REFERENCES

1. Allbright, C. S., F. G. Schwartz, and C. C. Ward. Diesel Fuel Stability Testing. Prepared for BuShips, Project Serial No. SR-001-06-02, Task No. 0600. BuMines Final Report, October 1966, 25 pp.

    Forty-one Navy diesel fuels were evaluated for storage stability at 43.3° C (110° F). Twenty-three fuels which contained cracked stock were tested for compatibility with a straight-run fuel during storage. Samples that contained cracked stock formed more gum in storage than the straight-run fuels. The amount of insoluble gum formed during storage for 36 weeks averaged 2.7 and 1.9 mg/100 ml, respectively, for cracked and straight-run samples. Two of the cracked fuels showed incompatibility with a straight-run fuel during the storage stability test.

    The 16-hour accelerated stability test at 95° C (203° F) was run on 43 fuels and the British Static Beaker test at 98.9° C (210° F) was run on 20 samples. Neither of these tests correlated with 12 weeks storage at 43.3° C (110° F).

    See Tables 44 and 45.

2. Allbright, C. S., F. G. Schwartz, and C. C. Ward. Fundamentals of Fuel Stability. Technical Report No. 20, Department of the Army Project 1A024401A106, Bureau of Mines, Bartlesville, OK, December 1969, 27 pp.

    The 16-hour accelerated gasoline stability test which had been developed was applied to additional gasoline samples, and the results were compared to the results of storage at 43.3° C (110° F) for periods up to 32 weeks. A total of 24 gasolines were tested by the 16-hour method, and the results correlated with the amounts of gum and lead precipitate that formed during storage at 43.3° C (110° F) for periods up to 32 weeks. As a result of the additional tests, some minor adjustments in the original correlations were made.

    See Tables 34, 35, and 36.

3. Allbright, C. S., F. G. Schwartz, and C. C. Ward. Storage Stability of Gasoline. Comparison of Storage and Rapid Bomb Aging. BuMines RI 7084, 1968, 33 pp.

    An accelerated stability test was developed in which gasoline samples were heated in a stainless steel bomb at 93.3° C (200° F) for 16 hours. Fuel deterioration

was determined from the amounts of soluble gum, insoluble gum, and inorganic residue formed. The results of this accelerated test were correlated with the results of storage at 43.3° C (110° F) for periods as long as 32 weeks.

The effect of several additives on gasoline stability in both the rapid 93.3° C bomb test and 43.3° C storage was investigated. N,N'-di-sec-butyl-p-phenylenediamine improved the stability of two unstable gasolines, but had little effect on two stable gasolines. 2,6-Di-tert-butyl-4-methylphenol improved the stability of only one of the unstable gasolines, and had no effect on the other three gasolines tested. Tetraethyllead decreased the storage stability of all four gasolines, both with respect to formation of gum and precipitation of inorganic sediment.

See Tables 25 through 31.

4. Allbright, C. S., M. L. Whisman, and F. G. Schwartz. Use of Tritium Tracer Techniques in Studies of Gasoline Storage Stability. BuMines RI 6373, 1964, 17 pp. NTIS No. N64-15607.

   Radioactive tracer techniques were used to gain a better knowledge of the types of compounds that cause gum formation in gasoline during storage. A selected organic compound was labeled with tritium and purified. An unstable gasoline was tagged by adding a small amount of the labeled compound. After storage of the gasoline at 43.3° C (110° F) for 16 weeks, the gum that had formed was recovered. The amount of the test compound converted to gum was determined by liquid scintillation counting. About 70 compounds, including several classes and types, were studied. The compounds, listed in order of descending reactivity in the test fuel, were sulfur compounds, nitrogen compounds, polycyclic hydrocarbons, olefins, alkylbenzenes, and saturates. In order of decreasing percentage of each in the gum, the compounds were mono-olefins, alkylbenzenes, sulfur compounds, polycyclic hydrocarbons, nitrogen compounds, and diolefins.

5. Armstrong, W. H., D. Milsom, H. P. Hebert, and A. R. Rescorla. Predict Fuel Oil Stabilities. <u>Petrol. Processing</u>, Vol. 12, No. 2, February 1957, pp. 88-93.

   A method was developed for estimating stability of fuel oil using optical density (absorbance) measurements. The oil was heated to 82.2° C (180° F) with air bubbling through it for various time periods. At the end of the heating period, the optical density of the oil was measured, the oil was filtered through a fine porosity fritted glass filter, and the optical density of the filtered oil was measured. The difference in optical density between the filtered and unfiltered oil was calculated, and this optical density difference was correlated with the amount of insolubles in the oil. A calibration curve was constructed by which the measured optical density difference could be used to estimate the length of time an oil would need to be held at 82.2° C to reach an insolubles content of 2 mg/100 ml. The time at 82.2° C to reach an insolubles content of 2 mg/100 ml could be converted, by previously developed correlations, to the time at any other temperature to reach the same insolubles content.

See Table 124.

6. Bartleson, J. D., and C. C. Shepherd. How to Select Gasoline Antioxidants. Hydrocarbon Processing & Petrol. Refiner, Vol. 43, No. 8, August 1964, pp. 153-158.

   Gasoline blending stocks from catalytic cracking and catalytic reforming and the use of alkylate in motor gasoline had increased the stability of this product. Unstable components such as cracked stocks and polymer gasolines had disappeared from use, so decomposition of lead antiknock compounds in gasolines had become the dominant stability problem. There is some discussion of storage of gasolines at 43.3° C (110° F) for testing the storage stability, but no experimental details or data are included.

7. Bassler, G. C., and J. R. Smith. Gum and Haze Formation in Motor Gasoline. Tech. Reports No. 1 to 11, Dept. of Army Ordnance Corps Contract No. DA-04-200-ORD-349, Stanford Res. Inst., Menlo Park, CA, May 1955 to December 1958.

   The formation of gum in gasoline or in pure alkanes and alkenes was accelerated by irradiation with UV light. A vacuum transfer technique was developed for recovery of gum from the liquids. Infrared analysis of the gum indicated the presence of carboxyl, hydroxyl, carbonyl, and ester functional groups. Vacuum distillation of the gum followed by functional group and elemental analyses of the distillate, residue, and original gum did not reveal any major differences between them. A three-step gum reduction process was developed in which the gum was reduced with lithium aluminum hydride, converted to iodo-compounds with potassium iodide, and the iodo-compounds reduced with zinc and hydrogen chloride. Infrared analysis of the reduced gum showed that oxygenated groups had been eliminated, indicating that the gum had been reduced essentially to hydrocarbons. The reduced gum appeared to be highly aromatic.

