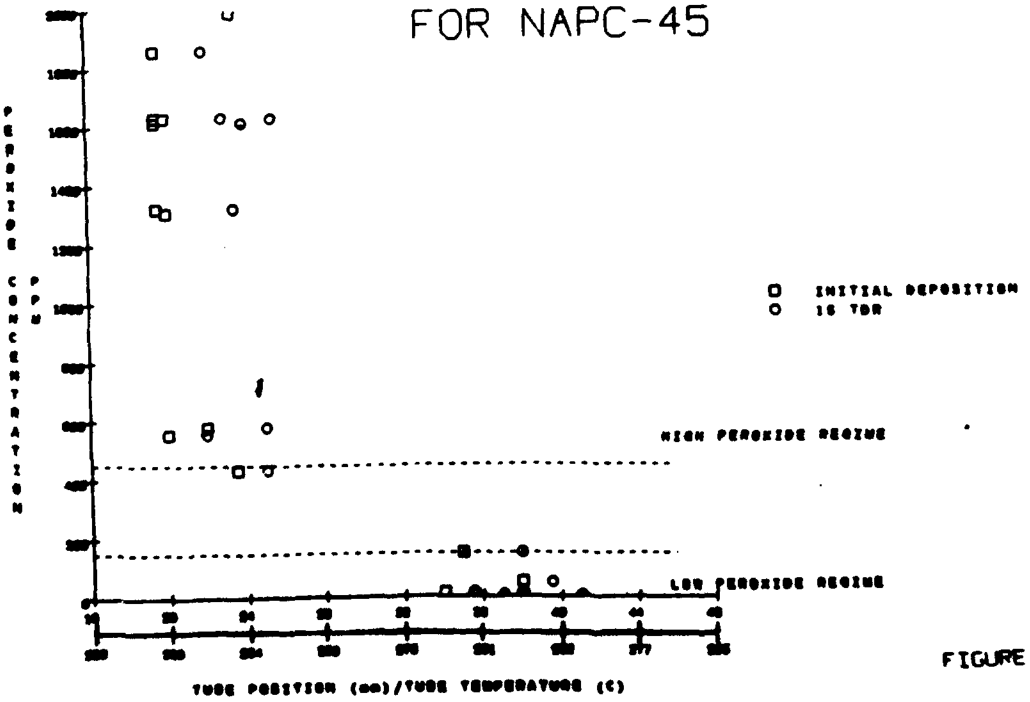
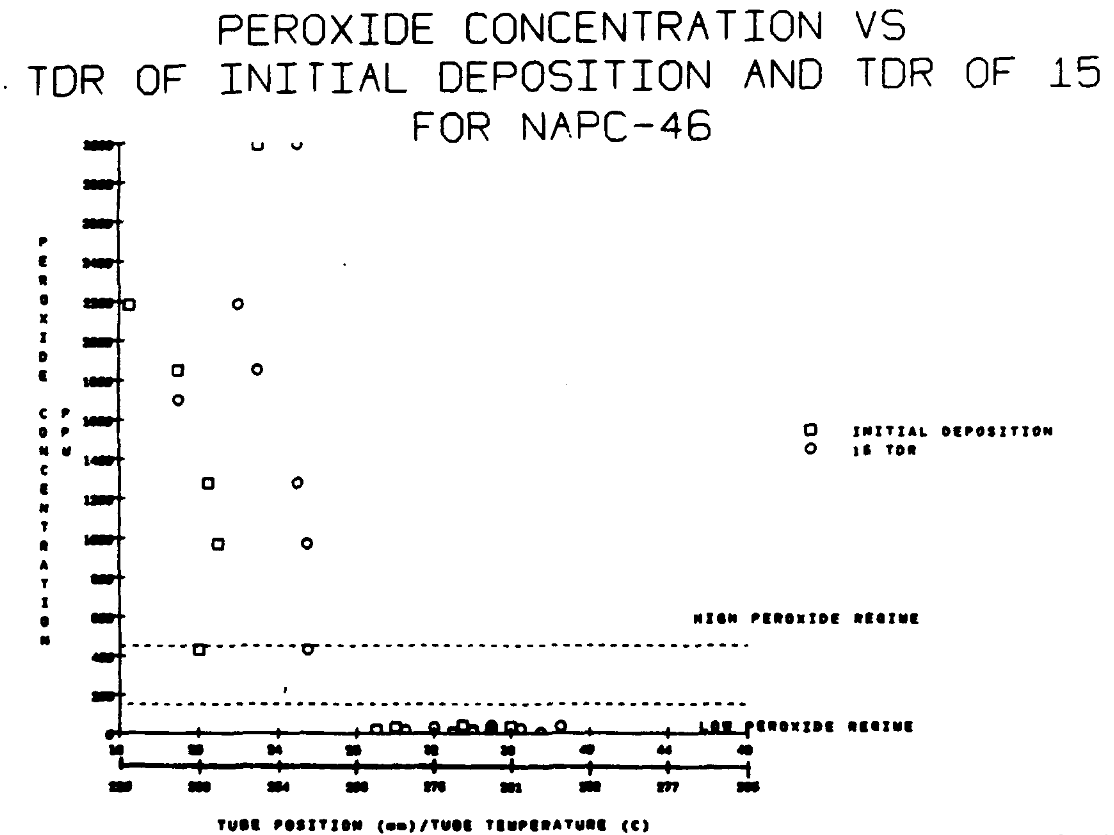


FIGURE 8



PEROXIDE CONCENTRATION VS TDR OF INITIAL DEPOSITION AND TDR OF 15 FOR NAPC-46

FIGURE 9

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RESEARCH ON PROBLEMS WITH THE USE OF CURRENT FUEL SYSTEM ICING INHIBITORS IN JET FUELS

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INTRODUCTION

To ensure that both aviation gasoline and aviation turbine fuels perform reliably in very cold environments such as those encountered in high altitude flight, military aviation fuels are normally treated with a fuel system icing inhibitor (FSII) [1-6]. The primary purpose of this class of additive is, as the designation implies, to prevent the formation of ice crystals in fuel tanks and lines that could cause in-flight fuel flow problems.

The two compounds currently used for most anti-icing applications are ethylene glycol monomethyl ether (EGME) and diethylene glycol monomethyl ether (DGME). These glycol ethers are commonly called cellosolves. EGME has the trade name of methyl cellosolve and a chemical name of 2-methoxyethanol. EGME is the FSII of choice for JP-4 fuel by virtue of its lower boiling point, while DGME is used in JP-5. The level of EGME required to prevent the formation of ice crystals is 0.1-0.15%, and DGME is added at a level of 0.15-0.2%.

Both EGME and DGME are slightly polar in character and have a hydroxyl functionality, making them extremely hydrophilic [7]. By virtue of these characteristics, glycol ethers are very effective in scavenging and dispersing traces of water from aviation fuels. However, these same characteristics result in fuel blending, handling, transfer, and storage problems. Small quantities of water in fuel storage systems, transfer lines, storage tanks, or vehicular fuel systems will readily extract the FSII additive from fuel, resulting in little or no low-temperature protection. To prevent this undesirable circumstance, aviation turbine fuels are tested at strategic distribution points and additional FSII is injected to maintain specified levels of the additive.

A primary source of FSII depletion occurs in large volume fuel storage tanks typically constructed with floating roofs. Rainwater or condensate water enters these storage tanks between the shell wall and the roof seal and settles to the bottom of the tank, extracting FSII in the process. The water and FSII mixture accumulates at the bottom of the tank and must be drawn off to prevent further depletion of the icing inhibitor at the fuel-water interface. A typical water from a JP-4 jet fuel storage tank will contain up to 22% EGME, while the water from a JP-5 storage tank may be as high as 35% DGME. In general, high volumes of wastewater (caused by residual rainfall) are usually associated with reduced FSII concentration.

The volume of water that must be removed from an aviation turbine fuel storage tank of moderate capacity can be as much as 15,000-20,000 gallons per year. If each fuel storage facility has 10 storage tanks, a total water volume of 200,000 gallons per terminal per year is a reasonable estimate. Some terminals generate as much as one million gallons of FSII-contaminated wastewater per year. In the past, this FSII/water mixture was released from time to time into diked areas around the storage tank where it evaporated or penetrated underlying media [8]. A host of recent studies that have shown these glycol ethers to be toxic now make this practice questionable based on both vapor inhalation toxicity and potential groundwater contamination.

Vapor inhalation, ingestion, and skin absorption of these glycol ethers have all been shown to have adverse health responses in laboratory animals. Dow Chemical Company issued a bulletin in 1981 to all Dow EGME customers warning that the Threshold Limit Value (TLV) in effect at that time (25 ppm) "may not provide an adequate margin of safety" [9]. The State of California issued a hazard alert in 1982 [10] for glycol ethers and specifically EGME. In 1984, the American Conference of Governmental Industrial Hygienists (ACGIH) lowered the TLV for EGME from 25 ppm to 5 ppm [11]. The U.S. Environmental Protection Agency (EPA) has only recently issued final water pollution control rules [12] on discharge limits for 66 pollutants. Although EGME is not specifically mentioned, the documented toxicity of this and related compounds makes them real candidates for future classification as hazardous materials. The EPA has referred EGME to the Occupational Safety and Health Administration (OSHA) for regulation, and OSHA has set an occupational exposure of 25 ppm as the Permissible Exposure Level for an 8-hour work shift. OSHA has also issued an Advanced Notice of Proposed Rulemaking asking for comments on further regulation of EGME [13]. The allowable limit of toxic materials discharged to water treatment facilities is currently 50 ppm. Entities sending wastes to water treatment plants will have three years to come into compliance with pretreatment standards, and those discharging wastes into rivers or streams will have to meet the standards as their pollution permits come up for reissue.

Disposal of wastewater as a hazardous waste is cost-intensive, ranging from $0.10-$10 per gallon. There are two ways to minimize these costs. The first is to find a technique for concentrating the nonaqueous components of these wastewaters into as small a volume as possible. This would make normal water treatment procedures possible on the bulk of the waste while the concentrated volume would be reduced to the point where disposal as a hazardous waste would not be excessively costly. In the most optimistic scenario, the FSII could be reclaimed, recycled, or sold for some industrial role. The second option is to cut down on the amount of waste generated. Both options are discussed below.

DISPOSAL OPTIONS

The options available for the treatment of wastewaters containing glycol ethers can be summarized in the following categories:

- Physical Treatment. Concentration of FSII into a small volume for disposal as a hazardous waste:
  a. distillation
  b. membranes

- Adsorption or Chemical Treatment. Extract or chemically alter FSII for disposal using:
  a. activated charcoal
  b. extraction by other adsorbents
  c. oxidation

- Microbial Action. Dilution below FSII bacterial biocide concentrations followed by microbial degradation of diluted FSII to meet water treatment standards

- Incineration

In theory, there are numerous techniques available for concentration of the FSII into a small volume which can be economically disposed of as a hazardous waste while discharging the bulk of the purified water to a water treatment facility. They include distillation (azeotropic and extractive) and membrane filtration (reverse osmosis). Adsorption and/or chemical treatment could be achieved with activated charcoal, clay, ceramic filters, or by oxidation and other chemical methods. Microbial degradation and other miscellaneous techniques including electrolysis and evaporation (solar, fossil energy) are potential techniques for eliminating or reducing residual FSII contamination. After an extensive literature search and preliminary engineering evaluations, bench-scale testing was carried out on those solutions showing the most promise. The technology and initial test results are discussed below.

Distillation

A mixture of two compounds can be separated by distillation if their boiling points are significantly different and they do not form an azeotrope (constant boiling mixture). The boiling points of DGME and EGME are 193.2° C and 124.3° C, respectively. Therefore, based on temperature differences, they should be separable from water by distillation.

Simple distillations were done on both DGME and EGME. In the DGME distillation, the 20% DGME/80% water (volume percent) mixture boiled at 99° C. After the separation was complete, the water fraction contained 0.97 weight percent DGME. Little additional treatment would be necessary before disposal of the water fraction.

The literature indicated that a simple distillation of EGME and water was not possible because of an azeotrope. This was confirmed on a 20% EGME/80% water (volume percent) blend. An azeotrope formed at 98° C. Samples were taken as each 100-ml portion was distilled. The "water" fraction of these samples contained 17.1±0.6% EGME, and the bottoms contained 20.8% EGME.

Hydrocarbons of nearly the same boiling point or constant-boiling mixtures cannot be separated readily by ordinary distillation. Therefore, a combination of fractionation and solvent extraction is one alternative. This extractive distillation can be particularly useful in separating EGME from water. A solvent is introduced at the top of the fractionating column and withdrawn at the bottom. The solvent is recovered from the bottoms by means of subsequent distillations. The solvent must be higher boiling than the EGME but not boiling so high that it is immiscible at the temperatures of the fractionation column.

Azeotropic distillation is a somewhat similar process. It involves the formation of a constant-boiling (azeotropic) mixture with the EGME and some added component. The azeotropic mixture can then be separated by distillation, but it must subsequently be treated by solvent extraction to recover the solvent or added component.

Although others have reported extractive and azeotropic distillation techniques for the separation of azeotropic mixtures of compounds [14-16], distillation appears to have little potential for application in separating EGME and water in a situation where simple processing is required.

Membrane Separation Processes

The earliest applications of membrane separation for water purification involved small-scale treatment of brackish waters for process and potable use. Technological advances have extended the utility of these processes to large-scale applications that range from seawater desalination to treatment of complex industrial wastes [17]. Ultrafiltration and reverse osmosis are the two most commonly used processes for removal of organic contaminants. They address different molecular weight ranges of organic matter typically found in wastewater.

A membrane is defined as a semipermeable barrier between two phases which can restrict the movement of molecules across it. The manner in which the membrane restricts molecular motion can take the form of size exclusion, differences in diffusion coefficients, electrical charge, and differences in solubility. Membrane separation is accomplished by a driving force and not by equilibrium between phases.

The driving force for separation is a hydrostatic pressure gradient. This pressure must be larger than any osmotic pressure gradient opposing the molecular motion. The feed solution flows to the membrane where small molecules are allowed to pass and large molecules are excluded. Typical pressure drops are 0.1 to 1.0 atm for microfiltration, 0.5 to 5.0 atm for ultrafiltration, and 20 to 100 atm for reverse osmosis [18].

Microfiltration and ultrafiltration techniques are useful for removal of molecules in the molecular weight range of 500 to 15,000 (1-1,000 nm) [18-20]. Molecules smaller than this are not expected to be significantly removed by ultrafiltration [21]. Therefore, ultrafiltration will not be directly applicable to the separation of FSII from wastewater due to the small size of the EGME and DGME molecules (molecular weights of 76.09 and 120.15, respectively).

Reverse osmosis has a lower cut point on the size of molecules to be removed (0.1 to 1 nm). Currently, the technique is used primarily to remove dissolved salts and uses an ionic charge to facilitate removal of ions. It is reported that reverse osmosis removes organic molecules larger than molecular weight 200 at a 99% rejection weight.

Reverse osmosis membranes are very susceptible to fouling with fine particulates (even tap water can be a problem) and growth of bacteria, due to the extremely small pores in the membrane. The membrane needs to be compatible with the solvent, and, even so, membrane replacement frequency is the principal factor in the economics of the process. Reverse osmosis has a relatively slow throughput and is therefore a time-intensive technique.

While acknowledging that reverse osmosis would be the best membrane technique for separating EGME and water, there was some question about its efficacy in separating the low molecular weight compound from water. However, Osmonics, Inc., was asked to do an applications test on a barrel of tank bottom water. Their preliminary bench-scale testing eliminated the need for the larger scale test. Seventy percent of the EGME [in a 20% EGME/80% water (volume percent)] was able to pass through the membrane at the very high osmotic pressure. Also, the flux was reduced from 24.2 gal/day at 77° F at the given pressure (gfd) at 400 psig on water to 4.3 gfd at 700 psig for the mixture. Therefore, reverse osmosis is not a viable option for separating the EGME from water.

