definite chemical reactions during aging. The changes were modest, however, for periods of eight weeks at 50° C. The authors concluded that one year of ambient storage should require no alteration of refining processes.

49. Hazlett, R. N., J. M. Hall, and J. Solash. Thermal Oxidative Stability of Synthetic Jet Fuels. Proc. Conf. on Composition of Transportation Synfuels: R&D Needs, Strategies, and Actions, CONF-7810176, U.S. Department of Energy, June 1979, pp. 112-125. NTIS No. CONF-7810176.

Shale oil fuel samples were extracted with acid to remove basic nitrogen compounds, followed by silica gel percolation to remove the remaining nitrogen compounds. The nitrogen free fuel was then spiked with the acid extracted basic nitrogen compounds to a concentration range of 8 to 125 ppm N. The spiked fuels were stored at 60° C for four weeks in glass jars. A small amount of water was also added to each jar. The jars were loosely capped with aluminum foil to permit breathing during storage. Thermal stability analyses of the samples before and after storage showed that small quantities of basic nitrogen caused the fuel to become unstable.

50. Heneman, F. C. The Effects of Organosulfur Compounds Upon the Storage Stability of Jet A Fuel. Masters Thesis, Colorado Sch. Mines, Golden, CO, August 1981, 87 pp. NTIS No. AD A103486.

The effect of sulfur-containing compounds on the storage stability of Jet A fuel was investigated. Test blends were prepared from Jet A fuel and a number of organic sulfur compounds of various types. The blends were stored in flint glass bottles at 121° C, 130° C, or 135° C for time periods ranging from 24 hours to 168 hours (7 days). The microscope cover slip technique developed by Worstell was utilized to determine the amount of insoluble deposits.

Thiols and thiophene derivatives increased the deposit formation rate compared to that of pure jet fuel, and the rate of deposition was a function of the concentration of the individual sulfur compounds. Alkyl sulfides and disulfides decreased the deposit formation rate. No induction period was observed with any of the test blends or temperatures studied. Arrhenius plots of deposition versus temperature were linear over the 121 to 135° C range studied. Measurement of relative basicities of the sulfur compounds by proton NMR in conjunction with the storage experiments suggested that alkyl sulfides and alkyl thiols influenced deposition rate through base catalysis. The inhibiting mechanism of alkyl sulfides appeared to be a result of sulfur's reactivity with intermediate soluble precursors to deposits in Jet A fuel.

See Tables 115, 116, and 117.

51. Henry, C. P. The duPont F21 149° C (300° F) Accelerated Stability Test. 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. 22-33.

    The duPont F21 149° C (300° F) Accelerated Stability Test for diesel fuel is described. In this test, a 50-ml sample of fuel is heated to 149° C for 1½ to 4½ hours, cooled, and filtered. The amount of insoluble sediment is estimated by visual comparison of the filter pad with standard pads. The test is useful for monitoring the relative stability of middle distillate fuels during refining, distribution, and storage. The reliability of the test to accurately predict storage stability is subject to error; however, useful correlations have been developed for specific applications where variables have been limited.

52. Hunt, R. A., Jr., T. B. Tom, and J. A. Bolt. Evaluating Additives for Distillate Fuels--Field Tests. Ind. and Eng. Chem., Vol. 48, No. 10, October 1956, pp. 1899-1903.

    The results of accelerated aging for 20 hours in open glass containers, aging at 32.2° C (90° F) in vented glass bottles, and storage in steel tanks at ambient conditions were compared. Two different additives were rated on their ability to prevent deposits in the accelerated aging tests and in tank storage.

53. Irish, G. E., and R. L. Richardson. Stability of Diesel Fuels Made from Shale Oil. 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. 76-83.

    A study was made to determine the type and degree of processing which will be needed to produce a stable diesel fuel from shale oil. The crude shale oil was produced by Union Oil Company retort technology, and solids and arsenic were removed. Diesel fuel fractionated from the crude shale oil was too high in sulfur and olefins and too low in cetane number to meet diesel fuel specifications.

    This shale oil diesel fuel was subjected to three different hydrotreatments. The fuel that was hydrotreated lightly to remove sulfur but not nitrogen (nitrogen level in the hydrotreated fuel was still over 2000 ppm) had unsatisfactory stability. When stored at 43° C for 12 weeks, it produced 31.7 mg of sediment per 100 ml of fuel. Fuel that was severely hydrotreated to reduce sulfur to 66 ppm and nitrogen to 119 ppm had good stability; there was less than 1 mg sediment per 100 ml fuel after 12 weeks storage at 43° C. Fuel that was hydrotreated by other conditions which reduced sulfur to 12 ppm and nitrogen to only 160 ppm also had good stability. The authors concluded that diesel fuel of good quality including excellent stability characteristics could be made from shale oil by hydrotreatment.