Several oxygen and nitrogen containing compounds were added to a synthetic system of 2-heptene and isooctane or to gasoline to determine their gum-forming potential during irradiation with UV light or in storage. The gums were studied by first reducing them to hydrocarbons, then analyzing the hydrocarbons by such techniques as fractional distillation, gas-liquid chromatography, UV absorption, and mass spectroscopy. Compounds identified in the fraction of reduced gum boiling up to 188° C were almost solely aromatic in nature, representing alkylbenzenes, indane, indene, and styrene. The higher boiling material was composed largely of naphthalenes, acenaphthenes, indanes, and indenes.

8. Bentur, S., M. Babitz, A. Manor, and A. Rocker. Storage Stability of Gas Oil. Israel J. of Technology, Vol. 5, No. 3, 1967, pp. 211-215.

Gas oil was stored in vented metal cans and in vented glass bottles at ambient temperatures for 3, 6, or 9 months. At the end of the storage period, gum was determined by filtration and other properties were determined by standard tests. All samples showed a continuous increase in color, acidity, and gum content. Samples stored in metal containers formed more gum than those in glass containers, indicating a catalytic effect by the metal.

Accelerated oxidation tests were conducted in which the oil was heated to 100° C with air bubbling through it for periods of 2 to 24 hours. Gum was determined by filtration. Gum content increased continuously with oxidation time. A plot of total gum versus oxidation time was linear up to a time of 8 hours, then the gum content began increasing more rapidly.

See Tables 137 and 138.

9. Bowden, J. N. Stability Characteristics of Some Shale and Coal Liquids. DOE/BETC/4162-10. Southwest Research Inst., San Antonio, TX, November 1980, 50 pp. NTIS No. DOE/BETC/4162-10.

Liquids derived from coal and from oil shale were stored in glass bottles for 32 weeks at 43° C. Periodically during the 32 weeks and at the end of the storage period, measurements were made of insolubles, soluble gum, dissolved oxygen content, and peroxide number. Some of the liquids were also analyzed by IR, NMR, and UV spectroscopy before and after storage.

Samples of coal-derived naphtha formed very large amounts of soluble gum and insoluble sediment during storage. Analyses of the naphtha and of the soluble and insoluble gum showed that the nitrogen, oxygen, and sulfur compounds present in the original naphtha became concentrated in the gum. The low carbon-hydrogen ratio of the gum indicated multi-ring aromatic compounds, and the molecular weight distribution suggested that most of the products in the gum were due to oxidation rather than polymerization.

The finished jet fuel and diesel fuel produced from shale oil formed very little gum and sediment, no more than typical petroleum products.

It was concluded that the shale oil products investigated were stable toward storage, while the coal derived products were unsuitable for storage but could be further refined to produce relatively stable material.

See Tables 152, 153, and 154.

10. Bowden, J. N. Stability Survey of Hydrocarbon Fuels. Final Report. DOE/BETC/1778-4, Southwest Research Inst., San Antonio, TX, October 1979, 30 pp. NTIS No. DOE/BETC/1778-4.

The purpose of this program was to develop storage stability data on currently available fuels to serve as reference data. Ten samples each of No. 2 diesel fuel, JP-4 jet fuel, unleaded gasoline, and leaded gasoline were obtained from 10 different locations across the United States. Each sample was evaluated for physical properties and elemental analysis. Then 10 280-ml portions of each sample were stored in 32 oz. amber glass bottles at 43.3° C (110° F). The bottles were aerated every four weeks. After 4, 8, 16, and 32 weeks of storage, two bottles of each sample were removed from storage and analyzed for soluble and insoluble gum and for precipitate. In addition, the thermal stability was measured on the jet fuel samples.

The JP-4 fuels were the most stable of the fuels tested. Unleaded gasoline ranked second in stability, leaded gasoline was third, and the diesel fuels were the least stable. None of the jet fuels showed any deterioration during the 32 weeks of storage at 43.3° C, while one unleaded gasoline, four leaded gasolines, and four diesel fuels appeared to have some instability. However, all the fuel types appeared to be reasonably stable for 32 weeks at 43.3° C, which translates into at least one year of storage at ambient conditions.

See Tables 39, 40, 53, and 112.

11. Bowden, J. N. Storage Stability of Federal Specification Gasoline. Final Report AFLRL No. 34, Contract No. DAAK-02-73-0221, U. S. Army Fuels and Lubricants Research Lab. Southwest Research Inst., San Antonio, TX, July 1974, 17 pp., NTIS No. AD 784282.

Eight drum samples of gasoline from various petroleum companies representing fuels meeting the requirements of Federal Specification VV-G-001690 (Army MR) Gasoline, Automotive, Low Lead or Unleaded, and four drums of European gasolines meeting the requirements of Federal Specification VV-G-76B, Gasoline Automotive, were stored for six months in sealed drums under cover at ambient conditions. Two of the VV-G-001690 gasolines were unleaded and six were low lead fuels. Analyses, bench and engine tests performed on these samples, prior to and after the storage period, indicated that gasolines meeting federal specification requirements have adequate storage stability for at least six months and probably for longer periods. Gasolines with high olefin content appeared to have less storage stability than those with lower olefin content. The work indicates that, from the standpoint of storage stability, combat gasoline in the military system could be replaced with federal specification gasoline with no adverse effects; however, a more severe oxidation stability requirement should be included in the Federal Specifications to insure adequate storage stability.

See Table 38.

12. Bowden, J. N., and D. W. Brinkman. Stability of Alternate Fuels. Hydrocarbon Processing, Vol. 59, No. 7, July 1980, pp. 77-82.

Samples of gasoline and jet fuel produced from coal, oil shale, or tar sands were stored in amber glass bottles for 32 weeks at 43.3° C (110° F), and the amounts of gum formed in each were determined. Samples of petroleum-derived gasoline and jet fuel were stored under the same conditions for comparison with the alternate fuels. The petroleum-derived fuels showed good storage stability, while most of the synthetic fuels developed high levels of deposits after 32 weeks.

Accelerated storage at 93.3° C (200° F) for 16 hours produced results that correlated well with the 43.3° C, 32 week storage for the gasoline samples, but not for the jet fuels. HPLC and GC analyses of the samples before and after storage indicated that the gasolines lost some of the lighter components during storage, but the jet fuels showed very little change in composition with storage.

IR and GPC analyses of the gums revealed a high concentration of oxygenated material and some high molecular weight material, indicating that gum formation is primarily the result of oxidation reactions with some polymerization. Elemental analyses showed that nitrogen and sulfur compounds tended to concentrate in the gum.