Adsorption

Wastewaters have been treated with granulated activated carbon to remove compounds which are health hazards, but this has been limited, for the most part, to trace quantities of organics [22-25]. Recovery of cellosolves from gas mixtures has been described by Fukabori [26] and Mitsubishi Heavy Industries [27] using adsorbents and/or activated charcoal. Ogasa and coworkers [28] passed waste gas containing various organic contaminants over activated carbon, and the recovery of various solvents was evaluated. The compounds recovered were ethyl acetate, methyl ethyl ketone, and acetone. Recovery of 90% from the activated charcoal was accomplished using steam.

It should be noted that removal of cellosolves from a gas stream is different from trying to remove them from a water mixture. Adsorption is a relative competition phenomenon, and cellosolve will partition in whichever media is most like itself. Thus, adsorption from air to carbon may be feasible, whereas separation from a polar solvent like water to a nonpolar carbon surface would be inefficient [29].

From the foregoing literature citations, all indications are that glycols would be poorly separated from water by adsorption processes. Calgon [30] has published a bulletin describing the use of granular activated carbon to clean up glycol of other more readily adsorbable compounds such as aliphatics.

It is generally true that the more soluble a compound is in water, the less efficient carbon adsorption is to remove it. Alcohols are generally poorly adsorbed, and some alcohols are purified by taking advantage of the preferential adsorption of organic contaminants onto carbon. However, carbon adsorption treatment to remove FSII contamination from wastewater was researched to establish the viability of such an approach.

The carbon adsorption studies show that the amount of carbon needed to remove the EGME in a typical tank bottom (10-15 weight percent EGME) would be too large to make this process feasible on a large scale. The adsorption isotherms show that 1.0 g of carbon will treat 0.76 g of liquid. In an actual flow system, the carbon would probably not perform to this level. However, it is possible that carbon could be used as a second step for polishing the water after some other treatment step.

Chemical Treatment

Chemical oxidation of wastewater is a process by which electrons are removed from a substance to increase its oxidation state [31]. Organic oxidation exhibits low rates of reaction that make complete oxidation generally impractical from an engineering or economic viewpoint. Oxidation processes tend to be energy-intensive and costly; therefore, their application in water and wastewater treatment is limited [32]. Increasing experience with ozone, permanganate, and chlorine compounds in water treatment, however, has demonstrated that combinations of oxidation reactions with other unit processes will often enhance overall organic removal efficiency.

At least two chemical treatments are presently being used for processing tank bottom water contaminated with FSII. In order to evaluate the efficacy of the two techniques, both are being simulated on a bench-scale basis. Initial tests indicate that the level of EGME is not affected by this processing. However, further experimentation is needed before drawing any definite conclusions.

Other chemical treatments involve extraction, large amounts of ozone, and supercritical fluids. None of these technologies is practical for use in tank bottom waters. They are either too expensive or require too much skilled manpower.

Microbial Degradation

Microorganisms are important agents in solubilization, precipitation, accumulation, and alkylation-dealkylation reactions involving organic and inorganic contaminants in environments associated with industrial process streams and wastes. As early as 1972, researchers at Dow Chemical [33] reported the use of microbes to remove salts and polyhydric organics from wastes. In 1978, Patel et al. [34] described microbial oxidation of methane and methanol. In 1985, Goud [35] published a bacterial profile of petrochemical industry effluents, and in 1986 Olson [36] brought attention to the importance of microorganisms as agents involving heavy elements in process streams and waste.

Biotransformation is a general term that specifies the alteration of a compound by living organisms. Biodegradation is more specific and refers to the removal of functional groups from a compound to form simple products through bacterial action.

Microorganisms can be classified according to their ability to exist with or without oxygen. The primary groups ordinarily mentioned are the aerobes which require oxygen and do not multiply in its absence and the anaerobes that grow only in the absence of oxygen. However, there are facultative anaerobes which can grow either in the absence or presence of oxygen by switching electron acceptors.

Aerobic microorganisms primarily produce carbon dioxide and water, while anaerobic metabolism produces oxidized simple organic substances including organic acids, methane, hydrogen gas, and carbon dioxide.

Aromatic compounds appear to be readily degraded as do normal alkanes in the range of C_5-C_8. Olefins have shown poor oxidation, but many of the mono-, di-, and trimethyl-substituted alkanes were degraded.

The primary role of microorganisms to achieve the goals of this research program would be to degrade glycol ethers into harmless products such as carbon dioxide and water. Nagashima [37] cultured A. cellosolvus M-11 microbial species on a specified medium containing methyl cellosolve (EGME) or ethyl cellosolve. About 0.[illegible]1-0.51 g of the carbon source (EGME) was consumed when cultured on a medium containing 1% EGME. This Alcaligenes species appears to have considerable potential for beneficial microbial action in destroying residual EGME contamination in wastewater.

The U.S. Army Environmental Hygiene Agency [38], in 1980, reported that dilute solutions of EGME were biotreatable. Two treatment methods were tested including: 1) simulated activated sludge and 2) selective sewage isolation, identification, and reinoculation of a pure culture into a minimal salt medium containing the FSII as the sole source of added carbon. Both systems showed 100% biodegradation of FSII after two to four days. However, no degradation took place when a solution containing 1,000 ppm EGME was shock-loaded into the system.

While dilute solutions of EGME in water have been successfully degraded with biological treatments, nothing is reported on the use of such treatments for more concentrated solutions. Therefore, some microbiological work on more concentrated solutions has been done at NIPER. In one case, a 10% EGME solution was decreased to 0.5% EGME after two weeks. However, this has not been repeated. Before a microbiological solution is considered, the maximum level for digestion needs to be defined. If the biological treatment is practical, such issues as shock loading and maintaining a constant supply will be addressed.

Incineration

Incineration offers a convenient and simple technique for disposing of wastewater contaminated with FSII, although general application of the technology may be limited by specific parameters. These parameters might include the total volume of wastewater, the assurance of complete conversion of FSII to CO_2 and water, and the hydrocarbon fuel required to incinerate the contaminated water.

Cement kilns represent an alternate incineration source which has seen limited used in the past for the disposal of wastewater containing FSII. When combusted at high temperatures, the FSII in wastewater readily decomposes to carbon dioxide and water.

A solution of 21% EGME in water will support combustion if the stack temperature is <540° C. At lower concentrations, the heat must be partially supplied in order to keep incineration going. Since there is no assurance that a 21% EGME solution could be provided, the energy costs could be considerable. Another problem could arise in the licensing of the incinerator. This is both time-consuming and expensive.

ELIMINATION/MINIMIZATION OF CONTAMINATED WASTEWATER

A logical alternative to disposal of wastewater contaminated with EGME and DGME is to avoid the production of, or minimize the quantity of, waste. Currently, rainwater that leaks into fuel storage tanks is the primary source of wastewater in fuel storage tank bottoms. The rainwater picks up FSII as it trickles through the fuel and continues to extract the glycol ether at the fuel-water interface.

At least three different routes can be taken to minimize or eliminate this contaminated waste. These are: 1) downstream injection of FSII, 2) geodesic domes, and 3) improved seals on floating roofs.

Alternate Blending Protocol for FSII in Jet Fuel

A logical approach to the generation of wastewater with FSII would be to eliminate the blending of FSII with finished jet fuel at the refinery. It is obvious that water cannot extract FSII if the additive has not yet been blended with the fuel.

Since this alternate approach has already been demonstrated as practical by application in several locations, the only questions at issue include: 1) the need for addition of a biocide at the refinery, 2) the optimum point in the distribution system for blending the additive with aviation turbine fuel, and 3) the quality control measures required to ensure appropriate blending ratios and adequate mixing procedures. The equipment required to inject FSII at a point remote to the refinery is available off-the-shelf and includes precise metering pumps and appropriate installation to ensure thorough mixing.

In a typical scenario relative to the distribution system for aviation turbine fuel, the fuel is manufactured at a refinery and placed in a fuel storage tank. The fuel is ultimately transferred from the fuel storage tank at the refinery by some form of transportation which can be truck, rail, barge, ship, or pipeline. At this point, the fuel is either placed in an intermediate storage tank or shipped to the final user.

In theory, the optimum downstream injection site is the final holding tank before delivery of fuel to the aircraft. This holding tank would be constructed such that rainwater infiltration would be eliminated. At this point, instead of the current practice of merely refortifying the fuel in rare cases to bring the FSII level back up to prescribed levels, the entire required amount of FSII would be introduced. It is obvious that, by merely changing the scope of this final operation, production of FSII-contaminated wastewater anywhere in the distribution system could be eliminated, the amount of FSII required would be reduced by eliminating losses enroute, and it would ensure sufficient FSII to prevent fuel icing problems in flight. The practice would also reduce the analysis and calculations required to determine the appropriate spiking of the fuel, since it would be known that the fuel did not contain additives. However, the mechanics and logistics of having such a large number of injection systems and reservoirs of FSII make this an impractical option. Moving the injection point back up the system to an intermediate level seems to be the most reasonable compromise.

One potential problem that must be addressed in a revised FSII injection protocol is the microorganism growth in the fuel which can produce corrosion and fuel flow problems [39-42]. Currently, a biocide is injected as part of the FSII package. Typically, dibutyl p-cresol at 75 ppm level is used to prevent the growth of fungus and bacteria in storage, transit, and on-board aircraft fuel tanks [43]. This is also the antioxidant additive required in military specifications. Other biocides that have been used include organoborates and p-hydroxybenzoates.

If alternate FSII injection logistics were adopted, it would be important that adequate training and safety equipment be provided for personnel charged with direct handling of the glycol ether(s), FSII injection, mixing, and sampling for analysis.

Coyne et al. [45] have provided an overview of protective equipment and its effectiveness for handling glycol ethers. The equipment specifically tested included gloves and respirators. In a glove permeation testing with EGME and DGME, breakthrough times ranged from 66 to 480 minutes. Permeation rates ranged from 0 to 13 $mg/M^2/sec$. Gloves offering the best protection were made from butyl rubber and heavy-duty neoprene. All charcoal respirators were effective in removing glycol ether vapors. At a vapor level of 1,000 ppm, the shortest breakthrough time in a charcoal respirator was one hour, and at 100 ppm the shortest breakthrough time was eight hours.

Because of the widespread use of glycol ethers in industrial processes and as fuel system icing inhibitors, there has been a great deal of published information describing analytical procedures for glycol ethers. The applications of glycol ethers have caused a need for both precise laboratory analyses and rapid, accurate field testing to ensure that fuel reaches an aircraft with sufficient icing inhibitor to prevent in-flight fuel flow difficulties.

It is now clear that injection of FSII downstream is not a new concept. Many facilities in the United States already have this capability, and many sites in Europe are forced into this operation due to the restrictions on additives in the multifuel pipelines. In an attempt to gain from those already using this approach, these operations were discussed with personnel at several facilities.

There seemed to be general agreement that downstream injection was not a problem. In fact, in Europe it is almost a requirement since the major multiproduct pipelines do not allow finished fuels with FSII to be transported. The key issues to be addressed are the optimal point of injection, quality control, and point-of-use limits for FSII.

Technically, it would be best to inject the FSII as the fuel is entering the aircraft. This would ensure that there is no opportunity for water to extract the additive or for the fuel/FSII mixture to degrade. Further, no analyses of the fuel would be necessary to determine the level required (such as that now done to determine the need for refortification), since it would be known that no FSII is present. However, the difficulties in having such a large number of facilities for injecting a hazardous material, the need for special quality control procedures to ensure adequate mixing and proper injection and the training required for such a large number of handlers makes this option logistically unattractive.

The next best option would seem to be to inject the FSII as the jet fuel leaves the various intermediate storage/transportation facilities. In this way, people trained to handle fuels and to blend in additives will be responsible. The number of injection points will be decreased dramatically. Yet, many of the advantages mentioned in the previous paragraph still hold. This type of approach is currently being used in selected sites successfully.

There is a wide range of approaches to quality control. One site did no testing at all because they only blended FSII into truck load deliveries and did that batchwise from buckets. Most use a refractometer method being considered by ASTM [46]. However, it is possible to get a system which will use a gas chromatograph to monitor and control the injection of the FSII.

Self-Supporting Geometric Domes for Fuel Storage Tanks

An alternative approach for minimization of fuel storage tank bottom wastewater which is contaminated with FSII is to minimize or eliminate the water that inadvertently finds its way into the fuel storage tanks. Most fuel storage tanks currently have floating roofs which are notorious for leaking at the seal between the roof and the tank side walls. One suggested solution to this problem is to construct a self-supporting geometric dome over the storage tank which would eliminate rainwater collection on the floating roof.

These geodesic all-aluminum polyframe dome structures have been described by Richter and others [47-50]. The domes, being constructed of a corrosion-resistant aluminum alloy, are light--weighing about 25 pounds per square foot--and are virtually maintenance-free. The geodesic concept implies a dome of optimum strength that can withstand windstorms, ice buildup, or drifting snow, and will shed water before it reaches the floating roof. These structures eliminate the need for support columns and their attendant penetrations through the floating roof.

Domes ranging in size from 20 to 180 feet in diameter have been constructed at a number of military and industrial sites [48-49]. Evaluation of these domes has led to the conclusion that they reduce vapor losses, shelter the tank contents, and eliminate the entry of water into the product. Their cost is materially less than the cost of a new tank and also less than the cost for replacing roofs on existing tanks using conventional pontoon design. Their disadvantage is the initial cost which can range from about $50,000 to $120,000, depending upon size and location.

Improved Floating Roof Storage Tank Seals

Engineering advances in recent years have provided the option of installing improved spring seal systems on floating roofs to provide an improved barrier against the leakage of rainwater. With a patented spring-loaded seal [51], tank leakage even in irregular and/or rebuilt tanks can be minimized. Reportedly, each spring-seal section can travel 12 to 15 inches radially to fill in gaps when the walls bulge outward, or give way when walls bulge inward. Each seal section moves independently of each other for maximum flexibility. Spring-seal sections can be installed in combination with standard wiper seal sections.

SUMMARY AND CONCLUSIONS

FSII is ethylene glycol monomethyl ether (EGME) or diethylene glycol monomethyl ether (DGME) (commonly referred to as cellosolves) to which a small amount of a growth-inhibiting antioxidant has been added. The glycol ethers serve as antifreeze to water contained in jet fuels (such as JP-4 and JP-5). The antioxidant limits the growth of bacteria and fungi in the fuel while preserving the FSII during storage before use.

A primary source of glycol ether depletion occurs in large volume jet fuel storage tanks typically constructed with exposed floating roofs. Rainwater enters these storage tanks between the shell wall and roof seal and settles to the bottom of the tank, extracting FSII in the process due to the extreme hydrophilic nature of glycol ethers. This water is typically drained from the tank on a daily or weekly basis.

Current disposal techniques include draining the bottoms water to diked areas, some of which have sealed bottoms to prevent soil permeation and others which are not sealed. Because of the toxic nature of the glycol ethers and recent evidence of groundwater contamination with FSII, this disposal option is no longer environmentally attractive. On the other hand, disposal as a hazardous waste can be cost-intensive. The volume of wastewater contaminated with FSII generated by various installations and the distance between them do not permit the construction of a central disposal facility. Therefore, the most attractive options for processing these wastes must necessarily be small scale, preferably portable, simple to operate, safe to operate, and efficient in the treatment of FSII-contaminated water. No off-the-shelf technology that complies with environmental regulations meets all technical and economic criteria is currently available for disposal of FSII-contaminated wastewater. However, some unit operations appear promising.

The alternative to waste reduction through treatment options is waste minimization and/or elimination. Engineering structures are available that would minimize the generation of fuel storage tank bottoms water. These include geodesic domes constructed to shelter tanks with floating roofs and improved seals between tank shell walls and floating roofs. Both of these options are cost-intensive and require extensive modification to existing structures.

The alternative that has already been demonstrated to be practical and which appears to have the greatest potential for elimination of fuel storage tank bottoms water contaminated with FSII would be to delay the point of injection of glycol ether into aviation jet fuels in the wholesale distribution system. The literature has little or no information that defines the optimum point for the addition of FSII in the aviation turbine fuel distribution system. However, site visits and contacts with appropriate government and private technical personnel have suggested that the glycol ether icing inhibitor should be injected at the time of delivery to a military facility. The optimum point of injection is somewhat site-specific.