54. Johnson, C. R., D. F. Fink, and A. C. Nixon. Stability of Aircraft Turbine Fuels. Ind. and Eng. Chem., Vol. 46, No. 10, October 1954, pp. 2166-2177.

This paper includes a general discussion of storage stability of jet aircraft fuels. Some comparisons are made between jet fuel and gasoline stability characistics. There is some discussion of tests for storage and of the factors affecting storage stability, such as hydrocarbon composition and concentration of minor components. However, there are no data from storage stability tests.

55. Johnson, J. E., A. J. Chiantella, and H. W. Carhart. Application of Light Scattering to Diesel Fuel Stability Problems. Ind. and Eng. Chem., Vol. 47, No. 6, June 1955, pp. 1226-1230.

The authors assumed that insoluble gum is formed in diesel fuel by unstable components of the fuel first reacting with oxygen or each other to form polymeric-type molecules. As the fuel ages, these large molecules continue to grow until they are no longer soluble in the fuel and form very small solid particles. These particles initially are suspended in the fuel, but as they grow they eventually become large enough to precipitate out as insoluble gum. A test method based on light scattering can detect the particles while they are still suspended in the fuel.

The diesel fuels for this study were stored in glass bottles at 43.3° C (110° F) or 54.4° C (130° F). Samples were removed from storage periodically and light scattering measurements made. The intensity of the scattered light increased with increasing storage time, indicating the formation of more particles. Large changes were observed for presumably unstable fuels, while fuels presumed to be stable showed very little change in light scattering with storage. However, there are no comparisons or correlation of light scattering data with other measures of stability.

See Table 41.

56. Johnston, R. K., and E. L. Anderson. Review of Literature on Storage and Thermal Stability of Jet Fuels. Tech. Documentary Report No. RTD-TDR-63-4270, Southwest Research Inst., San Antonio, TX, January 1964, 30 pp. NTIS No. AD 429937.

This review includes literature on both storage and thermal stability of jet fuels; however, most of the references on storage stability pertain to the effect of storage on thermal stability of the fuel. Literature on additives for improving thermal and storage stability is also covered.

57. Johnston, R. K., and C. M. Monita. Jet Fuel Stability and Effect of Fuel-System Materials. Tech. Report AFAPL-TR-68-20, Southwest Research Inst., San Antonio, TX, February 1968, 44 pp., NTIS NO. AD 828473.

The effect of storing jet fuel in contact with typical ground-fuel-system materials on the thermal stability of the fuel was investigated. A thermally stable, low volatility, naphthenic type jet fuel was stored in 55-gallon lined steel drums containing various metallic and nonmetallic specimens representing ground-fuel-system materials. Storage temperature was 54.4° C (130° F) and the length of storage ranged from 16 weeks to one year. At the end of each storage period, the fuel thermal stability was measured with a gas-drive fuel coker. The fuel itself remained thermally stable during storage and was not degraded seriously by steels, aluminum, coated steels, plug valve grease, or a filter separator element. Water or rusty steel, when present during storage, degraded the fuel thermal stability significantly. Brass, bronze, and butadiene-acrylonitrile rubbers of the type used for fuel hose gave the worst degradation of fuel thermal stability, accompanied by significant pickup of copper from the brass and bronze and of zinc and lead from the rubbers.

See Table 91.

58. Karn, F. S., F. R. Brown, and A. G. Sharkey, Jr. Aging Characteristics of Coal Liquids. Am. Chem. Soc., Div. Fuel Chem., Preprints, Vol. 22, No. 2, 1977, pp. 227-232.

Samples of coal liquid produced from West Virginia coal by the SYNTHOIL process were aged under a variety of conditions and the viscosity increase determined. The aging conditions included temperatures of 30° C, 45° C, or 61° C; atmospheres of oxygen, air, or nitrogen; stirring or no stirring; light or darkness; and time periods up to 56 days at 45° or 35 days at 61° C. The largest viscosity increases were in samples stored at 61° in an oxygen atmosphere. At all temperatures, samples stored under oxygen had a larger viscosity increase than samples stored in air or nitrogen. Samples stored under nitrogen showed a small viscosity increase, and those in air had a somewhat larger viscosity increase. Samples stored under oxygen or air and not stirred had a smaller viscosity increase than stirred samples in the same atmospheres. Stirring had no effect on samples stored under nitrogen. Light had no effect on the viscosity increase.