13. Bowden, J. N., and G. H. Lee, II. Syncrude Stability Study. Final Report. DOE/BC/10188-33, Southwest Research Inst., San Antonio, TX, 1983. NTIS No. DOE/BC/10188-33.

Six coal-derived liquids, three crude shale oils, and five hydrotreated shale oils were evaluated for storage stability. Samples were stored in borosilicate glass bottles at 43° C for periods up to 24 weeks, and the amounts of insolubles formed during storage were determined. The coal-derived naphthas and middle distillates produced less gum and precipitate than heavier coal-derived fractions, while a heavy distillate was the only fraction that showed a significant increase in viscosity during aging. Since the crude shale liquids were too viscous for measurement of precipitate and gum, deterioration was determined from heptane insolubles, which showed a small increase during aging. The hydrotreated shale oils were relatively stable during storage, but some increases in precipitate and adherent gum were observed. None of the shale oils showed significant changes in viscosity with aging.

Several samples of Occidental shale crude oil and intermediate refinery streams produced from this shale crude were tested for stability at 80° C over time periods of 3, 7, and 14 days. There was a wide range of stability between the materials; hydrotreated streams were significantly more stable than those not hydrotreated.

The storage stability of three petroleum-derived experimental referee broadened-specification (ERBS) fuels was investigated and compared to the stability of syncrudes. The ERBS fuels were much more stable in storage than the syncrudes, with insignificant amounts of gum and precipitate formed during 24 weeks of storage at 43° C.

Several other analytical techniques were evaluated for determining stability of coal and shale-derived liquids. Gas chromatography, proton NMR, and low-resolution mass spectrometry did not have sufficient resolution and sensitivity to measure the small changes in composition occurring during storage. Thermogravimetric analysis and differential scanning calorimetry appeared to be useful techniques for monitoring stability characteristics.

See Tables 194 through 202.

14. Bowden, J. N., E. C. Owens, D. W. Naegeli, and L. L. Stavinoha. Military Fuels Refined From Paraho-II Shale Oil. Interim Report AFLRL No. 131, Contract No. DAAK70-80-C-0001, U. S. Army Fuels and Lubricants Research Lab., Southwest Research Inst., San Antonio, TX, March 1981, 93 pp., NTIS No. AD A101069.

The storage stability of jet fuels and marine diesel fuel refined from Paraho-II shale oil was determined in an evaluation of these fuels for compliance with military specifications. The fuels were stored at 43° C in unvented glass bottles which were opened and aerated every four weeks. After storage periods of 4, 8, 16, and 32 weeks, soluble gum, insoluble gum, precipitate, peroxide number, and dissolved oxygen content were determined. Only small amounts of gum were formed in each sample. These fuels appeared to be stable through 32 weeks of storage at 43° C and compared favorably with petroleum-based fuels. Thermal stability tests by the JFTOT procedure before and after storage showed that the thermal stability of these fuels was not degraded by storage.

In an accelerated aging test at 150° C, the shale oil products formed less insoluble residue than petroleum products; however, at 80° C the stability of the shale fuels was poorer than that of petroleum-based fuels. Blends of shale oil fuels and petroleum fuels tested by the accelerated aging tests revealed no compatibility problems.

15. Bowden, J. N., and L. L. Stavinoha. Final Report on Crude and Product Storage: State-of-the-Art Review and Assessment. Interim Report AFLRL No. 110, Contract No. DAAK70-78-C-0001, U. S. Army Fuels and Lubricants Research Lab., Southwest Research Inst., San Antonio, TX, November 1978, 65 pp., NTIS No. AD A066605.

Report on Task 1 of a 4-task program to ensure that products being considered for storage in the Strategic Petroleum Reserve would be of a quality immediately usable and to identify likely quality assurance procedures. The first task reviewed and assessed the state-of-the-art in petroleum crude and product storage through literature review, questionnaires, and personal contacts. This report reviews the history of underground storage and briefly discusses the changes that occur in fuels during storage, but no data or test results are given. An extensive bibliography on gas storage and stability of petroleum and refined products is included.

16. Brinkman, D. W. Synfuel Storage and Thermal Stability Test Results. Proc. Naval Air Systems Command-Naval Research Laboratory Workshop on Basic Research Needs for Synthetic Hydrocarbon Jet Aircraft Fuels, Washington, D.C., June 15-16, 1978, pp. 155-162. In NTIS No. AD A060081.

The storage stability of a variety of different fuels and distillate cuts from both petroleum and oils derived from coal, oil shale, and tar sands was studied. The samples were tested in 43.3° C (110° F) storage stability tests; 32 weeks at 43.3° C was considered to be equivalent to at least 2 years of ambient storage.

Another test was an accelerated storage test in which the samples were sealed inside glass bottles and stored for 16 hours at 93.3° C (200° F). The oxygen consumption and amount of gum formed in the 16-hour test were used to predict the probable gum formation during 43.3° C storage. The predictions worked well for gasoline, but not for other fuels.

17. Brinkman, D. W., and J. N. Bowden. Stability of Some Coal and Tar Sands Syncrude Fractions. Fuel, Vol. 61, No. 11, November 1982, pp. 1141-1148.

Fractions of syncrudes derived from coal and tar sands were stored in borosilicate glass bottles at 43° C for periods up to 32 weeks, with aeration every four weeks. Precipitate, insoluble gum and soluble gum were measured periodically.

An SRC-II heavy distillate was extremely unstable, forming large quantities of total gum even when stored under ambient conditions. An SRC-II middle distillate formed much less gum in 43° C storage, but had a large increase in gum between 16 and 32 weeks. Three naphthas from coal-derived syncrudes had a large increase in gum content during the first 8 weeks of storage, followed by a more gradual increase to 32 weeks. A tar sands gas oil formed extremely large amounts of gum, and the rate of increase in gum between 16 and 32 weeks was very sharp.

Tar sands kerosene and naphtha were much more stable and formed much smaller quantities of gum in accelerated storage than the other syncrude fractions; however, they still formed more gum than equivalent petroleum fractions. Elemental analyses of gum samples showed that there was a significant increase in oxygen content of the gum over the original syncrude fraction. Liquids that originally contained sulfur and nitrogen showed substantial enrichment of these elements in the gum.

See Tables 163, 164, and 165.

18. Brinkman, D. W., J. N. Bowden, J. W. Frankenfeld, and W. F. Taylor. Synfuel Stability: Degradation Mechanisms and Actual Findings. Oil Shale, Tar Sands, and Related Materials, H. C. Stauffer, Ed., ACS Symposium Series No. 163, American Chemical Society, 1981, pp. 297-313.