This "downstream" injection protocol has the environmental advantage of elimination of most wastewater contaminated with glycol ethers. Technically, the downstream addition of FSII has already been demonstrated as a viable and feasible option. Economically, this alteration in the amount of FSII addition will be attractive by decreasing the labor and cost required to properly dispose of contaminated fuel storage tank bottoms water while reducing the use of FSII.

Safety considerations related to adding glycol ethers at an intermediate point rather than at the refinery are no more nor no less serious than current practice of refortifying the fuel with FSII. Adequate training and proper equipment (including protection from skin contact and inhalation) should be provided to all personnel who work with concentrated FSII.

Several analytical methods are documented in the literature for both field and laboratory applications to determine the concentration of glycol ethers in either jet fuel or in water extracts. Gas chromatographic analysis appears to be a very good laboratory technique and can be used in the field as part of a control system for the injection of FSII.

Since there are readily available injection/analytical systems that can be used to inject FSII into jet fuels, it would seem logical to focus increased effort on minimizing waste. The technological options need to be further evaluated in those situations where the waste must be processed.

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STABILITY PROPERTIES OF GASOLINE – ALCOHOL BLENDS

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ABSTRACT

The lead phase down for motor gasolines resulted in a search for alternative octane boosters, some alcohols and ethers being the most favoured candidates. The advantages and disadvantages of each of the oxygenates have been extensively studied, but the effect of oxygenates on the stability properties and long term storage stability of motor gasolines has been neglected. This paper summarizes the work done on the effect of some alcohols and ethers on degradation product formation in motor gasolines containing oxygenates.

Following are some specific points which have been investigated in the present work :

Effect of oxygenates on the conventional stability estimates and on stability properties of different types of gasolines has been examined ;

A reduction of methanol concentration has been noted during storage of some motor gasolines containing methanol, especially in case of catalytically cracked gasolines. It has been investigated whether this phenomenon is associated with formation of ethers due to a reaction of methanol with olefins present in some severely cracked stocks or whether this is due to commom phase separation;

The effect of peroxy radicals in gasolines containing alcohols on the behaviour of gasolines in storage and in use, such as formation of gumlike substances in inlet manifold systems of car engines, has been studied and is described in this paper;

The mechanisms associated with degradation products formation in the various types of gasolines containing alcohols have also been studied from the point of view of reactions of free RO· or HO· radicals, or peroxy radicals (ROO·), with alcohols to form either degradation products or inducing oxidation reactions of the alcohols.

INTRODUCTION

Use of alcohols and ethers as octane number boosters has increased in the last years. In spite of some controversial issues, the beneficial effect of alcohols on the performance of gasolines, as well as on ecological considerations, cannot be disputed.

In order to make full use of the beneficial effect of oxygenates admixed to motor gasolines, steps should be taken to prevent, or at least to minimize, some problems arising due to the presence of the oxygenates in gasolines; The increase in vapour pressures can be overcome by using less volatile gasoline components; the corrosive effect of methanol on some metals and elastomers should be borne in mind, but at methanol concentrations of 3–5% this problem is minimized, especially when corrosion inhibitors are added; finally, phase separation problems can be alleviated by adding co-solvents as tertiary butyl alcohols, methyl tertiary butyl ethers etc.

Methanol concentrations in gasoline tend to decrease during handling and storage. There are two main causes for this phenomena; The first is the possibility of leaching out of the methanol from the gasoline by moisture, the aqueous phase separating from the oily phase at concentrations from about 200 ppm upwards. The separated aqueous phase contains large amounts of methanol. When co-solvents are used, phase separation is diminished. For example, addition of 2% (in gasoline) of tertiaty butyl alcohol to 3% (in gasoline) of methanol, would raise the phase separation limit about tenfold, to approximately 2000 ppm of the aqueous phase in the gasoline before phase separation takes place. The second cause for methanol concentration reduction during storage is the possibility of its reacting with some olefins which may be present in the gasoline and forming the corresponding ethers. This reaction is at the given environmental conditions rather slow, but nevertheless under certain conditions it may take place.

The problem of corrosivity of gasolines containing methanol to some elastomers and some metals, as well as gum formation rate increase in gasolines containing alcohols has been observed in the past and is now specifically treated in this paper.

EFFECT OF ALCOHOLS ON STABILITY PROPERTIES OF MOTOR GASOLINES

One aspect which has not yet been dealt with properly is the effect of alcohols and ethers on stability properties and long term storage stabilities of motor gasolines in general and on degradation products formation in particular. The effect of oxygenates on these properties of motor gasolines has been therefore investigated in the present framework of gasoline stability studies and is reported in this paper.
The following gasoline types were used in this study :

1. Straight run gasoline (paraffinic nature).

2. Catalytically reformed gasoline (aromatic nature)

3. Catalytically cracked gasoline (olefinic nature)

The following oxygenate systems were added to each of the gasoline types :

	Blend 1	Blend 2	Blend 3	Blend 4
Methanol (%vol.)	0	3	3	3
Tert. butyl alcohol (%vol.)	0	0	2	0
Methyl tert. butyl ether (%vol.)	0	0	0	5
Phenolic antioxidant (ppm)	20/60*	20/60*	20/60*	20/60*
Lead (gr/1)	0.3/0.4**	0.3/0.4**	0.3/0.4**	0.3/0.4**

* In cracked gasoline
** In straight run gasoline

Characteristic results obtained in this study are summarized in Table 1.

Existent gum and potential gum of motor gasolines have not been affected significantly by addition of alcohols to straight run (paraffinic) or to catalytically reformed (aromatic) gasolines. However, when added to catalytically cracked (olefinic) gasolines, a significant increase of gum has been observed. Inlet manifold system deposit test (ISDT) results have been affected by oxygenates in cracked as well as in reformed gasolines. Oxygenates caused an increase in peroxide contents of all gasolines, but their effect has been larger in cracked gasolines. Characterictic results are summarized in Table 1 and Diagrams 1,2 . Use of sufficient amounts of suitable oxidation inhibitors may alleviate this problem appreciably (Table 2).

DISCUSSION OF RESULTS

Alcohols added to stable gasolines in which free radical formation is minimal, have no deleterious effect on the stability properties of such gasolines. However, alcohols added to gasolines which are susceptible to free radical formation, as for example peroxy radicals, enhance the instability of such gasolines. Polymerization chain reactions may be easily initiated in cracked gasolines, containing olefins. The free radicals so formed ($RH^{\cdot}$) in the initiation stage of the polymerization chain reaction react with oxygen to form peroxy radicals ($ROO^{\cdot}$), which, in turn, undergo one of the following changes:

A. Polymerization and degradation products formation;

B. Reaction with alcohols to form aldehydes and acids
$R^{I}OH + R^{II}OO^{\cdot} \rightarrow R^{I}O^{\cdot} + HO^{\cdot} + R^{II}O^{\cdot} \rightarrow RCHO \rightarrow RCOOH$

C. Termination of the polymerization chain reaction by mutual action of the free radicals or by the action of artificially added antioxidants; suitable antioxidants in sufficient quantities should be helpful in stiffling the progress of the polymerization chain reaction by eliminating the free peroxy radicals, which, when present, may oxidize primary alcohols to aldehydes and then to acids or secondary alcohols to acetone.

The initiation stage of the polymerization chain reaction is facilitated by the presence of olefins and diolefins in the catalytically cracked gasolines. The free radicals (R·) formed in the initiation stage lead to the propagation stage in which peroxy radicals are formed:

$R\cdot + O_2 \rightarrow ROO\cdot$

$ROO\cdot + RH \rightarrow ROOH + R\cdot$

The oxidation of alcohols by peroxy radicals mentioned in the foregoing represents one of the competing reactions taking place:

$ROO\cdot + RCH_2OH \rightarrow ROOH + RCH_2O\cdot$

$ROO\cdot + RCH_2OH \rightarrow ROOH + RC\cdot HOH$

$ROO\cdot + RH \rightarrow ROOH + R\cdot$

Under favourable conditions the hydroperoxides may form more free radicals RO· and HO· which react with the free radicals $RCH_2O\cdot$ and RC·HOH to form aldehydes, and by further oxidations, acids.

Some of the results obtained in the present work are summarized in Table 1 and illustrated in Figure 1 and Figure 2 and confirm the theoretical background of the processes described in the foregoing.

CONCLUSIONS

Stable gasolines in which free radical formation rate is insignificant, are not affected appreciably by presence of alcohols in respect of their stability properties. Catalytically cracked or other unstable gasolines, in which formation of free radicals and peroxy radicals takes place readily, tend to form degradation products in any case, but in presence of alcohols this tendency is greatly enhanced.

Free radicals and peroxy radicals are precursers to an oxidation of the alcohols to aldehydes and acids affecting thus the gasoline quality. The activity of such free radicals can be however stiffled by use of sufficient quantities of suitable inhibitors.

		Straight run gasoline				Aromatic gasoline				Olefinic gasoline			
Methanol	% vol	0	3	3	3	0	3	3	3	0	3	3	3
Tertiary butyl alcohol	% vol	0	0	2	0	0	0	2	0	0	0	2	0
Methyl tert. butyl ether	% vol	0	0	0	5	0	0	0	5	0	0	0	5
Antioxidant (phenolic type)	ppm	20	20	20	20	20	20	20	20	60	60	60	60
Tetra ethyl lead	gr Pb/l	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Density at 15°C	gr/ml	.7352	.7361	.7371	.7371	.7865	.7870	.7874	.7865	.7298	.7314	.7319	.7324
Reid vapour pressure	psi	6.5	8.1	8.0	8.2	5.4	7.0	6.5	6.6	13.3	14.4	15.0	14.4
Ex. gum: unwashed	mg/100 ml	0.4	0.4	0.3	0.4	0.6	0.8	0.7	0.9	1.2	1.5	3.0	2.8
washed	mg/100 ml	0.3	0.3	0.2	0.2	0.4	0.6	0.6	0.7	0.8	0.7	2.2	2.3
Pot. gum: unwashed	mg/100 ml	1.1	2.4	3.3	2.0	0.5	1.5	2.4	2.2	2.8	5.5	9.0	8.2
washed	mg/100 ml	0.7	1.5	1.8	1.7	0.3	1.0	2.0	1.9	1.9	2.6	7.0	5.2
Induction period	minutes	900	900	900	900	900	900	900	900	900	900	900	900
Peroxides	meq/l	0.1	0.2	0.5	0.6	0.3	0.4	0.6	1.1	0.5	0.8	1.2	1.3
I.S.D.T.: insol. in n-C$_7$	mg/100 ml	0.95	0.85	0.8	0.8	2.0	2.7	3.5	4.4	2.6	3.0	3.4	4.6
insol. in acetone	mg/100 ml	0.1	0.3	0.4	0.4	0.1	0.1	0.2	0.2	0.1	0.3	0.3	0.4
Phase separation at 0°C		no	yes	no	yes	no	yes	yes	yes	no	yes	yes	yes
Lead content	gr Pb/l	0.41	0.40	0.39	0.38	0.29	0.28	0.29	0.28	0.30	0.30	0.30	0.31
Motor octane number		82.7	83.9	84.4	85.0	89.0	89.4	89.7	90.1	84.8	85.1	85.4	85.9
Research octane number		84.9	86.3	87.0	87.8	97.5	98.1	98.8	99.5	96.0	96.4	96.8	97.5

TABLE 1 : Effect of oxygenates on stability properties of various types of gasolines.

Composition:										
Methanol	% vol	0	0	3	3	0	3	3	3	0
Tertiary butyl alcohol	% vol	0	0	0	0	0	0	2	2	0
Ethanol	% vol	0	0	0	0	0	0	0	0	7
Antioxidant (phenolic)	ppm	60	0	0	60	120	120	60	60	60
Antioxidant (aminic)	ppm	0	60	60	0	0	0	0	60	0
Tetra ethyl lead	gr Pb/l	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Density at 15°C	gr/ml	0.7325	0.7320	0.7348	0.7332	0.7330	0.7338	0.7354	0.7348	0.7335
Reid vapour pressure	psi	9.6	9.5	10.5	10.5	9.7	11.3	11.8	11.2	9.8
Ex. gum: Unwashed	mg/100 ml	0.7	1.2	5.0	6.3	0.9	2.0	5.5	2.2	2.5
washed	mg/100 ml	0.6	0.7	3.2	3.0	0.4	1.8	3.0	1.9	0 9
Pot. gum: unwashed	mg/100 ml	3.1	2.6	7.8	9.7	2.5	7.4	8.9	5.8	6.9
washed	mg/100 ml	0.8	1.1	6.0	9.0	1.3	4.1	7.1	4.0	4.8
Induction period	minutes	990	990	990	990	990	990	990	990	990
Peroxides	meq/l	0.14	0.20	0.85	1.10	0.08	0.66	0.95	0.65	0.65
I.S.D.T.: insol. in n-C_7	mg/100 ml	2.05	1.83	2.88	2.81	1.21	2.24	1.92	2.10	1.91
insol. in acetone	mg/100 ml	0.36	0.16	0.28	0.34	0.32	0.24	0.36	0.28	0.32

<u>TABLE 2</u> : Effect of antioxidants on a cracked gasoline containing oxygenates.