Solvent analysis of the original liquid and of stored samples indicated that there was no change in component distribution in samples aged under nitrogen, but samples aged under oxygen showed a decrease in pentane soluble and benzene soluble fractions with a corresponding increase in the benzene insoluble fraction.

See Table 147.

59. Kawahara, F. K. Composition of Gum in Cracked Naphtha. Ind. and Eng. Chem., Prod. Res. and Dev., Vol. 4, No. 1, 1965, pp. 7-9.

The types of oxygen and sulfur compounds in two simulated gasoline gums were determined. The first gum was produced by accelerated aging of naphtha in steel drums at 60° C for 12 weeks. The second gum was produced by aging naphtha in steel drums for two years at ambient conditions. The gum was separated from the gasoline and analyzed by several methods. Both gums contained thioether, dialkyl peroxide, and other groups, as well as ester, carbonyl, acid, hydroperoxide, and hydroxyl groups. Most of the sulfur in the gum was present as thioether. The rapidly aged gum had a high ether content, and the naturally aged gum had a high alcohol content. Oxygen appeared to be a major factor in gum formation, and disulfides and trisulfides appeared to be active promoters.

60. Kershaw, J. R., and D. Gray. Aging Studies of Coal Hydropyrolysis Liquids. Fuel, Vol. 59, June 1980, pp. 436-438.

A coal liquid was prepared by laboratory hydropyrolysis of coal, followed by separation of toluene soluble product. The toluene soluble product was further divided into oil and asphaltenes. The coal liquids were aged in test tubes in the dark, at various temperatures, with either oxygen or nitrogen bubbled through them. Deterioration was measured by change in viscosity. The increase in viscosity was much greater with oxygen than with nitrogen; the increase was also greater at elevated temperature than at room temperature. The combined oil and asphaltene fraction deteriorated much more rapidly than the oil alone, especially in the presence of oxygen. NMR, IR, and ESR were also used to study the aging process. While oxygen had a significant effect on the viscosity change during aging, no change in the products could be detected by the spectroscopic methods between the oxygen-aged samples and the nitrogen-aged samples.

The fact that coal liquids also age under a nitrogen atmosphere, although much more slowly than under oxygen, may indicate that hydrogen bonding increases with aging. This may explain why asphaltenes cause an acceleration in the aging rate, since asphaltenes readily take part in hydrogen bonding.

61. Kitchen, G. H. Fuel Storage Life. Tech. 66-14, Presented at National Petroleum Refiners Association Annual Meeting, San Antonio, TX, March 28-30, 1966, 14 pp.

> Studies on gum inhibitors for kerosine and diesel fuel for standby engines are described. Different inhibitors identified only in general terms, such as "oxygenated amine dispersant and stabilizer" were studied; effectiveness was determined in a heat stability test run at 98.9° C (210° F), and in a 12-week corrosion stability test at 48.9° C (120° F) in the presence of water. The most effective inhibitor was a combination of an anionic dispersant-stabilizer combined with a metal deactivator such as N,N-disalicylidene-1,2-propane-diamine or a heterocyclic sulfur-nitrogen compound.

62. Kolobielski, M. Estimation of Dipole Moment of Oxidized Gasolines: A Potential Method for Evaluating Effectiveness of Additives. Am. Chem. Soc., Div. Petrol. Chem., Preprints, Vol. 21, No. 4, September 1976, pp. 898-903.

> A sample of gasoline was oxidized by heating to 100° C, with a beginning oxygen pressure of 100 psi, for a period of 24 hours. The oxidized gasoline was filtered to remove precipitate, and the amount of oxygen consumed was calculated from the pressure drop. The dielectric constant and refractive index of the oxidized liquid and of the starting gasoline were measured. A "Polarization Index" (PI) was computed from the dielectric constant and refractive index, and the difference in PI between the starting gasoline and oxidized gasoline was calculated.
>
> This PI difference was correlated with the amount of oxygen consumed in the oxidation. It had been previously shown that a relationship existed between the amount of gum formed in storage and the oxygen consumption; therefore, this method could be used to assess storage stability of gasoline and to evaluate antioxidant properties of additives.

63. Kolobielski, M., and F. McCaleb. Gasoline and Engine Oils: Literature Review, New Laboratory Oxidation Method, and Significance of Olefins in Fuel. Report 2296, U.S. Army Mobility Equipment Research and Development Command, Fort Belvoir, VA, March 1980, 73 pp.