The effects of various nitrogen compounds on the stability of diesel fuel and JP-8 jet fuel were investigated. The nitrogen compounds were rated according to their relative tendencies to form sludge when they were added to the petroleum-derived fuels. Deleterious compounds were those which contained heterocyclic nitrogens with an alkyl group adjacent to the nitrogen.

Interactions between compounds were investigated. Preliminary results suggest that interactions can occur between 2,5-dimethylpyrrole (DMP) and various other nitrogen-containing species. In some cases, the interaction was positive, with the total sediment formed being more than would be expected if the two compounds acted independently; in other cases it was negative, with less sediment produced than expected if the compounds acted independently. Interactions with several sulfur and oxygen compounds were also investigated; thiols produced significant negative interactions with DMP.

A number of synfuels and syncrude liquids were stored at 43.3° C (110° F) for up to 32 weeks. Those fuels refined to meet the requirements of petroleum-derived fuel specifications generally showed relatively good stability.

19. Brinkman, D. W., J. N. Bowden, and H. N. Giles. Crude Oil and Finished Fuel Storage Stability: An Annotated Review. DOE/BETC/RI-79/13, February 1980, 67 pp. NTIS No. DOE/BETC/RI-79/13.

Literature pertaining to the effects of storage on the quality of crude oils and fuels was reviewed. The review includes 270 references, which were located through a computer search of eight literature data bases. The emphasis of the review is on underground storage; however, some studies of laboratory storage of fuels are also included.

20. Brinkman, D. W., M. L. Whisman, and J. N. Bowden. Stability Characteristics of Hydrocarbon Fuels from Alternative Sources. BETC/RI-78/23, March 1979, 36 pp. NTIS No. DOE/BETC/RI-78/23.

Samples of gasoline and jet fuels produced from coal, oil shale, and tar sands were investigated for storage stability and compared to petroleum-derived samples. The samples were stored in amber glass bottles for 32 weeks at 43.3° C (110° F). The petroleum-derived fuels showed good storage stability, but most of the synthetic fuels developed high levels of deposits after 32 weeks.

These fuels were also tested in a 16-hour, 93.3° C (200° F) accelerated aging test, and the results were used to predict the amount of gum that would be formed in 32 weeks of storage at 43.3° C. Correlations between the predicted and actual gum values for 43.3° C storage were good for the gasoline and naphtha samples, but poor for the jet fuels.

HPLC and GC analyses before and after storage indicated that the gasolines lost some lighter components during storage, but there was very little change in the jet fuels. Analysis of the gums by infra-red spectroscopy revealed the presence of oxygenated compounds.

See Tables 148 and 149.

21. Brinkman, D. W., and E. W. White. Future Distillate Fuels: What, When, Where, and How Stable? _Distillate Fuel Stability and Cleanliness_, L. L.

Stavinoha and C. P. Henry, Eds., ASTM STP 751, American Society for Testing and Materials, Philadelphia, PA, 1981, pp. 84-91.

A general discussion of some of the factors that must be considered in converting from the present petroleum-based fuels to synthetic fuels from coal or oil shale is presented. Stability of the fuel is suggested as one factor that will need to be considered, and the authors suggest that a stability test requirement may need to be included in purchase specifications. Fuels from synthetic crudes are considered to have poorer storage and thermal stability than petroleum-derived fuels because of higher levels of nitrogen, sulfur, and oxygen compounds. However, not all heteroatom compounds are equally deleterious. Certain compound types, such as alkyl-substituted pyrroles, are more active toward gum formation than other compound types.

22. Brown, F. R., and F. S. Karn. Stability Studies of Coal-Derived Liquids. Fuel, Vol. 59, June 1980, pp. 431-435.

Coal liquids obtained from the one half ton per day process development unit at Pittsburgh were aged under various combinations of temperature, gaseous environment (nitrogen, air, or oxygen), stirring, and light or darkness. Viscosity was the primary measurement of deterioration. The viscosity increased with aging for all samples; the rate of viscosity increase was much faster for samples stored under oxygen than for samples stored under nitrogen. The higher the storage temperature, the faster the rate of degradation.

Solvent analysis of fresh and aged samples showed that samples aged under oxygen showed large increases in the amount of benzene-insoluble materials, decreases in oil components, and a relatively constant amount of asphaltenes. Solvent analysis of samples aged under nitrogen showed very little change.

Oxygen determinations on the solvent-separated fractions of the unaged and oxygen-aged samples showed that there was an increase in oxygen content with aging. Infrared analysis showed formation of C=O and C-O groups. Although the amount of asphaltenes stayed relatively constant with aging, the oxygen content of the asphaltenes greatly increased, indicating that the asphaltenes were chemically changed.

This oxidative degradation probably proceeds by auto-oxidation through a free-radical mechanism. Coal-derived liquids are so complex it may be futile to attempt to define actual mechanisms. However, some understanding of the chemical processes involved is needed so that the materials can be stabilized. Seventy-four additives for petroleum-derived oils have been tested on coal liquids; none were effective in inhibiting oxidative degradation.

See Table 155.

23. Buttrill, S. E., Jr., F. R. Mayo, B. Lan, G. A. St. John, and D. Dulin. Oxidation and Formation of Deposit Precursors in Hydrocarbon Fuels. NASA Contractor Report 165534, SRI International, Menlo Park, CA, January 1982, 25 pp. NTIS No. N82 18402.

The objective of this study was to determine the mechanism of deposit formation in hydrocarbon fuels. A fuel oil and pure n-dodecane were oxidized at 130° C, and the oxidized fuels and the deposits were analyzed by field ionization mass spectrometry. The authors concluded that oxygen is required to produce deposits from hydrocarbon fuels (except at pyrolysis temperatures). The process proceeds mainly through monomer oxidation and coupling of these oxidation products to form polymers. The products become insoluble in the fuel at molecular weights around 600.

When fuel containing soluble deposit precursors is heated, especially with oxygen, oxidation and condensation become rapid and precipitates form. The oxidations are probably conventional free radical chain reactions; the coupling of monomer units probably involves both a free radical coupling mechanism and a nonradical condensation. Nitrogen and sulfur compounds concentrate in the precursors and deposits because they are more reactive in oxidation and condensation, and probably less soluble in the fuel.

24. Christian, J. G., A. J. Chiantella, J. E. Johnson, and H. W. Carhart. The Glass Effect in Distillate Fuel Stability. Ind. and Eng. Chem., Vol. 50, No. 8, August 1958, pp. 1153-1156.