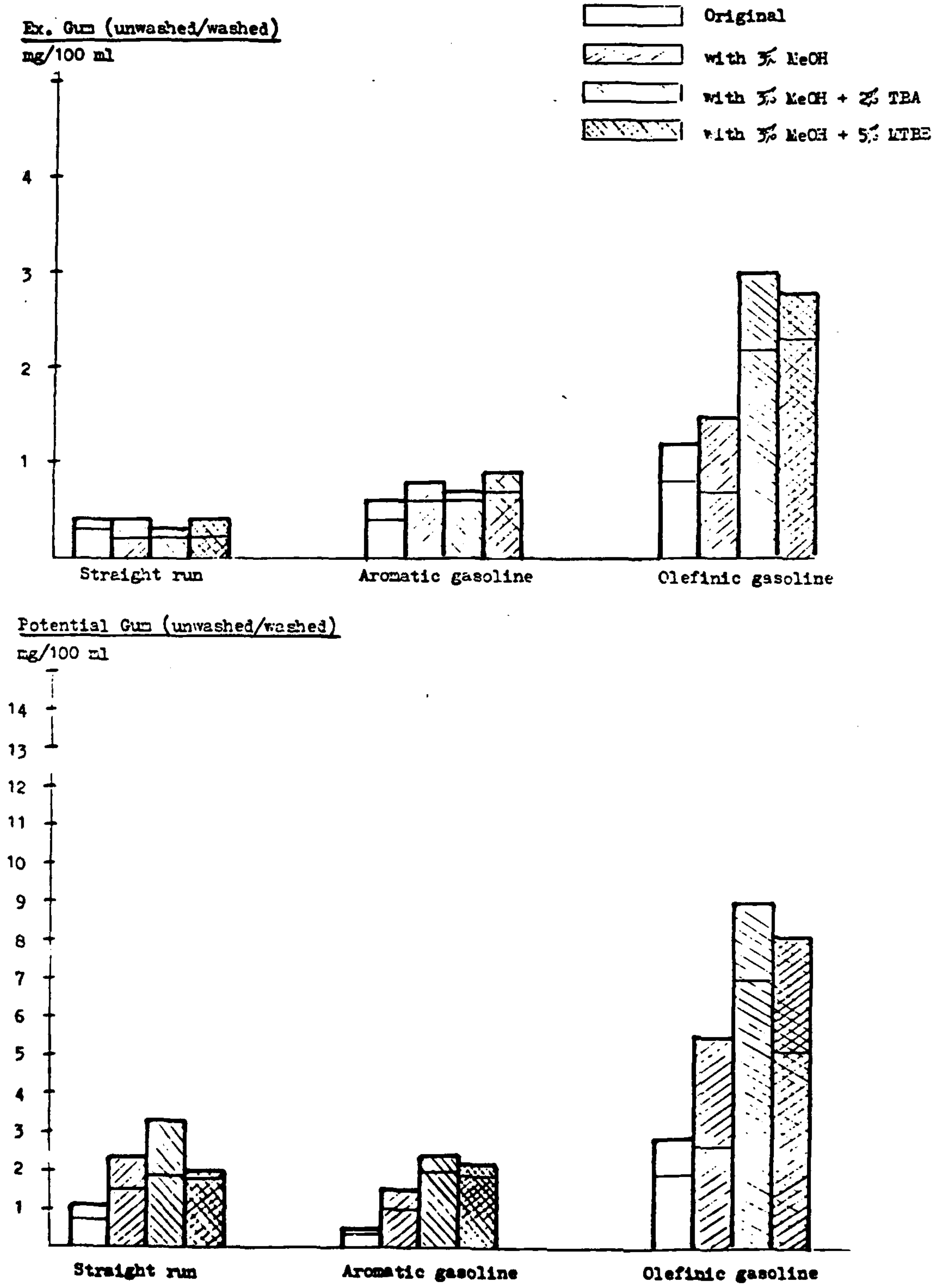

FIGURE 1: Effect of oxygenates on Ex. and Pot. gum of various gasoline types

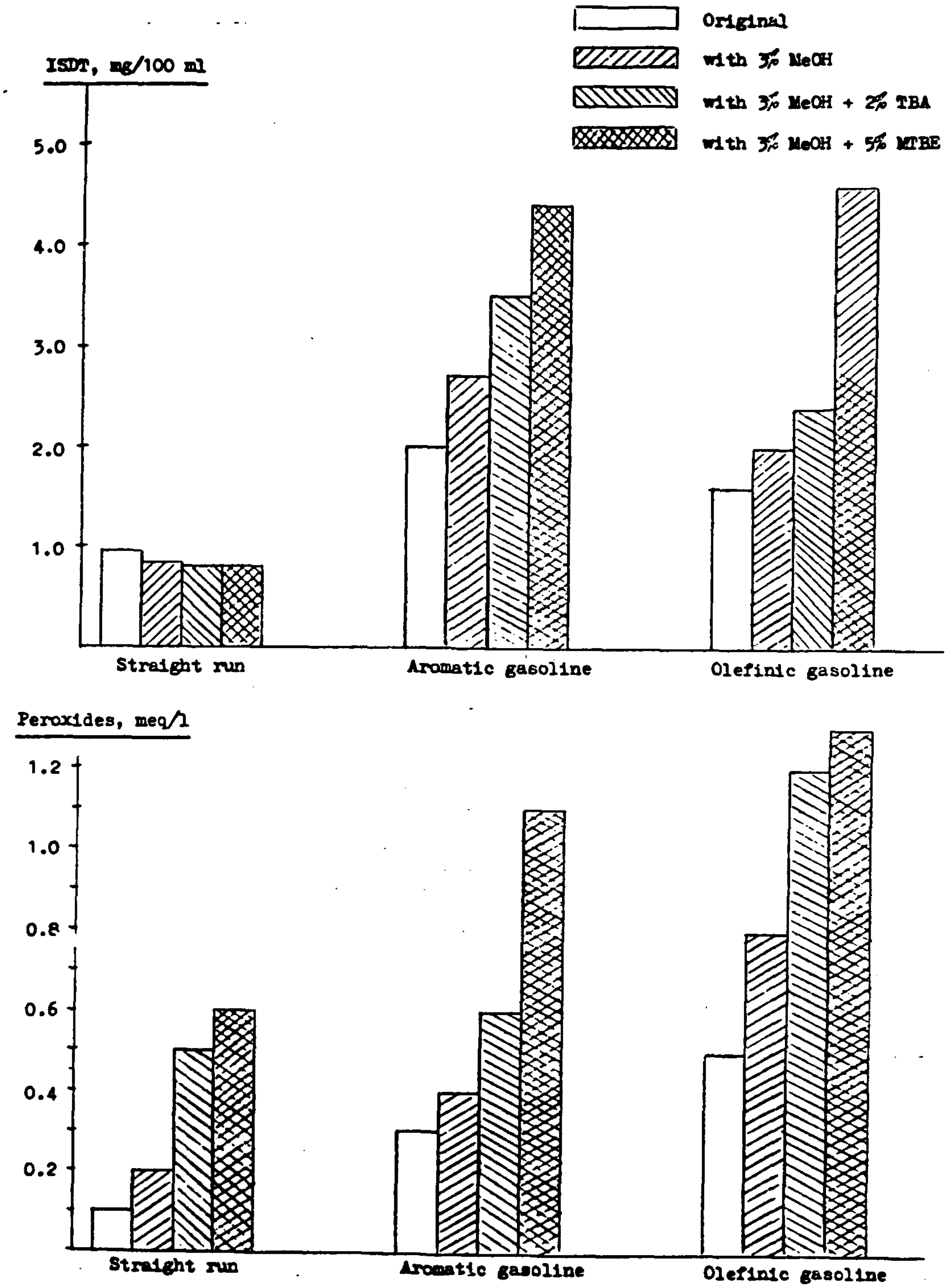

FIGURE 2: Effect of oxygenates on Inlet Manifold System Deposit Test results and on peroxide contents of various gasoline types.

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EVALUATION OF MOTOR GASOLINE STABILITY

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ABSTRACT

This paper presents current results of an on-going storage program whose primary goal is the development of improved methods for evaluating motor gasoline stability. Several existing and potential predictive tests were applied to both individual refinery components of gasoline, selected laboratory blends, and commercial gasolines for which ASTM D 525 induction periods ranged from 75 to >5000 minutes. Darkroom storage was commenced at 43°C, 54°C, and ambient temperatures, for varying periods which will ultimately reach 4 years.

Results to date confirm the findings of earlier researchers that ASTM D 525 is not viable as a predictive device by virtue of a low coefficient of determination between induction period and gum formed in storage at 43°C for periods up to 1 year. It is recognized, however, that ASTM D 525 is not likely to be abandoned as a specification stability test. Based upon the data generated to date under the four phases of this storage stability program including supporting data obtained from literature sources and current surveillance information on both military and industry practices, the method to be adopted for evaluating stability of commercial/military motor gasoline will consist of the modified ASTM D 873 Method using a 6-hour aging existent gum maximum limit of 20 mg/100 mL. The ability of this test to distinguish between stable and unstable low induction period fuels and/or components is discussed.

In evaluating the individual potential gasoline components, a pyrolysis naphtha was shown to be generally an order of magnitude less stable than all other streams, and coker naphtha was shown to possess poor stability characteristics. LCC and HCC naphthas

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* No longer at Southwest Research Institute.

which make up the bulk of unleaded gasoline have lower stability than the remaining components. Reformate showed definite acceleration of deterioration during storage. Synergistic effects exist, particularly between LCC and HCC naphtha blends.

INTRODUCTION

Efforts are being made by North Atlantic Treaty Organization (NATO) nations to adopt NATO Code No. F-57 (commercial low lead gasoline) as a replacement for NATO Code No. F-46 (military gasoline) under which the United States provides MIL-G-3056 (1)* product. The NATO Code Nos. and U.S. Military Specifications which pertain to this program are detailed in TABLE 1.

TABLE 1. Selected Stability-Related Parameters for NATO Code and U.S. Military Specification Gasolines

Code or Specification	NATO F-46	NATO F-57	MIL-G-3056
Gasoline Type	Military	Commercial	Military
ASTM D 525 Induction Period, minutes, min.	480	360	480
ASTM D 381 Unwashed Gum, mg/100 mL, max.	4	--	4
Washed Gum, mg/100 mL, max.	--	4	--
Corrosion Inhibitors	Required	Optional	Optional
Oxidation Inhibitors	Optional	Optional	Required
Metal Deactivators	Optional	Optional	Required

The change from F-46 to F-57 is being driven by a number of factors, including maximal use of commercially available fuels, simplification of fuel procurement, and increased flexibility in maintaining war reserve requirements. However, with respect to the stability issue, one principal difference of major concern between current F-46 and the proposed F-57 guide codes is the ASTM D 525 induction period requirement. F-46 calls for 480 minutes minimum, whereas F-57 specifies a 360-minute minimum. A second difference associated with this stability issue is the requirement for addition of 8- to 15-lb/1000-bbl antioxidant in MIL-G-3056 but not in either F-46 or F-57 (which allow but do not require antioxidant). It is necessary that the United States protect gasoline stocks already procured in compliance with MIL-G-3056 (e.g., approximately 2.1 MM barrels at a value of $94 MM are in storage for the United States in Central Europe) from contamination with inferior product. Additionally, it is desired to prevent inferior gasoline from being placed in vehicles and small storage containers that are exposed to more severe deterioration conditions of heat and breathing.

A survey of MIL-G-3056 gasolines available at military installations in the United States was conducted during the 1950's.(2) The bulk of these gasolines had induction periods in excess of 1440 minutes. Commercial gasoline specification ASTM D 439 allows commercial gasoline to have induction periods as low as 240 minutes.

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* Underscored numbers in parentheses refer to the literature citations at the end of this paper.

Surveillance data were previously presented from the Central European Operating Agency (CEOA) which demonstrated that a gum specification for procurement was inadequate protection against fuel instability.(3)

By suitable modification to ASTM D 873, it may be possible to combine features of D 525 and D 381 to accomplish what either test alone cannot: i.e., ensure a stable gasoline. A program was designed and subsequently initiated within the United States to provide the necessary data for accomplishing these objectives. Such a program is designed to determine:

1. Viability of a modification to ASTM D 873 as a means to accurately predict the long-term storage stability of motor gasolines, and
2. Stability characteristics and engine depositing tendencies of gasoline possessing ASTM D 525 induction periods in the range of 360 minutes.

BACKGROUND

At the U.S. Army request, the Coordinating Research Council CRC) conducted three desert storage tests on motor and aviation gasoline during 1943-1945. The findings in that work (4) indicated that gasoline stability could be evaluated using ASTM tests for induction period (D 525) and oxidation stability (D 873). Also, it was determined that 480 minutes represented a realistic minimum induction period specification for commercial gasolines of that era, and that an acceptable correlation existed between results obtained via laboratory storage at 43°C and desert storage results. The work employed a "5-hour aging gum test" and 6 months as the predictable storage period.

In another CRC program conducted in 1944 and 1945 in Texas and California (5), gasolines with gum levels of 1.5, 7, 10, 25, and 50 mg/100 mL were used in several vehicles for up to 500 hours of operation. Results showed that most of the vehicles operating with gasolines having 7 mg/100 mL gum (or more) failed after relatively few hours of operation. Such failures were due to excessive intake valve manifold and port deposits.

Work conducted at the U.S. Bureau of Mines, Bartlesville, OK, resulted in the development of a 16-hour "oven test" at 95°C (200°F). Test results were correlated with 43°C storage for various periods of time.(6) This procedure was never generally accepted by industry, although some techniques for analyzing stored samples have been adopted from this work.

Schrepfer and Stansky utilized a "4-hour accelerated gum" test.(7) Results of this test were correlated with results after 3-month darkroom storage at 43°C. A statistical procedure was devised to ascertain the stability of various gasoline samples. The "4-hour accelerated gum" test is a modification of ASTM D 873 and is essentially the method adopted for the work reported here.

The data of Schrepfer and Stansky were originally presented in graphical form and have now been digitized for verification through statistical analysis. Fig. 1 presents the result in graphical form. The findings reinforce the conclusion that D 525 is a poor predictor of stability. Fig. 2 recreates these data over the range of induction periods of most interest for this program. A coefficient of determination of 0.003 (by linear regression) was obtained.

Correlation results of the modified D 873 test with gum after 3-month dark storage at 110°F, shown in Fig. 3, convey a coefficient of correlation of 0.26.

However, Schrepfer and Stansky make the interesting observation from Fig. 3 that 98 percent of the samples that result in a 4-hour gum of 5.0 mg/100 mL (or less) generate less than 3.0 mg/100 mL in the 3-month 110°F storage test.