> A new laboratory oxidation test for gasoline was developed. The gasoline sample was heated in a stirred autoclave under 100 psi oxygen pressure at a temperature of 100° C for 24 hours. The oxygen consumed in the test was measured, and at the end of the test the dielectric constant and refractive index of the gasoline were measured and a "Polarization Index (PI)" calculated. The oxygen consumption and PI parameters were assumed to indicate the susceptibility of gasoline to form gum in storage, and therefore could be used to predict storage stability of gasoline.

A brief literature review is included covering gasoline storage stability, accelerated aging tests, oxidation tests, the effects of gasoline components and impurities on gum formation, and mechanism of gum formation.

64. Konrad, W. A., T. S. Tutwiler, and N. L. Shipley. New Fast Test Method for Distillate Storage Stability. Petrol. Proc., Vol. 11, No. 9, September 1956, pp. 145-149.

An accelerated filter plugging test for measuring storage stability of distillate fuels is described. Four and one half gallons of the test oil was placed in a tin-plated steel can and heated for 16 hours in a heating cycle in which the oil temperature started at 23.9° C (75° F) and reached 112.8° C (235° F) at the end of the 16 hours. The oil was then cooled to 23.9° C over a period of 3.5 to 4 hours. Twelve liters of the cooled oil was filtered through a woven felt filter. Pressure drop across the filter was measured and the sediment deposited on the filter was weighed. These two parameters were related to the stability of the fuel.

65. Kwong, G. W. Y. Additives for Hydrocarbon Oils. U.S. Pat. 4,239,497, December 16, 1980.

An additive consisting of the reaction product of poly (oxyalkylene)amine with an epihalohydrin was claimed to inhibit sedimentation and retard discoloration in hydrocarbon fuels such as gasoline, diesel fuel, jet fuel, other aviation fuel, burner oil, furnace oil, kerosene, and naphtha.

66. Kwong, G. W. Y., and J. Levy. Additives for Hydrocarbon Oils. U.S. Pat. 4,284,415, August 18, 1981.

An additive comprised of the reaction product of an alkoxyalkylamine and an epihalohydrin was claimed to reduce formation of sediment and discoloration during storage of hydrocarbon fuels such as gasoline, diesel fuel, jet fuel, other aviation fuel, burner oil, furnace oil, kerosene, and naphtha.

67. Lander, H. R., Jr. Stability of High-Temperature, Hydrocarbon Jet Fuels During Storage. Tech. Documentary Report No. APL-TDR-64-107, Air Force Aero Propulsion Lab., Research and Technology Division, Air Force Systems Command, Wright-Patterson Air-Force Base, OH, November 1964, 52 pp., NTIS No. AD 610591.

The effect of storage on the thermal stability of fuels for high-speed aircraft was investigated. Eighteen JP-6 jet fuels and nine fuels meeting the specifications for Thermally

Stable jet fuel were stored in 55-gallon steel drums at ambient conditions for periods up to 18 months. The thermal stability of the fresh fuels and of the fuels after storage was determined with a standard ASTM-CRC coker. All of the JP-6 fuels passed the thermal stability requirements when they were procured; however, after only 30 weeks of storage 8 of these fuels failed the thermal stability test. The other 10 JP-6 fuels showed little change in thermal stability quality during storage for periods as long as 66 weeks. Of the 9 Thermally Stable jet fuels evaluated, 3 failed the thermal stability test when fresh and again after 20 weeks of storage. The remaining 6 Thermally Stable fuels maintained their thermal stability during storage for periods up to 78 weeks.

68. LePera, M. E. Investigation of the Autoxidation of Petroleum Fuels. CCL Report No. 204, U.S. Army Coating and Chemical Lab., Aberdeen Proving Ground, MD, June 1966, 24 pp., NTIS No. AD 641270.

The deterioration of petroleum fuels was studied by investigation of their autoxidation susceptibilities. Four federal and military specification gasolines, two military jet fuels, and six commercial gasolines were used in this investigation. The fuels were stored in amber glass bottles at 150° F (65.6° C) with an oxygen atmosphere above the fuel. Each week for six weeks one bottle of each fuel was removed from storage and the hydroperoxide content determined. The resulting peroxide-time curves revealed that autoxidation tendencies varied considerably. A lead-free federal specification gasoline had the highest rate of autoxidation, the other automotive gasolines showed intermediate rates, and a military specification aviation gasoline had a very low rate of autoxidation. The two jet fuels formed almost no hydroperoxide during the six weeks of storage.