Diesel fuels were stored in glass bottles at 54.4° C (130° F) or at 98.9° C (210° F). Some of the bottles were soft glass; some were borosilicate glass. Fuel degradation was measured by the change in light transmission and light scattering and by the amount of insoluble residue and soluble gum formed.

Diesel fuel stored in borosilicate glass bottles deteriorated much more rapidly than the same fuel stored in soft glass bottles. Additional experiments showed that soft glass inhibited fuel degradation, while borosilicate glass was essentially inert toward the fuel.

The effect of soft glass varied with the fuel. Soft glass greatly improved the stability of some fuels, but had almost no effect on other fuels. Therefore, storage of fuels in soft glass bottles could give misleading results in assessing the relative stabilities of distillate fuels.

See Tables 129, 130, 131, and 132.

25. Clinkenbeard, W. L. How Distillate Fuel Stability is Measured and Controlled. Symposium on Stability of Distillate Fuel Oils, ASTM STP 244, American Society for Testing and Materials, Philadelphia, PA, 1958, pp. 32-40.

> This is a general discussion of fuel oil storage stability. It includes discussion of the contribution of catalytically cracked stocks to fuel instability, the effects of instability and sediment formation, how stability can be controlled by proper processing and by use of additives, and methods of measuring storage stability. No experimental details or data are presented.

26. Coordinating Reseach Council. CRC Literature Survey on the Thermal Oxidation Stability of Jet Fuel. CRC Report No. 509, Coordinating Research Council, Inc., Atlanta, GA, April 1979, 141 pp.

> Two hundred eleven references from the period 1951 to 1978 are reviewed in this survey of literature on the thermal stability of jet aircraft fuels.

27. Coordinating Research Council. Navy-CRC Barge Storage Program. CRC Project No. CG-1-58, Coordinating Research Council, Inc., Atlanta, GA, September 1959, 70 pp.

> The Navy-CRC barge storage program was initiated to investigate the scale-up factor in going from bottle or drum storage to bulk storage in tanks. Seven base distillate fuels were used to make 12 test fuel blends of varying stability. About 5,000 gallons of each blend was prepared and stored for 24 months in a clean tank in one of two U.S. Navy vessels. Portions of the 12 test fuel blends were also stored in steel drums at ambient temperature, in glass bottles at ambient temperature, and in glass bottles at 43.3° C (110° F).
>
> Samples of each of the test blends, both fresh and at intervals during storage, were sent to 14 cooperating laboratories for determination of soluble gum, insoluble gum, and percent light transmission. Bottle and drum storage at ambient temperature produced soluble gum and percent light transmission values very similar to barge storage. Bottle storage for one week at 43.3° C (110° F) was equivalent to bottle, drum, or barge storage at ambient temperature for one month. The insoluble gum values from barge storage were much lower than obtained in bottle and drum storage; this probably reflects difficulties in sampling insoluble gum from the barge tanks rather than any inherent differences in the amount of insoluble gum.
>
> See Tables 133, 134, and 135.

28. Cummings, A. L., P. Pei, and S. M. Hsu. Measurement Techniques for Fuel Stability Characterization. Report from National Bureau of Standards, 28 pp. To be published as ASTM STP, possibly in mid-1983.

Differential scanning calorimetry (DSC) at high pressure was used to measure oxidation onset temperature and gum-forming tendency of shale derived diesel and jet fuels. Less than 1 mg of fuel was required for each test. For measuring oxidation onset temperature the scanning mode of the DSC instrument was used, with a heating rate of 40° C per minute and oxygen pressure of 520 psia. For measurement of gum-forming tendency, the fuel was first oxidized in the DSC at 170° C and oxygen pressure of 650 psia. The oxidized residue was then heated slowly in a thermogravimetric analyzer and the gum content computed from the weight loss curve.

The DSC results for the shale-derived fuels were compared to the results for a petroleum jet fuel. It was found that the shale-derived marine diesel fuel was less resistant to oxidation and formed more gum than the petroleum jet fuels. The shale-derived jet fuels were more stable than the petroleum jet fuel. The results of the DSC tests were also compared with accelerated stability tests and JFTOT tests. There was qualitative correspondence between the DSC test results and the accelerated stability and JFTOT results.

29. Dahlin, K. E., S. R. Daniel, and J. H. Worstell. Deposit Formation in Liquid Fuels. 1. Effect of Coal-Derived Lewis Bases on Storage Stability of Jet A Turbine Fuel. Fuel, Vol. 60, June 1981, pp. 477-480.

An accelerated storage test was developed in which sediment formation was estimated from the amount of sediment deposited on a microscope cover slip. This method was used to study the effect of nitrogen compounds and coal liquid extracts on deposits.

A weighed glass microscope cover slip was placed in a soft glass storage jar, the test fuel was added, and it was stored at 121° C (250° F). At the end of the storage period, the cover slip was removed, dried, and weighed. The weight gain of the cover slip divided by the area of the slip was taken as representative of the amount of deposited gum. Dissolved gum was determined by evaporating 1 ml of the filtered fuel and weighing the residue.

A Lewis-base extract was prepared from coal-derived liquid by a ligand-exchange procedure. The concentration of nitrogen in the extract was determined with an elemental analyzer. The extract was added to jet fuel in amounts equivalent to 10 to 300 ppm nitrogen, and the storage stability of the mixtures was determined. The extract decreased the storage stability of the jet fuel, with more gum formed as more extract was added.

Addition of individual heterocyclic nitrogen compounds to the jet fuel produced a decrease in storage stability comparable to that obtained by addition of the extract at the same nitrogen level.

See Table 113.

30. Daniel, S. R., and J. H. Worstell. Mechanisms of Nitrogen Heterocycle Influence on Turbine Fuel Stability. Aircraft Research and Technology for Future Fuels, NASA Conf. Publication 2146, National Aeronautics and Space Administration, 1980, pp. 185-194. NTIS No. N80 29300.

Lewis bases were extracted from a syncrude by ligand exchange. Addition of this extract to petroleum jet fuel at levels as low as 5 ppm produced deterioration of stability in both JFTOT and accelerated storage tests (7 days at 121° C). Comparable effects on jet fuel stability were obtained by addition of pyridine and quinoline, while pyrrole and indole were less detrimental. These four compounds represent the main compound types in the extract. The weight of deposit produced in the accelerated storage tests was proportional to the concentration of added nitrogen compound.