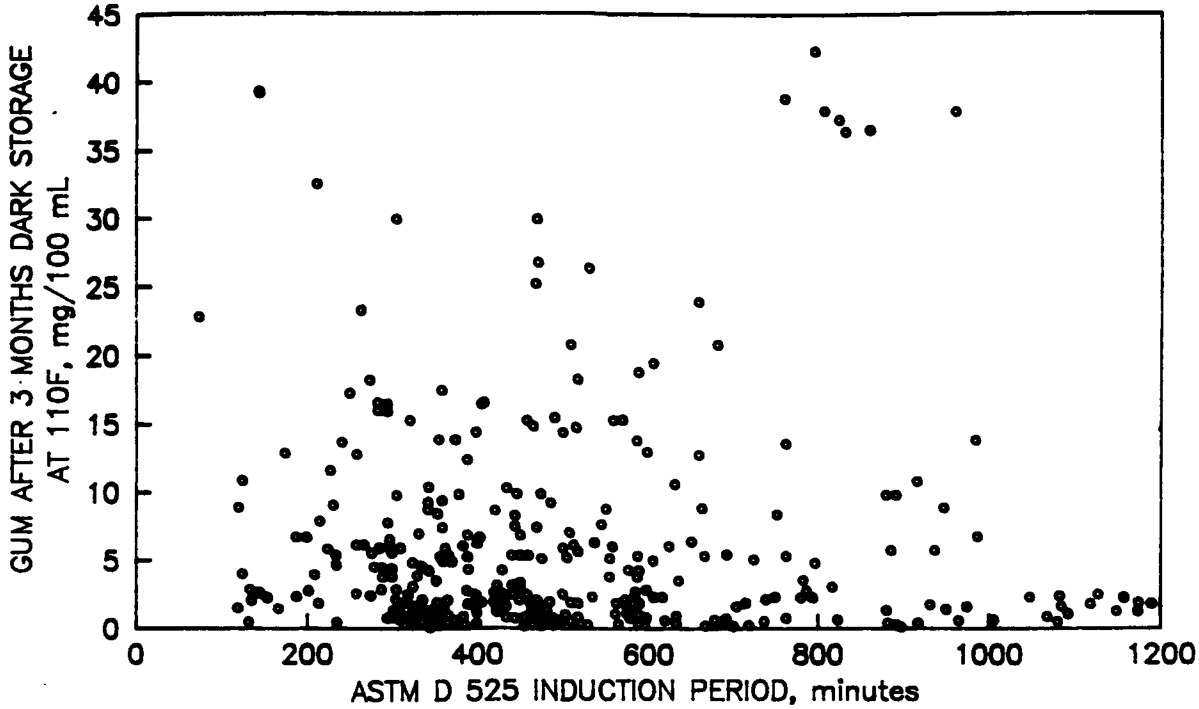

Figure 1. UOP induction period correlation for 3-month dark storage at 100°F

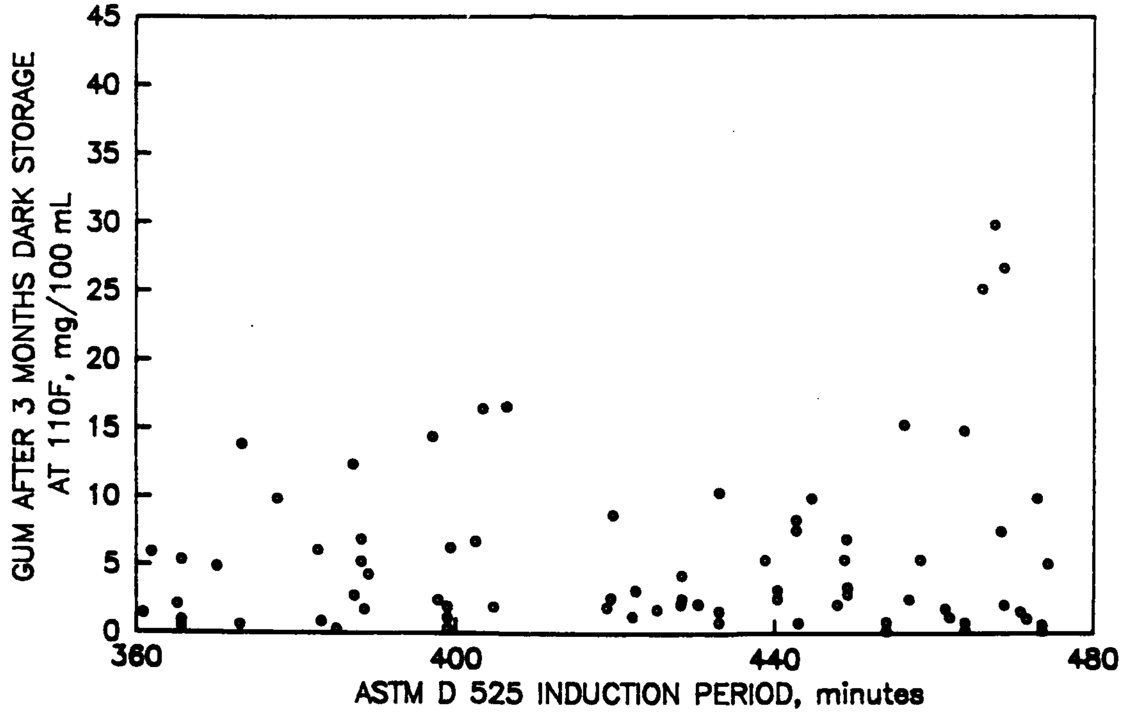

Figure 2. UOP induction period correlation for 3-month dark storage at 110°F

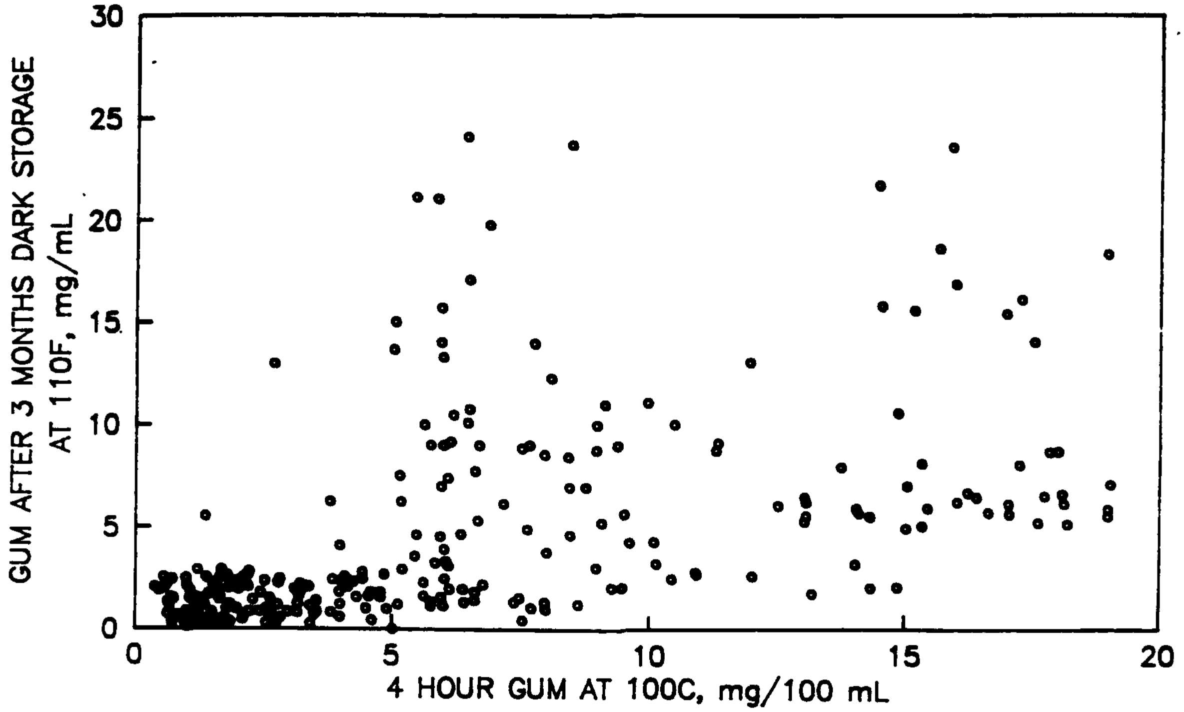

Figure 3. UOP potential gum correlation for 3-month dark storage at 110°F

EXPERIMENTAL

This program encompassed darkroom storage of test fuels at ambient (San Antonio, TX), 43°C (110°F), and 54°C (130°F) for time periods up to 4 years. Samples were subjected to a battery of physical and chemical tests prior to storage and again at selected storage times. These tests included determination of (1) Induction Period (ASTM D 525), (2) Unwashed and Existent Gum (ASTM D 381), (3) Peroxide Number (UOP Method 33-82), (4) Color (ASTM D 1500 and D 156), and (5) Induction System Deposit (ISD) Rating (Method 500 Federal Test Method Standard 791B). Wall-adhered insoluble gum and filterable precipitate were obtained, where appropriate, by a modification to U.S. Bureau of Mines methodology.(6) Additionally, ASTM D 873 methodology was applied to all blends prior to storage.

In the modified D 873 "X-hour" aging procedure, the 100-mL sample (after "X-hour" aging) is transferred to a flask, the sample container is washed twice with 10-mL portions of gum solvent (toluene-acetone mixture) also placed in the flask. The flask material is divided equally into two gum beakers and the unwashed gum determined by ASTM Method D 381 (air jet). The sum of the increase in weight of the two gum beakers is reported as "X-hour" total unwashed gum in mg/100 mL and washed gum in mg/100 mL.

The program has evolved into four distinct test phases, numbered sequentially. Each test phase is carried out with samples uniquely selected to permit several approaches to be made.

Phase I: An unstable (via caustic treating) light catalytically cracked naphtha blendstock was incorporated into a stable, leaded, regular gasoline to provide five fuel blends, plus the original two materials, for initial study.

Phase II: An unleaded gasoline plus nine refinery components (which make up gasoline) were obtained. Five "hand blends" of the components were also prepared, and two miscellaneous materials of interest (the reference gasoline of MIL-G-53042, and a pyrolysis naphtha from a chemical plant) were included to provide 18 total samples for this test phase.

Phase III: Eight "artificial" fuel blends were prepared whose commonality is a "low" induction period, but which represent both "good" and "bad" fuels based on D 381 gum data and D 873 modified potential gum.

Phase IV: This final test phase incorporated four "low" induction period fuels that were commercially available, a debutanizer bottom sample, and a blend of debutanizer bottom with regular leaded gasoline.

CURRENT STATUS

A. TABLE 2 is a summary of code numbers and descriptive information for the samples in test phases I through IV.

B. Research on Phase I Samples

Phase I storage stability testing was carried out on a leaded regular gasoline, a LCC naphtha, and five intermediate blends of these two components. TABLE 3 is a summary of induction period (D 525), unwashed gum (D 381), and existent gum for samples stored at 43° and 54°C, modified D 873 results for "X-hour" aging and results to date for samples stored at ambient temperatures.

C. Observations for Phase I Samples

1. For a LCC naphtha, leaded regular gasoline, and five intermediate blends, induction periods have slowly changed during a 128-week period of ambient storage. As the amount of stable, leaded regular gasoline, in the blends increases, they actually show more tendency to have a declining induction period, up to about 60-percent gasoline.

2. Similar trends are evident for Induction System Deposit (ISD) rating data, Unwashed Gum and Existent Gum by ASTM D 381, and by the UOP Peroxide Number test. A sample containing 60-percent leaded regular gasoline and 40-percent LCC naphtha apparently deteriorates faster than either ingredient alone and faster than other blends.

3. These samples, when subjected to storage at 43°C, show similar patterns emerging after 32 to 40 weeks; roughly three times faster than for ambient storage. At 43°C, the most rapid deterioration seems to be for samples containing even more (65- to 70-percent) leaded regular gasoline. Peroxide numbers for these samples began to increase significantly after 16 to 24 weeks at this test condition.

4. At 54°C, significant changes are observed after only 8 weeks, some five times faster than at ambient. However, the changes seem most evident among the samples containing the most LCC naphtha.

5. From statements 2, 3, and 4, it is deduced that a different reaction is taking place at 54°C than the one which occurs at 43°C and/or ambient temperatures.

6. Using the relationship,

TABLE 2. Summary of Sample Characterization Data

AL-Code No.	Sample Description	Induction Period, D 525, minutes	Gravity, °API	Distillation, °F								Hydrocarbon Type, FIA, vol%			Octane No.		RVP
				IBP	10% E	20% E	50% E	90% E	EP	Res	Loss	Sats	Olef	Arom	RON	MON	
Phase I																	
14158-G	100% LCC Gasoline	240	54.8	115	150	168	235	380	427	1.0	1.0	39.5	34.9	25.6	--	--	--
14388-G	75% LCC, 25% Regular Leaded Gasoline	250	55.0	111	153	175	239	376	447	1.0	1.0	--	--	--	--	--	--
14389-G	50% LCC, 50% Regular Leaded Gasoline	345	56.3	103	147	173	234	351	422	1.0	1.0	--	--	--	--	--	--
14390-G	40% LCC, 60% Regular Leaded Gasoline	465	56.6	101	145	174	234	347	420	1.0	1.0	--	--	--	--	--	--
14391-G	35% LCC, 65% Regular Leaded Gasoline	900	57.0	100	147	175	233	342	416	1.0	1.0	--	--	--	--	--	--
14392-G	30% LCC, 70% Regular Leaded Gasoline	>960	56.4	101	152	180	234	333	414	1.0	1.0	--	--	--	--	--	--
14893-G	100% Regular Leaded Gasoline	>960	58.9	99	134	165	226	295	366	0.5	0.0	71.1	0.9	28.0			
Phase II																	
15271-G	HC Naphtha	>2490	82.4	95	108	111	123	152	170	0.0	1.0	98.1	0.0	1.9	84	81	12.5
15272-G	Reformate	>6015	42.2	103	178	212	261	329	418	1.0	1.0	34.1	1.5	64.4	100	88	6.1
15273-G	HSR Naphtha	>5835	59.6	190	227	226	260	314	349	1.0	0.0	88.0	0.7	11.3	54	53	1.1
15274-G	LSR Naphtha	>4620	79.6	89	109	113	129	177	224	0.0	1.0	97.3	0.0	2.7	75	73	12.6
15275-G	Alkylate	>2640	64.3	99	133	151	207	327	477	1.0	1.0	90.8	1.1	8.1	72	70	7.5
15276-G	No-Lead Gasoline	870	58.3	89	123	142	205	327	397	1.0	1.0	49.5	20.6	29.9	93	81	8.8
15277-G	HCC Naphtha	900	48.3	108	176	205	266	348	401	1.0	0.0	38.0	18.5	43.5	94	81	4.7
15278-G	LCC Naphtha	435	60.4	93	122	139	185	297	368	1.0	1.0	34.8	32.7	27.5	95	81	9.5
15279-G	Coker Naphtha	105	80.8	89	104	109	122	162	202	1.0	1.0	52.1	46.3	1.6	85	74	13.7
15280-G	Raffinate	4440	76.8	139	155	150	167	188	200	1.0	0.0	95.4	2.7	1.9	63	62	5.5
15281-G	Pyrolysis Gasoline	105	51.7	97	111	116	136	315	370	1.0	1.0	17.0	40.7	42.3	97	80	10.6
15282-G	Referee Blend, MIL-G-53042	795	68.6	203	214	216	223	244	253	1.0	0.0	79.6	19.2	1.2	38	37	1.6
15283-G	1/3 HC, 1/3 Ref, 1/3 HSR	4560	57.6	105	144	162	226	321	390	1.0	1.0	73.4	0.7	25.9	79	74	6.5
15284-G	1/3 Ref, 1/3 HSR, 1/3 LSR	6000	57.4	100	142	162	226	312	381	0.5	0.0	73.1	0.7	26.2	76	71	6.6
15285-G	1/3 HSR, 1/3 LSR, 1/3 Alkylate	4574	65.2	102	133	149	207	312	420	1.0	0.0	92.0	0.6	7.4	67	65	7.0
15286-G	1/3 HSR, 1/3 Alkylate, 1/3 LCC	1275	59.7	104	147	171	231	318	425	0.5	0.0	72.9	11.5	15.6	74	68	6.0
15287-G	1/2 HCC, 1/2 LCC	750	53.9	97	140	164	232	334	414	0.5	0.0	38.9	25.6	35.5	95	81	7.1
15288-G	Coker Naphtha Plus Antioxidant	1770	80.3	90	106	110	123	168	228	0.5	0.0	52.1	46.3	1.6	86	74	13.7
Phase III																	
15707-G	Ashland MPFI Batch No. 4	240	59.0	76	111	138	220	364	427	1.0	1.0	54.3	15.0	30.7	91	81	11.2
15815-G	MIL-G-53042 Reference Gas + 0.25% Diolefin	435	66.7	210	216	218	226	250	265	1.0	1.0	79.1	19.2	1.7	45	43	1.5
15949-G	Champlin Coker Naphtha	240	52.4	194	229	245	291	364	401	0.5	1.0	46.3	38.7	15.0	64	60	1.3
15963-G	55% Coker Naphtha, 45% No-Lead Gasoline (15276-G)	315	54.7	110	162	192	264	355	408	1.0	2.0	48.8	29.0	22.2	78	70	4.7
15964	55% Coker Naphtha, 45% Light Cat. Cracked	315	55.5	110	157	185	257	354	400	1.0	2.0	45.1	33.9	21.0	79	70	5.2
16004-G	Chevron Coker Naphtha	75	81.5	95	107	--	119	155	193	--	--	55.2	43.2	1.6	85	75	13.2
16021-G	65% Ashland MPFI Batch No. 4 + 25% No-Lead Gasoline (15276-G)	360	58.0	87	117	140	218	367	459	1.0	2.0	52.2	16.3	31.5	92	81	9.7
16023-G	67% Chevron Coker (16004-G) + 33% No-Lead Gasoline (15276-G)	375	72.7	95	111	126	135	270	380	1.0	3.0	51.4	37.9	10.7	88	77	11.4
Phase IV																	
16798-G	Debutanizer Bottoms	195	58.7	102	134	149	208	337	402	0.5	0.5	40.4	33.5	26.1	--	--	6.9
16813-G	Commercial Co. A Unleaded Gasoline	705	58.6	--	--	--	--	--	--	--	--	59.8	9.6	30.6	--	--	--
16815-G	Commercial Co. B Regular Unleaded Gasoline	315	61.4	--	--	--	--	--	--	--	--	58.6	14.9	26.5	--	--	--
16816-G	Commercial Co. B Regular Leaded Gasoline	315	62.9	--	--	--	--	--	--	--	--	60.5	13.5	26.0	--	--	--
16817-G	Commercial Co. C Regular Unleaded Gasoline	780	57.6	--	--	--	--	--	--	--	--	45.7	24.7	29.6	--	--	--
16832-G	45% Debutanizer Bottoms, 55% Unleaded Gasoline (13892-G)	345	58.7	--	--	--	--	--	--	--	--	60.3	11.3	28.4	--	--	--