Deposition rate increased with basicity of the added nitrogen compound within a given compound class, but there was no correlation of deposition rate with basicity between compound classes. Compounds in which the nitrogen atom is sterically hindered were much less detrimental than expected on the basis of basicity.

31. Davis, J. W., F. G. Schwartz, and C. C. Ward. Effects of Polar Components of a Petroleum Distillate Fuel on Storage Stability. BuMines RI 5798, 1961, 11 pp.

Polar compounds, including most of the nitrogen, oxygen, and sulfur compounds, were separated from a distillate fuel by liquid chromatography on silica gel. Removal of polar compounds improved the storage stability of the fuel. The insoluble gum content of the depolarized fuel was only 10 percent as much as that of the original fuel after both had been stored for 39 weeks at 43.3° C (110° F) in vented soft glass bottles. Soluble gum formation in the depolarized fuel was much lower than in the original fuel through 26 weeks of storage, but then it increased rapidly during the 26- to 39-week period. After 39 weeks at 43.3° C, the soluble gum in the depolarized fuel was nearly as high as in the original fuel.

Blending the polar compounds with the original fuel and with the depolarized fuel in the same ratio as they existed originally and at two and three times the original ratio increased the amount of gum present before storage, but had little effect on the formation of additional gum during storage.

See Table 136.

32. Dimpfl, L. H., J. E. Goodrich, and R. A. Stayner. Evaluating Additives for Distillate Fuel Oil--Storage Tests. Ind. and Eng. Chem., Vol. 48, No. 10, October 1956, pp. 1885-1891.

Two tests are described for determining the effectiveness of additives in preventing deterioration of distillate fuels during storage. The first test was an accelerated aging test in which the fuel was stored in glass bottles at 60° C (140° F) for four weeks. At the end of the storage period, the fuel was filtered and the insoluble residue weighed. The other test was a full scale pumping test in which about 100 gallons of fuel was recirculated through a screen for a period of several weeks to several months and the deposits on the screen determined.

33. Dinneen, G. U., and W. D. Bickel. Gum Formation in Shale-Oil Naphtha. Ind. and Eng. Chem., Vol. 43, No. 7, July 1951, pp. 1604-1607.

Shale oil distillates rapidly become dark colored and form large quantities of gum. Analysis of the gum from shale oil naphtha indicated that it contained about 8 percent nitrogen. The nitrogen in the gum comes from pyrrole and pyridine type compounds in the naphtha.

An accelerated oxidation method was developed in which the naphtha was heated to 100° C (212° F) under an oxygen pressure of 100 psi. The gum formed in the accelerated oxidation was compared to the gum formed in storage. About the same amount of gum was obtained after eight hours of accelerated oxidation as was formed in three weeks of storage at room temperature. Elemental analysis of the gums indicated that the nitrogen and sulfur contents were very similar, but the gum from accelerated oxidation contained more oxygen.

34. Elmquist, E. A. A Review of the Distillate Fuel Stability Problem. Symposium on Stability of Distillate Fuel Oils, ASTM STP 244, American Society for Testing and Materials, Philadelphia, PA, 1958, pp. 26-31.

This is a general, semi-technical discussion of the history of distillate fuels, the effect of catalytic cracking on fuel quality, storage stability of catalytically cracked fuels, testing to improve stability, and stability measurement. Catalytically cracked fuels are less stable in storage than straight-run fuels. Instability appears to be due to the presence of three substances--oxygen, an aromatic mercaptan, and a reactive hydrocarbon. Certain nitrogen compounds have deleterious effects on stability when present in fuels containing aromatic mercaptans, but appear to be harmless in thiol-free oils.

35. Finseth, D., M. Hough, J. A. Queiser, and H. L. Retcofsky. An ESR Characterization of Asphaltenes Formed During the Aging of Coal Liquids. Am. Chem. Soc., Div. Fuel Chem. Preprints, Vol. 24, No. 4, September 1979, pp. 979-981.

Electron spin resonance was used to investigate the role of radical reactions in the aging of coal liquids. Centrifuged coal liquids were aged in oxygen and in nitrogen atmospheres. Asphaltenes were separated from both the fresh and aged liquids and analyzed by ESR. The spin concentrations of the aged asphaltenes were larger than on the unaged asphaltenes; this was interpreted as indicating an aging mechanism which concentrated radicals in the asphaltenes excluding radical recombination as a primary mechanism. The g-value for the oxygen-aged asphaltene was higher than for the unaged or nitrogen-aged asphaltenes, indicating greater heteroatom involvement with the unpaired electrons. It was concluded that the ESR data were consistent with an aging mechanism involving condensation of small heteroatom-rich molecules in the presence of oxygen to form higher molecular weight insolubles and asphaltenes.

See Tables 150 and 151.

36. Frankenfeld, J. W., and W. F. Taylor. Alternate Fuels Nitrogen Chemistry. Final Tech. Report, Report No. EXXON/GRUS.1KWC.77, Department of the Navy, Naval Air Systems Command, Contract N00019-76-C-0675, Exxon Research and Engineering Co., Linden, NJ, November 1977, 54 pp. NTIS No. AD A053299.

The effect of nitrogen compounds on sediment formation was investigated. Nitrogen compounds studied included 2,5-dimethylpyrrole, indole, carbazole, and a number of aromatic and aliphatic amines. The nitrogen compounds were added to n-decane at a concentration equivalent to 2000 ppm nitrogen. Duplicate sample blends were prepared in glass bottles; one was stored in darkness at ambient temperature (24° C) and the other was irradiated with UV light. Samples were removed from storage periodically and the sediment filtered and weighed. 2,5-Dimethylpyrrole produced the largest amount of sediment, indole and carbazole produced a small quantity of sediment, and the other nitrogen compounds tested produced none or just a trace.
Exposure to UV light increased the amount of sediment formed. Addition of carboxylic acids significantly increased the rate of sediment formation with both DMP and indole, while addition of phenols reduced sediment formation.

Analysis of the sediments from DMP and n-decane blends indicated that sediments obtained from a variety of storage conditions had very similar characteristics. The data suggested that the sediments were made up largely of repeating units of oxidized dimethylpyrrole. Storage conditions affected the rate of formation and the quantity of sediment, but did not alter the characteristics of the sediment.

See Tables 219, 220, and 221.

37. Frankenfeld, J. W., and W. F. Taylor. Continuation Study of Alternate Fuels Nitrogen Chemistry. Final Tech. Report, Report No. EXXON/GRU.2KWC.79, Department of the Navy, Naval Air Systems Command, Contract No. N00019-78-C-0177, Exxon Research and Engineering Co., Linden, NJ, February 1979, 50 pp. NTIS No. AD A069011.