TABLE 3. Test Data Summary for Phase I Samples

AL-Code No.	Sample Description	Induction Period, D 525, minutes	Gum, D 381, mg/100 mL Unwashed				Gum, D 381, mg/100 mL Existent				ISD Rating				Peroxide No.				4-Hour Modified D 873 Gum, mg/100 mL		6-Hour (or Other) Modified D 873 Gum, mg/100 mL	
			A*	B*		C*	A*	B*		C*	A*	B*		C*	A*	B*		C*	Unwashed	Existent	Unwashed	Existent
				24 wk	40 wk			24 wk	40 wk			24 wk	40 wk			24 wk	40 wk					
Phase I 14158-G	100% LCC Gasoline	240	11.8	13.4	41.7	98	1.9	4.5	37.2	56	1.0	1.8	8.3	10.2	0.3	1.5	5.1	9.9	58.9	--	--	--
14388-G	75% LCC, 25% Regular Leaded Gasoline	250	8.5	10.8	23.0	68	1.4	3.9	15.4	53	0.6	1.1	17.7	11.2	0.3	1.3	7.5	8.4	25.0	--	54.1 (4.5 hr)	--
14389-G	50% LCC, 50% Regular Leaded Gasoline	345	5.5	6.5	105	42	0.2	4.1	103	38	0.4	0.6	11.6	9.4	0.3	1.0	22.9	8.8	8.3	--	48 (4.8 hr)	--
14390-G	40% LCC, 60% Regular Leaded Gasoline	465	5.3	5.5	67.7	41	1.1	2.2	67	38	0.5	0.4	14.6	7.3	0.3	1.5	21.0	9.0	4.7	--	32.9	--
14391-G	35% LCC, 65% Regular Leaded Gasoline	> 900	3.9	45.9	302	35	0.0	41	264	32	0.5	7.2	32.8	4.6	0.2	18.5	33.0	10.5	5.2	--	15.6	--
14392-G	30% LCC, 70% Regular Leaded Gasoline	> 960	4.7	63	296	39	3.2	54	262	36	0.2	8.2	54.4	5.1	0.2	28.0	32.9	10.2	5.3	--	17.0	--
13893	100% Regular Leaded Gasoline	> 960	0.6	1.4	6.3	2.0	0.5	0.2	0.3	0.9	0.5	0.8	0.7	5.2	0.0	0.3	0.4	1.2	2.0	--	1.5	--

AL-Code No.	Sample Description	Induction Period, D 525, minutes	Ambient Storage												
			24-Wk			48-Wk			96-Wk			144-Wk			
			Gum, mg/100 mL		ISD, mg/100 mL	Gum, mg/100 mL		ISD, mg/100 mL	Gum, mg/100 mL		ISD, mg/100 mL	Gum, mg/100 mL		ISD, mg/100 mL	Peroxide No.
			Unwashed	Existent		Unwashed	Existent		Unwashed	Existent		Unwashed	Existent		
Phase I 14158-G	100% LCC Gasoline	240	10.0	4.1	0.5	8.9	2.8	1.0	10.5	2.3	1.1	10.5	4.7	3.2	1.4
14388-G	75% LCC, 25% Regular Leaded Gasoline	250	7.6	3.2	0.6	6.8	2.4	0.8	8.1	1.6	1.4	8.8	4.2	2.3	1.4
14389-G	50% LCC, 50% Regular Leaded Gasoline	345	6.1	2.4	0.3	3.6	1.5	0.6	6.0	2.0	1.1	7.7	4.9	2.1	1.7
14390-G	40% LCC, 60% Regular Leaded Gasoline	465	6.3	2.5	0.3	3.4	2.0	0.5	7.0	3.4	2.3	24.9	23.8	8.0	8.9
14391-G	35% LCC, 65% Regular Leaded Gasoline	> 900	4.6	1.9	0.4	2.8	1.2	0.4	4.9	1.5	1.3	7.8	6.8	2.8	2.4
14392-G	30% LCC, 70% Regular Leaded Gasoline	> 960	3.3	1.6	0.4	2.4	0.7	0.3	3.7	0.8	1.0	4.2	3.2	1.0	1.1
13893	100% Regular Leaded Gasoline	> 960	2.0	0.8	0.0	0.4	0.0	0.1	1.4	0.2	0.2	0.8	0.2	0.5	0.1

---

* A = initial; B = 43°C; C = 20 weeks at 54°C.

$$\ln [C] = \frac{Ea}{RT} + \ln A$$

where [C] = test result after storage,
R = the gas constant (1.9872 cal./$^{\circ}$K-mol.),
T = the storage temperature in $^{\circ}$K,
A = a numerical constant, and
Ea = the Energy of Activation

for phase 1 samples, the Energy of Activation, Ea, ranges from 12 to 20 kcal. per mole, depending upon sample composition and the particular test employed to measure "deleterious product formation," i.e., gum, ISD, or peroxide number.

D. Research on Phase II Samples

In an attempt to devise a test that might be applicable (and sensitive) to a broader range of materials, a second testing phase was developed. Samples were collected that represent both typical and extreme potential gasoline blend components. These were evaluated for stability characteristics by the standard and proposed tests, and then subjected to storage. Because it was expected that some of these potential gasoline components would deteriorate more rapidly than phase I samples, the storage times (12 weeks at 54°C; 24 weeks at 43°C) were shortened from those employed in phase I (20 weeks at 54°C; 48 weeks at 43°C). Most components, however, proved to be quite stable.

These samples were obtained from a total of three plant sites; two refineries and one chemical plant. An effort was made to conduct the ASTM D 525 induction-period test to completion for each sample. As seen from TABLE 1, many of the samples failed to yield a distinct break point (as called for by the test) despite sample stress times of up to 100 hours. Most of the components collected from these particular sources are of high quality, and for such samples, the induction-period test does not lead to values that are amenable to statistical treatment.

A total of 18 samples were subjected to storage. An unleaded gasoline was stored as a base case sample. From the refinery that produced the base case gasoline, eight potential gasoline components were obtained for storage, and an additional potential component (raffinate) was obtained from a second refinery. Pyrolysis gasoline from a chemical plant and the reference gasoline of MIL-G-53042 were included as fuels of interest. Five remaining samples were "hand-blends" or approximate gasolines made up by equal-volume blending of different components. This permitted an examination of synergism and mixing effects as part of the study. The final sample was the component known as coker naphtha but included a commercially available antioxidant.

These 18 samples are named below, including abbreviated nomenclature used throughout this report:

HC; Hydrocracked naphtha
Ref; Reformate
HSR; Heavy straight run
LSR; Light straight run
Alky; Alkylate
No-lead; Unleaded gasoline
HCC; Heavy cat-cracked
LCC; Light cat-cracked
Coker; Coker naphtha

Raffinate
Pyrolysis gasoline
Referee blend
1/3 HC, 1/3 Ref, 1/3 HSR
1/3 Ref, 1/3 HSR, 1/3 LSR
1/3 HSR, 1/3 LSR, 1/3 Alky
1/3 HSR, 1/3 Alky, 1/3 LCC
1/2 HCC, 1/2 LCC
Coker + AO (antioxidant)

Of the 10 individual components, only 3 have induction periods lower than the unleaded gasoline fuel. One of these is pyrolysis naphtha from the chemical plant; the remaining two are coker and light catalytically cracked naphthas. This finding is consistent with the stability literature. In addition, LCC and HCC naphthas have induction periods close to unleaded gasoline and, therefore, probably constitute the bulk of the total gasoline volume.

E. Observation for Phase II Samples

1. From the data in TABLE 4, it is apparent that pyrolysis naphtha and coker naphthas are generally an order of magnitude less stable than other gasoline components. In ambient storage, the unleaded gasoline began to show deterioration after 40 to 64 weeks, evidenced by D 381 Gum formation and ISD rating. Among the components, only alkylate and a heavy catalytically cracked (HCC) naphtha showed similar trends. Pyrolysis naphtha gave erratic results, suggesting that sampling is inconsistent. Hand-blends of components which contain alkylate and/or HCC naphtha also seem to be deteriorating, based on limited data.
2. When these samples were subjected to 43°C storage, the unleaded gasoline did not deteriorate after 24 weeks, while HCC naphtha and reformate samples did experience declines in some parameters. Pyrolysis naphtha showed profound changes after as little as 8-week storage. A hand-blend containing HCC naphtha also deteriorated rapidly.
3. At 54°C, the unleaded fuel showed substantial increases in both soluble (unwashed) and existent (washed) gum content after 8 to 12 weeks of storage. It is deduced that 54°C is superior to 43°C for accelerating the formation of gum. A referee blend which had not declined markedly at ambient temperature did show change in gum formation after 24 weeks at 43°C and after 12 weeks at 54°C, it showed an increasing ISD rating but a steady amount of gum.

F. Research on Phase III Samples

In order to evaluate low-induction period streams, eight samples having induction periods in the range of 240 to 425 minutes were prepared. TABLE 5 provides a summary of test data for phase III and IV samples. A coker naphtha similar to the one employed in phase II is included in three of the samples. A test fuel specialty prepared for port fuel injector fouling tests (Ashland Batch No. 4) was included, and the reference fuel spelled out in MIL-G-53042 was adulterated with diolefin in order to lower the induction period and round out the test matrix. Note that none of these samples constitute or are derived from commercially available fuel.

These fuels are of interest because they possess low-induction periods, but also because they cover a relatively wide range of ISD ratings plus unwashed and existent gum. It is this fact that should enable further evaluation of the proposed, modified D 873, test. By subjecting these samples to the proposed test, it should become apparent if the test correlates with (is predictive of) any of the variables, and if it can distinguish between "good" and "bad" low-induction period fuels. As an additional interest, it may become apparent whether the proposed test should be carried out for 4-, 6-, or 8-hour duration.

G. Observations for Phase III Samples

1. The eight low-induction period fuels were prepared and placed in ambient storage. Among these noncommercial materials and blends, only a coker naphtha of 75-minute induction period is exhibiting deterioration after 32 to 48 weeks of storage.

TABLE 4. Test Data Summary for Phase II Samples

AL-Code No.	Sample Description	Induction Period, D 525, minutes	Gum, D 381, mg/100 mL Unwashed			Gum, D 381, mg/100 mL Existent			ISD Rating			Peroxide No.			4-Hour Modified D 873 Gum, mg/100 mL		6-Hour Modified D 873 Gum, mg/100 mL		8-Hour Modified D 873 Gum, mg/100 mL		Ambient Storage 24-Wk			Ambient Storage 48-Wk			Ambient Storage 88-Wk			
			A*	B*	C*	A*	B*	C*	A*	B*	C*	A*	B*	C*	Unwashed	Existent	Unwashed	Existent	Unwashed	Existent	Gum, mg/100 mL Unwashed	Gum, mg/100 mL Existent	ISD, mg/100 mL	Gum, mg/100 mL Unwashed	Gum, mg/100 mL Existent	ISD, mg/100 mL	Gum, mg/100 mL Unwashed	Gum, mg/100 mL Existent	ISD, mg/100 mL	Peroxide No.
Phase II																														
15271-G	HC Naphtha	>2090	0.8	0.0	0.5	0.5	0.0	0.4	0.0	0.1	0.0	0.17	0.08	0.10	0.5	--	0.1	--	0.9	--	0.5	0.1	0.0	0.0	0.0	0.0	0.4	0.7	0.0	0.05
15272-G	Reformate	>6015	1.5	13.6	19.9	0.1	1.9	3.9	0.4	2.1	3.6	0.29	0.86	1.90	4.0	--	2.9	--	3.0	--	2.6	6.6	0.3	0.8	0.4	0.3	1.8	1.7	0.1	<0.05
15273-G	HSR Naphtha	>5835	2.6	0.8	2.2	0.4	0.0	0.3	0.0	0.2	0.0	0.25	0.20	0.16	3.2	—	3.7	--	2.9	--	2.2	0.4	0.2	1.3	0.0	0.3	2.2	0.0	0.0	<0.05
15274-G	LSR Naphtha	>4620	0.2	0.0	0.4	0.0	0.0	0.3	0.0	0.0	0.1	0.13	0.08	0.32	1.2	—	0.5	--	1.2	--	0.2	0.0	0.0	0.3	0.0	0.0	0.8	0.0	0.0	<0.05
15275-G	Alkylate	>2640	0.4	0.9	0.8	0.0	0.0	0.2	0.2	0.0	0.1	0.20	0.32	0.27	1.9	—	1.3	--	2.0	--	0.7	0.1	0.3	1.0	0.2	0.2	1.2	0.9	0.1	0.09
15276-G	No-Lead Gasoline	870	1.2	1.3	2.5	0.0	0.4	1.6	0.2	0.2	0.5	0.18	0.89	0.38	2.4	--	3.5	--	5.7	--	0.8	0.5	0.2	1.5	0.5	0.5	1.9	1.9	0.2	0.19
15277-G	HCC Naphtha	900	0.9	5.0	4.5	0.4	5.2	4.2	0.3	1.7	2.3	0.20	1.23	1.31	4.3	--	6.9	--	13.1	-	1.0	0.7	0.7	3.4	2.5	1.7	3.1	3.1	0.6	0.59
15278-G	LCC Naphtha	435	0.6	1.5	1.3	0.0	1.7	1.4	0.1	1.1	0.6	0.15	0.88	0.90	2.6	--	4.2	--	14.5	-	0.8	0.5	0.2	1.6	0.7	0.8	1.3	1.1	0.1	0.70
15279-G	Coker Naphtha	105	13.8	16.4	21.3	0.6	2.2	1.6	0.0	0.2	0.3	0.15	1.75	0.96	48.7	--	NR**	--	NR	--	13.7	0.7	0.1	14.3	0.9	0.0	11.9	0.7	0.0	1.46
15280-G	Raffinate	>4440	1.3	1.6	1.0	0.5	0.8	0.2	0.0	0.0	0.1	0.15	0.27	0.11	2.0	--	0.4	--	1.5	--	0.6	0.2	0.1	0.6	0.0	0.0	0.3	0.1	0.0	0.12
15281-G	Pyrolysis Gasoline	105	22.8	255	832	5.1	13.8	88	4.1	119	301	0.20	1.89	1.09	775	--	NR	--	NR	--	10.0	8.7	3.9	17.6	5.4	5.2	19.1	16.6	4.8	0.61
15282-G	Referee Blend	795	1.5	2.1	1.1	0.6	1.7	0.9	0.0	0.6	43	1.87	4.34	3.18	0.0	--	0.1	--	0.0	--	0.4	0.0	1.4	0.3	0.0	0.0	0.3	0.4	0.1	0.45
15283-G	1/3 HC, 1/3 Ref, 1/3 HSR	>4560	3.1	1.4	1.5	0.6	0.9	0.4	0.3	0.0	0.1	0.15	0.82	0.14	1.9	--	2.2	--	2.9	--	0.7	0.4	0.0	1.3	0.1	0.3	0.9	0.1	0.0	0.32
15284-G	1/3 Ref, 1/3 HSR, 1/3 LSR	>6000	1.5	1.1	0.8	0.7	1.2	0.2	0.0	0.3	0.0	0.09	0.42	0.15	1.1	--	2.1	--	1.6	--	1.2	0.6	0.3	1.5	0.1	0.2	1.2	0.6	0.0	0.10
15285-G	1/3 HSR, 1/3 LSR, 1/3 Alky	>4570	0.7	1.1	0.6	0.6	0.5	0.0	0.1	0.1	0.2	0.09	0.35	0.07	2.0	--	1.1	--	1.5	--	0.3	0.2	0.0	0.8	0.1	0.0	1.0	0.4	0.1	0.08
15286-G	1/3 HSR, 1/3 Alky, 1/3 LCC	1275	0.8	1.7	1.6	0.4	1.5	0.5	0.2	0.3	0.3	0.09	0.53	0.08	1.9	--	1.9	--	2.0	--	0.3	0.2	0.2	0.9	0.6	0.3	1.1	0.1	0.0	0.15
15287-G	1/2 HCC, 1/2 LCC	750	1.3	4.3	3.0	0.4	4.0	2.9	0.2	1.4	1.7	0.15	1.30	0.07	4.0	—	5.3	--	11.2	--	1.3	1.2	0.3	1.5	1.3	0.8	2.5	2.2	0.6	0.32
15288-G	Coker + A.O.	>1770	16.4	16.5	13.9	0.8	1.8	0.7	0.2	0.2	0.6	0.13	0.69	0.10	7.2	—	15.0	--	12.4	--	13.8	0.7	0.0	14.1	0.5	0.0	14.9	0.5	0.1	0.19

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* A = initial; B = 24 weeks at 43°C; C = 12 weeks at 50°C.

** Not Run.

TABLE 5. Summary of Data for Phase III and IV Samples

AL-Code No.	Sample Description	Induction Period, D 525, minutes	Gum, D 381, mg/100 mL Unwashed			Gum, D 381, mg/100 mL Existent			ISD Rating			Peroxide No.			4-Hour Modified D 873 Gum, mg/100 mL		6-Hour Modified D 873 Gum, mg/100 mL		Ambient Storage 24-Wk			Ambient Storage 48-Wk			
			A*	B*	C*	A*	B*	C*	A*	B*	C*	A*	B*	C*	Unwashed	Existent	Unwashed	Existent	Gum, mg/100 mL Unwashed	Gum, mg/100 mL Existent	ISD, mg/100 mL	Gum, mg/100 mL Unwashed	Gum, mg/100 mL Existent	ISD, mg/100 mL	Peroxide No.
Phase III 15707-G	Ashland MPFI High Deposit Fuel Batch No. 9	240	7.5	38.2	22.9	4.5	5.1	13.5	0.9	3.4	3.1	0.27	0.71	0.89	173.7	169.3	--	--	14.6	8.0	1.4	11.8	8.5	1.3	1.32
15815-G	MIL-G-53062 Reference Gasoline + 0.25% Distalin	435	0.8	2.4	2.0	0.2	0.4	2.1	0.0	0.2	0.2	0.56	2.70	2.53	15.2	14.9	64.9	64.4	1.3	0.1	0.0	1.9	1.5	0.2	0.84
15949-G	Champlin Coker Naphtha	240	34.5	35.4	29.3	34.4	34.1	29.0	11.8	20.1	14.0	Dark	Dark	Dark	279.9	274.8	--	--	38.2	34.2	13.1	32.9	32.5	14.1	Dark
15963-G	35% Champlin Coker Naphtha (15949) 65% Unleaded Gasoline (15276)	315	15.6	19.1	18.1	15.1	18.4	17.6	6.3	10.3	8.7	Dark	Dark	Dark	154.9	154.0	--	--	20.9	18.4	7.9	17.5	17.3	9.5	Dark
15964-G	35% Champlin Coker Naphtha (15949) 65% LCC Naphtha (15278)	315	18.8	19.1	17.2	18.4	18.7	16.2	7.5	11.8	9.2	Dark	Dark	Dark	148.1	143.7	--	--	19.0	16.9	8.3	15.8	15.5	7.9	Dark
16004-G	Chevron Coker Naphtha	75	2.0	3.5	18.1	0.6	1.4	0.8	0.0	0.4	0.2	0.48	1.10	0.61	317.8	310.0	--	--	2.9	2.6	0.0	4.4	3.7	0.2	1.96
16021-G	75% Ashland (15707) + Unleaded Gasoline (15276)	360	8.8	17.5	23.8	4.5	8.2	9.3	1.5	2.3	3.2	0.28	0.98	0.63	29.8	17.9	125.1	112.0	10.5	3.4	1.3	6.1	2.9	0.9	1.42
16023-G	67% Chevron Coker Naphtha (16004) + Unleaded Gasoline (15276)	375	0.6	1.9	2.4	0.4	1.4	1.5	0.2	0.6	0.4	0.36	0.76	0.95	4.5	3.7	35.3	32.4	1.0	0.2	0.2	0.8	0.7	0.0	0.68
Phase IV 16798-G	Debutanizer Bottoms	195	2.9	7.9	18.0	1.6	5.0	6.3	0.3	2.5	2.4	--	1.07	1.31	231.0	225.0	--	--	2.0	1.7	0.5				
16813-G	Commercial Co. A Unleaded	705	13.8	14.3	33.1	0.0	0.2	1.9	0.6	0.0	0.2	1.23	0.99	0.48	15.8	0.4	15.4	0.3	15.2	1.9	0.1				
16815-G	Commercial Co. B Regular Unleaded	315	21.0	25.2	47.3	0.0	2.5	3.4	0.0	3.3	1.9	1.64	0.72	0.34	28.5	16.2	94.4	87.9	16.6	0.3	0.1				
16816-G	Commercial Co. B Regular Unleaded	390	14.4	19.3	33.8	0.1	2.5	4.7	0.1	2.4	2.2	2.62	0.76	0.24	52.2	35.6	153.6	115.9	9.9	0.6	1.9				
16817-G	Commercial Co. C Regular Unleaded	780	5.2	6.4	22.3	0.0	2.6	2.7	1.2	2.4	1.8	0.66	0.31	0.21	5.3	2.5	7.5	4.5	5.9	0.6	2.1				
16832-G	65% Debutanizer Bottoms/35% of 13892-G (Reg. Loaded Gasoline)	345	3.8, 1.5	4.4	11.7	3.1, 0.9	3.8	5.5	0.4	1.1	0.9	0.30	2.99	0.79	11.7	10.2	66.6	64.6	1.4	1.2	0.6				

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* A = initial; B = 24 weeks at 43°C; and C = 24 weeks at 54°C.

2. At 43°C, a high-deposit reference fuel and a blend containing the fuel declined after as little as 4-week storage. Another reference fuel, containing conjugated diolefins, deteriorated somewhat after 16 to 24 weeks.

3. At 54°C, the high-deposit reference fuel and a blend containing the fuel again declined after 2 to 4 weeks, as did the reference fuel containing conjugated diolefins.

H. Research on Phase IV Samples

In this final test phase, an attempt was made to obtain "low" induction period commercial fuels to test the validity of the modified D 873 test and establish limits for use in a specification. Of the twelve commercial gasolines procured from various locations (in the U.S.) where low-induction fuels had been obtained previously, only two were in the 360-minute range with two in the 700-minute range, and the rest were above 960 minutes. The four lowest induction period fuels plus a debutanizer bottom stream from a refinery (both neat and mixed with regular leaded gasoline) were also used in this test phase.

For this set of samples, a decision was made to not aerate the 43° and 53°C samples at the sampling time periods as was done with the three previous phase samples. This condition would represent air (oxygen) starved systems such as large bulk underground storage tankage. The D 873 test represents a condition with abundant oxygen; granted, it also represents a very high temperature of 100°C. The effect on gum formation in oxygen deficient systems compared aerated samples has been previously demonstrated to have a significant effect.(8) Corrections to gum formation rates have also taken into account ullage oxygen concentration in the 95°C "oven test."(6)

I. Observations for Phase IV Samples

1. Data summarized in TABLE 5 for the four low-induction period commercial gasolines and two additional hand-blends that have been stored for 24 weeks at ambient conditions, and provide no conclusions about these materials.

2. When the materials were stored at 43°C, a sample of cracked naphtha and a mixture of that naphtha with leaded regular gasoline, both deteriorated over a 4- to 16-week period. Three of the four low-induction period gasolines showed increases in the insoluble gum formation after as little as 8 weeks, but only one of these samples did so after 4 weeks. The fourth sample seems stable after at least 16 weeks at this condition.

3. At 54°C, three of the four commercial gasolines and both samples containing cracked naphtha showed various indications of deterioration after as few as 4 weeks storage.

4. Both of the low-induction period gasolines showed high deposits in the oxygen-rich D 873 test.

CONCLUSIONS AND RECOMMENDATIONS

The results completed to date have demonstrated the proposed storage stability test, a modification of ASTM D 873, to be acceptable in predicting motor gasoline stability. This method has been shown to correlate with both unwashed and existent gum formations of gasolines stored in excess of 2 years under ambient storage. Based on the data generated to date under the four phases of this storage stability program including supporting data obtained from literature sources and current surveillance information on both military and industry practices (see TABLE 6), the method to be adopted for evaluating stability of commercial/military motor gasoline will consist of the modified

TABLE 6. Specification and Surveillance Limits for Various Gasolines

	Aviation Gasoline Specification Limits		Motor Gasoline Specification Limits			Surveillance Limits			
						DOD			
Requirement	MIL-G-5572E	ASTM D 910-85	MIL-G-3056	ASTM D 439	NATO F-57	MIL-G-5572(3)	MIL-G-3056	Switzerland(1) Gasoline	UOP(2) Gasoline
Induction Period, minutes, max	NR*	NR	480	240	360	NR	NR	360	NR
Unwashed Gum, mg/100 mL, max	NR	NR	4	NR	NR	NR	7	NR	5
Existent Gum, mg/100 mL, max	3.0	NR	NR	5	4	6.0	NR	5	5
Potential Gum, 16-hour aging, mg/100 mL, max	6.0	10	NR	NR	NR	NR	NR	NR	NR
Potential Gum, 4-hour aging, mg/100 mL, max	NR	NR	NR	NR	NR	NR	NR	NR	5
Potential Gum, 5-hour aging, mg/100 mL, max	NR	6	NR	NR	NR	NR	NR	NR	NR
Potential Gum, 6-hour aging, mg/100 mL, max	NR	NR	NR	NR	NR	NR	NR	10	NR

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* NR = No Requirement.

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(3) Canceled and replaced by ASTM D 910.

ASTM D 873 Method using a 6-hour aging existent gum maximum limit of 20 mg/100 mL. The 20-mg/100-mL limit represents a compromise in predicting storage stability for a 4-year period for military gasolines; i.e., F-46 gasolines are now required to meet both an ASTM D 525 limit of 480 minutes minimum and an ASTM D 381 unwashed gum limit of 4 mg/100 mL maximum. The new F-57 military/civilian gasoline will also require both the modified ASTM 873 limit of 20 mg/100 mL maximum after a 6-hour aging period and the ASTM D 381 existent gum limit of 4 mg/100 mL maximum. The final adoption of this new methodology is contingent upon approval by other NATO nations.

Analysis of ambient stored samples is continuing. A detailed analysis of all data is planned for the latter part of fiscal year 1989.

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STORAGE STABILITY OF AVIATION GASOLINE

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Aviation gasoline specifications include accelerated ageing tests with the intention to forecast in advance the storage life of the fuel and to ensure its stability for a reasonable period of time (1 -2 years).

The problematic question in this matter is for how long the fuel would be suitable for use if it is stored under adverse and unusual conditions and how the deterioration , if any , would influence the engine performance. The purpose of this study is to find the answer to this questions when the storage conditions are set in advance.

Aviation gasoline according to MIL-G-5572 grade 100/130 with and without 5% lubricating / preservative oil are stored under regular and severe conditions in two kind of containers: (1) 200 liters steel drums (2) 2 liters polyethylene bags .

A test program for the different samples include gasoline specification properties, analytical methods to record possible chemical changes in the gasoline and functional tests. Parallelally, a two stroke cycle engine will be run with the fuels under test and it's performance recorded and correlated against laboratory test data.

At each stage of the study the test results would be compared with the starting properties and chemical composition of the fuel

Finally the data would be statistically elaborated in order to establish the influence of the different parameters and the expected stability of the gasoline under specified storage conditions.

INTRODUCTION

Gasoline in general and aviation gasoline in particular are considered unstable products under storage conditions.

Even the specifications refer to the stability issue by including accelerate ageing tests with the intention to forecast in advance the storage life of the product. For the user, it is of great importance to be protected and to avoid the use of a fuel that will be unuseable shortly after storage.

The conventional field storage conditions for gasolines are in a way a compromise between the needs of the user and the expected storage stability of the product.

It is widely agreed that for proper and safe field storage of aviation gasoline, it can be maintained in 200 liters steel drums for a period of 1 year provided that:

(1) The initial properties of the product are not close to the specification limits.
(2) The environmental conditions are not too extreme.

Beside the limitations and restrictions this kind of storage impelled upon the user, it has been proved as correct and reliable from the product stability point of view.

The main purpose of this study is to find out in what manner the quality of the aviation gasoline would be influenced if the mentioned field storage conditions are changed and in what way deterioration if any, would affect the performance of an engine.

Our approach was to change sharply the storage parameters in order to get extreme conditions in a short time and to enabel an accelerated ageing. The product received was tested and compared against the specification limits and its performance checked by means of engine tests.

The parameters which have been chosen are:

(1) Type of container - polyethylene vs. steel.
(2) Surface/Liquid ratio - 1 liter bottle vs. 200 liter drum.
(3) High environment temperature - 40°-50° C vs. 20° C.
(4) 5% lubricant oil in the avgas.

PROCEDURE

Three different samples sets have been tested along the study:

(1) Aviation gasoline according to MIL-G-5572 grade 100/130 stored in a 200 liter drum under conventional environmental conditions.
(2) Aviation gasoline according to MIL-G-5572 grade 100/130 stored in 1 liter polyethylene bottles at 40°-50° C temperature.
(3) A mixture of 5% oil according to MIL-L-24435 and aviation gasoline stored under regular and extreme conditions as explained in paragraphs. (1), (2).

The plastic bottles were filled to the top, sealed and stored for different periods of time in a compartment in which the temperature and humidity could be controlled.

The total storage period for the study was set to 32 weeks with an option to continue it to up of 1 year long.

At specified time periods and one at a time, the containers were removed from the compartment and the avgas checked for specification and analytical tests in order to record possible changes in the properties or the chemical composition of the product. Table 1 & 2 summarize the tests and their timing.

In addition, at the end of the 32 storage period, the following tests were performed:

(1) Engine performance with a 5% oil/avgas fresh mixture.
(2) Engine performance with a stored 5% oil/ avgas mixture.
(3) Thermal and analytical analysis of the polyethylene containers after storage.

TABLE 1

TESTS FOR AVIATION GASOLINE STORED UNDER CONVENTIONAL CONDITIONS

TEST	ASTM METHODS	TIME IN WEEKS						
		0	4	8	16	24	32	54
APPEARANCE	------	*	*	*	*	*	*	*
SP. GRAVITY	D-287	*	*	*	*	*	*	*
DISTILLATION	D-86	*	*	*	*	*	*	*
COPPER CORROSION	D-130	*	*	*	*	*	*	*
EXISTENT GUM	D-381	*	*	*	*	*	*	*
POTENTIAL GUM	D-873	*	*	*	*	*	*	*
WATER REACTION	D-1094	*	*	*	*	*	*	*
ANILINE GRAVITY	D-611	*					*	*
SULPHUR CONTENT	D-1266	*					*	*
LEAD CONTENT	D-526	*					*	*
AROMATICS	D-1319	*					*	*
FREEZING POINT	D-2386	*					*	*
OCTANENUMBER	D-2700	*					*	*
U.V	------	*		*			*	*
FTIS	------	*		*			*	*

TABLE 2

TESTS FOR AVIATION GASOLINE STORED UNDER EXTREME CONDITIONS

TEST	TIME IN WEEKS								
	0	1	2	4	8	16	24	32	54
APPEARANCE	*	*	*	*	*	*	*	*	*
SP. GRAVITY	*	*	*	*	*	*	*	*	*
DISTILLATION	*	*	*	*	*	*	*	*	*
COPPER CORROSION	*	*	*	*	*	*	*	*	*
EXISTENT GUM	*	*	*	*	*	*	*	*	*
POTENTIAL GUM	*	*	*	*	*	*	*	*	*
WATER REACTION	*	*	*	*	*	*	*	*	*
ANILINE GRAVITY	*							*	*
SULPHUR CONTENT	*							*	*
LEAD CONTENT	*							*	*
AROMATICS	*							*	*
FREEZING POINT	*							*	*
U.V	*		*			*	*	*	*
FTIS	*		*			*	*	*	*

The results obtained were compared with those received at the beginning of the study.

Finally the data received was elaborated to find a relation between storage condition/ fuel properties and engine performance.

TEST RESULTS

The results are divided into 4 categories: (1) specification (2) analytical (3) engine performance (4) container properties.

Specification properties

Some aviation gasoline properties are considered to have a tendency to change during storage, other ones related to the basic composition of the product or to the content of the added compounds remain unchanged.

The "unstable" properties were checked periodically. The test results are summarized in table 3 together with the respective figures from MIL-L-5572 specification and the deterioration limits of the product according to MIL-HDBK-200.

Table 4 contains the fuel tests for avgas at the beginning and the end of the storage period (regular and severe).

Analytical tests

The analytical tests include the following:

(1) U.V spectra for the avgas and the oil/ avgas mixture at the beginning of the storage and after 32 weeks.
(2) F.T.I.R spectra (figure 1).

According to the test results received no changes were detected in the chemical composition of the product before and after storage.