Investigation was continued on sediment formation with nitrogen compounds in n-decane. The test compound-decane blends were stored in glass bottles at 24° C, in the dark or under UV light.

Pyrrole and indole derivatives increased sediment formation, but other nitrogen compounds such as anilines, pyridines, alkyl amines, quinolines, and isoquinolines did not produce any appreciable sediment. Position of substituents on the pyrrole and indole greatly influenced sediment formation; compounds with alkyl groups in the 2 and 5 position were the most active and produced the most sediment. Storing the blend under UV light greatly increased sediment formation compared to dark storage. Removal of dissolved oxygen from the test blend significantly reduced sediment formation, in both dark and light storage.

Other compounds were added to the DMP (or indole) and decane test blend, and the effect on sediment formation was determined. Other hydrocarbons (olefins, aromatics, and cycloparaffins) had very little effect on sediment formation. Carboxylic acids (benzoic, decanoic, cyclohexane carboxylic) increased sediment formation; the increase was greater in dark storage than in light storage. Phenols reduced sediment formation, the most effective were those with large, bulky groups in the 2 and 6 positions. Sulfides had little effect on sediment formation, while thiols appeared to reduce sediment formation.

See Tables 222 through 230.

38. Frankenfeld, J. W., and W. F. Taylor. Effects of Nitrogen Compounds on Deposit Formation During Synfuel Storage. Am. Chem. Soc., Div. Fuel Chem., Preprints, Vol. 23, No. 4, 1978, pp. 205-214.

This paper is essentially a summary of the material in References 36 and 37.

39. Frankenfeld, J. W., and W. F. Taylor. Fundamental Synthetic Fuel Stability Study. Final Report, DOE/BC/10045-23, Exxon Research and Engineering Co., Linden, NJ, March 1982, 111 pp. NTIS No. DOE/BC/10045-23.

This report summarizes a multi-year study on the storage stability of synthetic fuels derived from oil shale and coal. A variety of organic nitrogen, sulfur and oxygen compounds were evaluated for their tendencies to promote sediment in hydrocarbon fuels under accelerated storage conditions. Three diluents were employed in model compound studies--n-decane, petroleum-derived jet fuel, and petroleum-derived diesel fuel. In addition, several fuels derived from shale liquids were tested and the results compared to the model compound studies. The fuel and mixtures were stored in Pyrex flasks at 43.3° C (110° F) or 65.6° C (150° F) in the dark, and sediments were determined gravimetrically.

The most deleterious species to fuel stability were alkylated heterocyclic nitrogen compounds, and the most reactive of those were compounds with two or more alkyl groups, at least one of which was on a carbon adjacent to the nitrogen. Other nitrogen compounds were not deleterious when tested by themselves; however, several of these interacted with reactive nitrogen compounds to promote sediment formation.

With the exception of sulfonic acids and aromatic thiols, none of the sulfur or oxygen compounds studied produced sediment when tested by themselves. However, carboxylic acids interacted with nitrogen compounds to increase sediment formation, while aromatic thiols interacted with nitrogen compounds to reduce sediment formation.

Shale-derived middle distillates with nitrogen content over 3000 ppm were very unstable, while those with nitrogen content less than 500 ppm were stable for extended periods. However, there was no direct correlation between total nitrogen content and rate of sediment formation.

See Tables 67 through 87, 118, and 158 through 162.

40. Frankenfeld, J. W., and W. F. Taylor. Storage Stability and Nitrogen Chemistry. Proc. Naval Air Systems Command-Naval Research Laboratory Workshop on Basic Research Needs for Synthetic Hydrocarbon Jet Aircraft Fuels, Washington, D.C., June 15-16, 1978, pp. 149-154. In NTIS No. AD A060081.

Nitrogen compounds of the type found in shale oil caused formation of significant quantities of sediment in n-decane in a relatively short time. The type of nitrogen compounds in the fuel was important, as not all classes of nitrogen compounds were deleterious. Pyrroles and some amines were the principal deleterious classes. Structure of the pyrrole derivative affected the sediment formation rate. Light had a strong catalytic effect on sediment formation. The interaction of nitrogen compounds with other trace impurities exerted a strong but complex effect on the rate of sediment formation. Carboxylic acids accelerated the rate of sediment formation, while phenols reduced the rate of sediment formation.

41. Frankenfeld, J. W., W. F. Taylor, and D. W. Brinkman. Storage Stability of Synfuels from Oil Shale. Submitted to Ind. and Eng. Chem., Prod. Res. and Dev.
Part I. General Features of Sediment Formation in Model Fuel Systems.
Part II. Effects of Nitrogen Compound Type and the Influence of Other Non-Hydrocarbons on Sediment Formation in Model Fuel Systems.
Part III. Studies With Actual Shale-Derived Middle Distillates.

This three-part paper is a summary of material previously published in a Government report (Reference 39).

42. Garner, M. Q., and E. W. White. Correlation of Long-Term Storage and Accelerated Stability Tests. Distillate Fuel Stability and Cleanliness, L. L. Stavinoha and C. P. Henry, Eds., ASTM STP 751, American Society for Testing and Materials, Philadelphia, PA, 1981, pp. 34-46.

Three-year outdoor bottle and column storage tests have been completed on four Navy distillate fuels. It was concluded that the results of bottle storage and column storage are in sufficient agreement to permit the use of bottle storage for long-term storage tests. The total insolubles found in bottle storage depended on both duration of storage and geographic location. The location effect was probably a function of the average ambient temperature at the location. The total insolubles were a linear function of the time in storage in both the bottle tests and in accelerated tests. One week of beaker storage at 43.3° C (110° F) was equivalent to one month of bottle storage at an average temperature of 19.4° C (67° F). Beaker test results were thus indicative of long-term storage results.

43. Gattuso, M. J. Substituted Tetrahydropyrimidines. U.S. Pat. 4,003,718, January 18, 1978.

Mono- and disubstituted tetrahydropyrimidines are proposed as additives for petroleum distillates such as gasoline and fuel oil to protect the distillate from deterioration during storage. In addition, it is claimed they help maintain cleanliness in the engine, protect against icing, and act as corrosion inhibitors and dispersants.

44. Gutnikova, L. P., T. P. Vishnyakova, I. A. Golubeva, A. G. Pechenkin, and L. I. Bugaeva. N-Acyl Derivatives of N-Substituted Ureas as Stabilizers for Jet Fuels. Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 9, September 1982, pp. 23-25. UDC 665.753.2.038. Plenum Publishing Corp., 1982.