Engine performance

A two stroke cycle gasoline engine was run with different types of fuels. Each run was for a total of 30 minutes long and different engine performance parameters were checked. The fuels used for the test included:

(1) A 5% MIL-L-24435 oil / avgas fresh mixture .
(2) A 5% oil/ avgas mixture prepared from avgas stored for 32 weeks in normal conditions.
(3) A 5% oil/ avgas mixture stored under severe conditions.

The engine tests results are summarized in table 5.

Container tests

The mechanical properties and thermalanalysis characteristics of the polyethylene containers after the storage period of 32 weeks were tested and compared with those of new ones.No differences were detected for the tensile strenght and elongation of the samples, the thermal behavior of the polyethylene before and after storage was essencially the same (figure 2).

TABLE 3 : TEST RESULTS OF "UNSTABLE" AVGAS PROPERTIES

PROPERTY	TIME IN WEEKS							MIL-G-5572	MIL-HDK-2000
	0	1	2	4	8	16	32		
APPEARANCE	B&C	B&C	B&C	B&C	B&C	B&C	B&C	B&C	------
DISTILLATION (C)									
IBP	40	45	42	44	44	44	46	Report	------
10%	73	73	75	77	77	78	80	min at 75 C	0.40% at 75 C
40%	98	97	99	101	99	99	99	max at 75 C	-47% min at 105 C
50%	102	100	102	104	102	101	101	min at 105 C	-87% min at 135 C
90%	113	111	116	121	112	112	113	min 135 C	------
FBP	140	133	145	150	144	142	138	170 max	176.7
SUM 10% AND 50%	175	173	177	181	179	179	181	135 min	------
R.V.P. (psi)	5.8	5.7	5.5	5.3	5.1	4.8	4.6	5.5 - 7.0	5.0 - 7.25
WATER REACTION	1(1)	1(1)	1(1)	1(1)	1(1)	1(1)	1(1)	2(2)	------
COPPER CORROSION	1A	1A	1A	1A	1A	1A	1A	1	3
EXISTENT GUM mg/100 cc	1	1	1	1	1	2	9	3.0 max	6.0 max
POTENTIAL GUM mg/100 cc	1	1	1	1	2	10	30.0	6.0 max	------

TABLE 4: TESTS RESULTS AT BEGGINING AND END OF THE STUDY

PROPERTY	WEEK			MIL-G-5572
	0	32(DEV)	32(REF)	
APPEARANCE	B&C	B&C	B&C	B&C
SP. GRAVITY	0.7078	0.7075	0.7075	Report
DISTILATION°C				
IBP	40	46	44	------
10%	73	80	78	min at 75 C
40%	98	99	98	max at 75 C
50%	102	101	101	min at 105 C
90%	113	113	113	min at 135 C
FBP	140	138	138	170 max
R.V.P (psi)	5.8	4.6	4.9	5.5 - 7.0
W.R	1(1)	1(1)	1(1)	2(2)
COPPER CORROSION	1A	1A	1A	1
EXISTENT GUM mg/100ml	1	9	3	3.0 max
POTENTIAL GUM	1	30	5	6.0 max
ANILINE GRAVITY PR.	10558	10600	10600	7500 min
AROMATICS (%)	7	7	7	5 min
FREEZING POINT (C)	-72	-72	-72	-60 max
LEAD CONTENT (g/gal us)	0.54	0.54	0.54	2.12 max
SULFUR CONTENT (%)	0.04	0.04	0.04	0.05 max
OCTANE NUMBER	101	100	101	

TABLE 5

ENGINE TESTS

PROPERTY	FRESH MIXTURE MIXTURE (32 WEEKS)					REGULAR STORAGE MIXTURE (32 WEEKS)					SEVERE STORAGE MIXTURE (32 WEEKS)				
R.P.M.	5000	5500	6000	6500	7000	5000	5500	6000	6500	7000	5000	5500	6000	6500	7000
C.H.T. (RIGHT) °C	177	187	195	210	222	168	185	196	201	220	177	183	194	208	222
C.H.T (LEFT) °C	165	177	184	202	215	159	176	188	205	211	165	173	186	201	215
FUEL CONSP. liter/ hour	3.36	4.32	6.30	7.89	11.07	3.53	4.04	6.28	8.00	16.10	3.12	4.07	6.41	7.95	11.36
MAX R.P.M	7300					7300					7300				
STARTABILITY	FIRST TRY					FIRST TRY					FIRST TRY				
REACTION TO FULL ACCEL.	VERY GOOD					VERY GOOD					VERY GOOD				
MOTOR BEHAVIOR	VERY GOOD					VERY GOOD					VERY GOOD				
REMARKS	NONE					NONE					NONE				

FIGURE 1: FTIR SPECTRA FOR FRESH AND STORED GASOLINE.

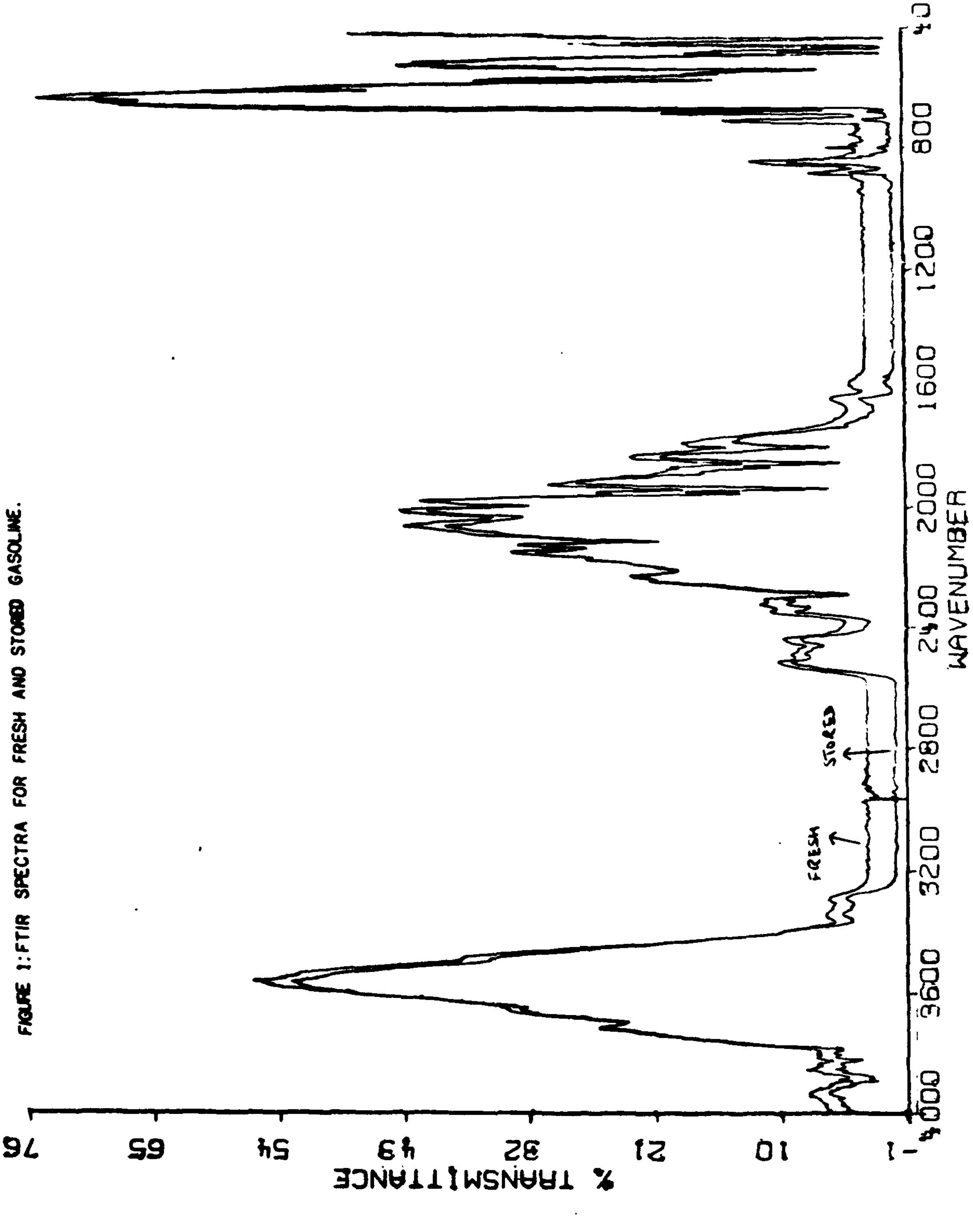
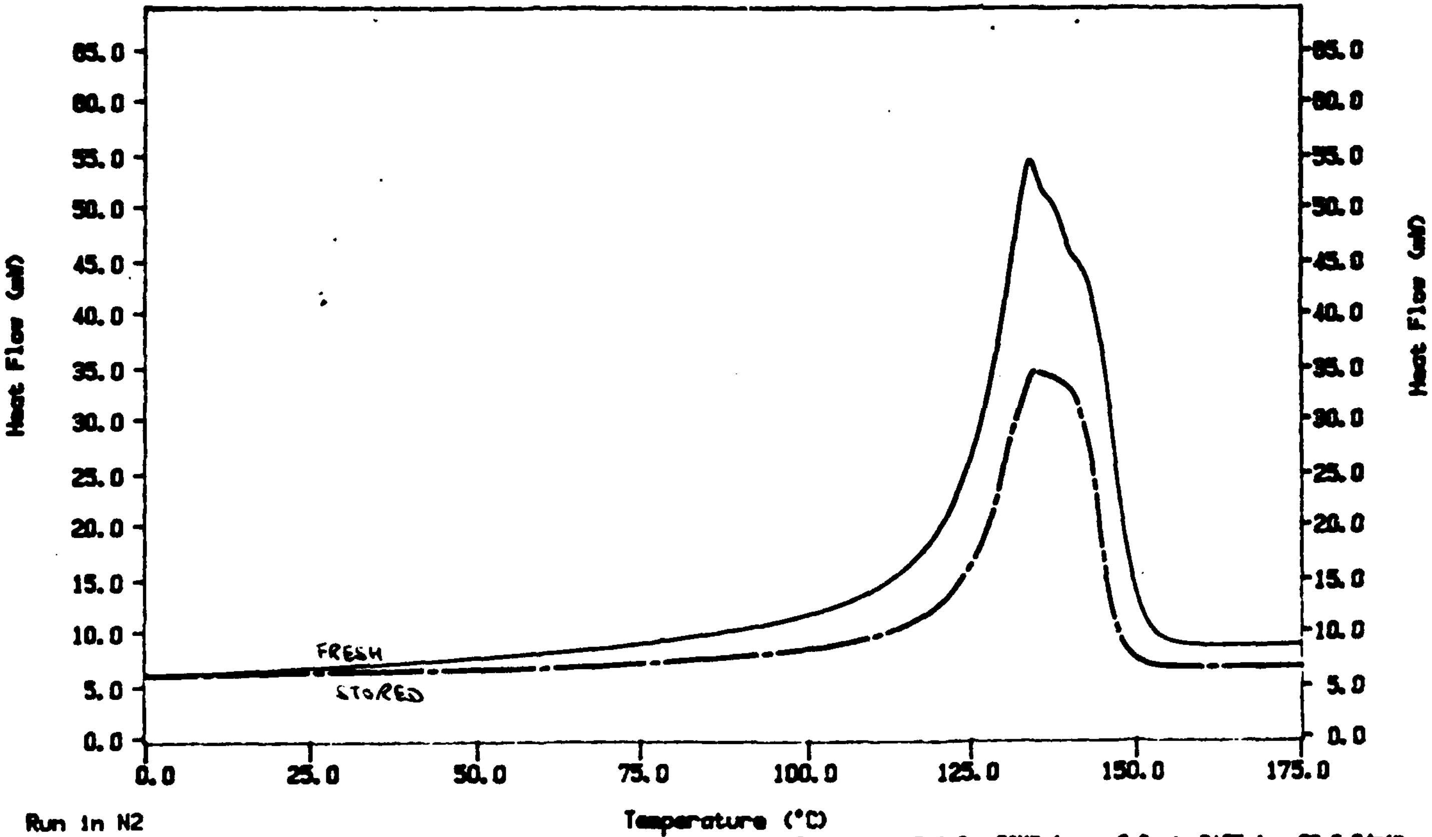


FIGURE 2: THERMAL ANALYSIS OF POLYETHYLENE CONTAINERS

DSC Data File: pe32
Sample Weight: 15.500 mg
Wed Aug 10 12:36:11 1988
P.E. - after 32 weeks

PERKIN-ELMER
7 Series Thermal Analysis System

DSC Data File: perel
Sample Weight: 8.200 mg
Wed Aug 10 11:23:47 1988
P.E. - reference



Run in N2
TEMP 1: -25.0 C TIME 1: 0.0 min RATE 1: 20.0 C/min
TEMP 2: 180.0 C

TEMP 1: -25.0 C TIME 1: 0.0 min RATE 1: 20.0 C/min
TEMP 2: 180.0 C TIME 2: 0.0 min

DISCUSSION

A wide number of parameters influence the storage stability of the gasoline, between them we can mention the crude source, the distillation process and sweetening, storage conditions prior to use, environment, etc. The main purpose of this study was to evaluate uncommon storage conditions and the perfomance of a deteriorated product in comparision with "conventional" storage as a first step for further investigation.

We have to point out that the results received here are limited and restricted to the parameters checked and it is possible that with a different type of fuel, different containers or other engines the conclusions and results would not be the same.

From Tables 3-5 and figures 1-2 we can conclude the following:

(1) The deteriorated properties along storage in steeldrums or polyethlene containers are essencially the same: potential and existent gum, distillation and R.V.P.

(2) The gum formation for gasoline stored in plastic plastic containers is much severe than for avgas stored in

(3) The loss of volatile fractions stored in plastic containers is mush more severe.

(4) For the gasoline stored in plastic containers the change in the potential gum was detected after 8 weeks and it was out of spec after 16 weeks. Regarding the existent gum, the main change happened between week 16 and 32 when it changed from 2 mg/100 cc to 9 mg/100cc.

(5) The gasoline stored in the 200 liter drum was on spec at the end of the 32 week storage period besides the R.V.P and 10% distillation. The gasoline is still proper for use according to the deterioration limits specified under MIL-HDBK-2000.

(6) No chemical changes were detected in the gasolines or mixtures stored.

(7) No differences were detected in the engine performance between fresh, regular stored and severe stored types of mixture.

(8) There is no deterioration in the polyethlene containers after storage (mechanical properties and thermal anylysis behavior).

We can conclude that the two main issues regarding product deterioration are concerned with volatility loss and gum formation.

Loss of volatile fractions of gasoline is normal and expected under storage, specially if the container is not properly closed or not filled to the top. We can explain the differences in the distillation and R.V.P as function of time between the two types of storage by the following explanation:

(1) The drum wasn't full to the top and was periodically open to take samples.

(2) The poltethylene containers filled with avgas had been exposed to heat and as a result of that their volume increased. Althogh they were at the beginning filled to the top, because of the volume change, gasoline vapor formation became possible and loss of volatile product happened when the bottle was opened for testing.

The gum formation in gasoline under storage in a known problem. In our opinion the first step to be taken into account before a decision about storage is made is to check whether the initial existent and potential gum results are suitable enough. The next step should be to consider the conditions and time period for the storage (how many months or years) and finally the intended use of the product (type of engine).

In our case if we take into account that the date of production of the gasoline was 5-6 months before the study started we can conclude that a 1 year storage period in steel drums is reasonable and the product reach the limit of the specification after 1 year storage as expected.

The storage in polyethlene containers is in our opinon better than we expected, specially if we realize the temperature conditions, the small volume of the containers (ratio plastic/ gasoline) etc. The main problem found was the production of gum which we believe should be less severe if the environmental temperature is kept low.

According to the results received in this study and the limitations mentioned, there is no reason to reject the idea of avgas storage in plastic containers for a period of time of 12 month.

We can certainly say that the avgas stored under the abnormal conditions described here is still proper to run a two stroke engine without any trouble and this fact has to be considered for further studies or operational steps in the future for storage of aviation gasoline in small quantities.

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