The authors compared the effectiveness of N'-acylaminoacyl and N'-acylalkyl derivatives of N-substituted ureas to 2,6-di-tert-butyl-4-methylphenol in the stabilization of T-6 jet fuel toward oxidation in storage.

The test compounds were added to the T-6 fuel in a concentration of 0.003 percent by weight. Their effectiveness in stabilizing the fuel was evaluated in a 12-cycle heating test at 120° C; samples were taken every 12 hours for the determination of acidity and optical density.

The fuel without additive showed considerable deterioration, as shown by changes in acidity and optical density, after only 12 hours of heating. The N'-acylalkyl derivatives had adverse effects on the oxidation stability. The N'-acylaminoacyl derivatives were high in antioxidant efficiency, comparable to 2,6-di-t-butyl-4-methylphenol.

The most effective compounds were also investigated at higher temperatures. At 140° C, these additives improved the oxidation stability of the fuel considerably, but at 180° C the results with the additives were the same as without additives.

45. Gyrath, F. W., F. R. Dunn, Jr., and A. C. Smith, Jr. One-Day Stability Test for Distillate Fuel Oils. Am. Chem. Soc., Div. Petrol. Chem., Preprints, Vol. 3, No. 3, August 1958, pp. 135-144.

A one-day stability test is described. One liter of oil was placed in a glass bottle along with several steel strips, the bottle was purged with oxygen, sealed, and placed in an oven at 100° C (212° F) for 24 hours. At the end of the test, the oil was cooled and filtered, and the sediment on the filter was dried and weighed. The results of the one-day test were correlated with the results of storage tests in which oil samples were stored for six months at 29.4° C (85° F) in 30-gallon steel drums or in glass bottles containing steel strips. At the end of storage, sediment was measured by filtering and weighing. The one-day stability test was also compared with storage in 100-barrel tanks at ambient temperature. The one-day stability test was in good agreement with the storage tests, and could be used to predict the amount of sediment that would be formed in storage.

See Table 126.

46. Hara, T., L. Jones, N. C. Li, and K. C. Tewari. Aging of SRC Liquids. Fuel, Vol. 60, December 1981, pp. 1143-1148.

An SRC-II middle distillate and a 30/70 blend of SRC-I (solid) with SRC-II (liquid) were aged at elevated temperature with either oxygen or nitrogen bubbled through the liquid, in either light or darkness. Changes due to aging were monitored by viscosity measurement, solvent fractionation, elemental analysis, IR, and NMR.

The viscosity of the blend increased significantly when it was aged under oxygen, while exposure to nitrogen and light had only a small effect. GPC profiles of the blend and its fractions showed that on aging with oxygen larger molecular-size components formed in the toluene-insoluble fraction but not in the pentane-soluble oil fraction.

Infrared spectra of isolated toluene-insoluble and asphaltene fractions from both unaged and oxygen-aged blend showed that the aged blend had an additional absorption band which is characteristic of carbonyl. This band did not appear in the aged oil fraction, indicating that oxygen was incorporated preferentially into the toluene-insoluble and asphaltene fractions.

Aging of the SRC-II middle distillate required the presence of copper shavings. Bubbling with oxygen without copper had little effect, but when copper shavings were included, the results for the middle distillate were similar to the results for the blend.

Oxidative coupling of phenols was proposed as an aging mechanism for coal liquids.

47. Hazlett, R. N., J. V. Cooney, and E. J. Beal. Mechanisms of Syncrude/Synfuel Degradation. First Annual Report, September 15, 1981 to September 30, 1982. Naval Research Lab., 115 pp.

The effect of nitrogen compounds on the storage stability of middle distillate fuels was studied. The base fuel was a diesel fuel marine refined from Paraho crude shale oil. 2,5-Dimethylpyrrole (DMP) was added to the base fuel in concentrations ranging from 45 to 450 ppm nitrogen and the blends were stored in borosilicate glass flasks in the dark at 43.3° C, 65° C, or 80° C for time periods ranging from 4 days to 179 days. At the end of each storage period insoluble sediment was determined by filtering and weighing. The amount of insolubles that formed was directly proportional to the initial concentration of DMP, to the storage time, and to the storage temperature. The presence or absence of antioxidant in the base fuel made almost no difference in the amount of insolubles formed in the fuel-DMP blends. There was no detectable difference between vented and non-vented storage.

Elemental analysis of the sediment revealed that the sediment and DMP had nearly identical carbon to nitrogen ratios, indicating that the sediment was for the most part derived directly from DMP. Nitrogen balance calculations showed that approximately 92 percent of the total initial nitrogen was accounted for in the sediment and filtrate after stressing.

The hydroperoxide concentration of the blends increased with increasing storage time and with higher storage temperature. At all conditions, the hydroperoxide concentration was much higher in the undoped fuel than in the fuel-DMP blends. It appeared that DMP either inhibited formation of peroxide or depleted peroxide by reaction.

Twenty-seven other nitrogen compounds were surveyed as fuel dopants. Each of these compounds was added to the diesel fuel at a concentration equivalent to 450 ppm nitrogen, and the blends were stressed at 80° C for 14 days or at 43° C for 80 days. Substituted pyrroles containing 2 or more alkyl groups produced large amounts of sediment, 3-methylindole formed some sediment, and the other compounds produced only very small amounts of insoluble material. Most of these compounds formed less sediment in the fuel with antioxidant than in the fuel without antioxidant.

Interactions between several of these other nitrogen compounds and 2,5-dimethylpyrrole in diesel fuel were studied. No significant synergistic effects were discovered; however, there appeared to be several negative interactions between DMP and other nitrogen compounds.

Seven Exxon shale liquids containing up to 480 ppm nitrogen were screened for storage stability in an accelerated test in which the liquids were stored at 80° C for 14 days. There was very poor correlation between initial total nitrogen and the amount of insolubles formed in storage. Several shale fuels produced by the Navy shale program and containing much higher levels of nitrogen were also tested. The storage stabilities of these fuels differed markedly.

See Tables 166 through 193, and 231

48. Hazlett, R. N., J. M. Hall and J. C. Burnett. Aging Behavior of Crude Shale Oil. NRL Memorandum Report 3844, Naval Research Laboratory, Washington, D. C., August 1978, 11 pp. NTIS No. AD A062420.

Crude Paraho shale oil was stored for eight weeks at 50° C, corresponding to at least one year at ambient conditions. There were modest increases in the viscosity and in the content of high molecular weight compounds as measured by GPC. IR, GC, and LC did not reveal any significant differences between the stressed and unstressed products.

The measured changes showed that the shale oil underwent