See Table 24.

69. LePera, M. E. Investigating the Elastomer Environmental Effects on the Storage Stability of Military Fuels. CCL Report No. 279, U.S. Army Aberdeen Research and Development Center, Coating and Chemical Lab., Aberdeen Proving Ground, MD, April 1970, 32 pp., NTIS No. AD 704707.

The effects of the elastomers in collapsible fuel containers on the quality of the stored fuels was investigated. Six fuels common to military fuel supply systems, including a gasoline, a turbine-engine fuel, and four diesel fuels, were stored in collapsible 500-gallon drums at ambient conditions for one year. Control samples of each fuel were stored in 55-gallon steel drums at ambient temperature and in 1-gallon containers at controlled laboratory temperature. Aliquots of each fuel were taken from each type of storage container at initial fill and after 4, 6, 8, and 12 months of storage for determination of gum and other properties. Four of the six fuels stored in the collapsible containers contained more gum and showed more deterioration in other properties than the control samples, indicating evidence of contamination and degradation resulting from elastomer-fuel interactions.

See Tables 37, 46, 47, 48, 49, and 100.

70. LePera, M. E., and J. G. Sonnenburg. How Stable is Diesel in Storage? Hydrocarbon Processing, Vol. 52, No. 9, September 1973, pp. 111-115.

The storage stability characteristics of four diesel fuels meeting the requirements of Federal Specification VV-F-800a (Fuel Oil, Diesel) were investigated. Two straight-run fuels and two fuels containing catalytically cracked fractions were stored in 100 bbl above-ground steel tanks for two years. The fuels were sampled initially and periodically during storage; each sample was analyzed for existent gum, particulates, and ASTM D2274 stability.

Two of the fuels maintained satisfactory storage stability throughout the entire two-year storage period. One fuel was considered marginal with respect to storage stability since its initially low values for gum and particulate contamination were followed by gradually increasing values. The fourth fuel exhibited a cyclic pattern of gum and particulate values typical of unsatisfactory storage stability.

These results indicated that production diesel fuels meeting the requirements of Federal Specification VV-F-800a might not have satisfactory storage stability.

See Tables 50, 51, and 52.

71. LePera, M. E., and J. G. Sonnenburg. Storage Stability of Automotive Diesel Fuels. CCL Report No. 315, U.S. Army Mobility Equipment Research and Development Center, Coating and Chemical Lab., Aberdeen Proving Ground, MD, October 1972, 27 pp. NTIS No. AD 752906.

This Government report presents the same material as Reference 70, with additional details.

72. Loveland, J. W., G. R. Dimeler, L. G. Bostwick, and L. J. Cali. Use of Light Scattering, Electron Microscopy, and Polarography in Oil Stability Studies. Proc., Am. Petrol. Inst., Vol. 40, 1960, Section III, pp. 410-415.

Fuel oils and electrical oils were aged in both borosilicate and soft glass bottles at 43.3° C (110° F). The aged and fresh fuels were examined by light-scattering methods and the results compared. The ability of light-scattering measurements to detect a small difference in the number and size of particles made it a rapid and convenient tool for following the rate of sludge formation in its early stages. In an unstable oil, differences in light scattering could be detected after as little as two days of aging. However, when large quantities of sludge were formed, leading to aggregation of small particles into large particles and precipitation of sludge, the light-scattering method was no longer valid. The primary application of light scattering would be for sludge determination after short aging times where filtration methods lack the required sensitivity.

In addition to the light-scattering measurements, the aged oils were centrifuged and the separated sludge particles examined by electron microscopy.

There was no mention of any difference in results between borosilicate and soft glass bottles for aging the oils.

73. MacDonald, J. W., and R. T. Jones. Predictive Type Tests for Storage Stability and Compatibility of Diesel Fuels. Symposium on Stability of Distillate Fuel Oils, ASTM STP 244, American Society for Testing and Materials, Philadelphia, PA, 1958, pp. 5-14.

    Brief, semi-technical discussion of laboratory aging tests was presented, including simulated field storage tests, predictive tests for insolubles and gum, and filterability tests. Aging tests involve the storage of fuel in some type of container. Although metal cans are sometimes used, they may cause inaccuracies because of the formation of iron rust as well as gum. Borosilicate glass is the preferred container; soft glass has been shown to have an inhibiting effect on some unstable fuels.

    The development of a suitable specification test has been handicapped by the multiplicity of tests that are being used, which make comparison of data extremely difficult. An appendix gives experimental details for 26 different test methods.

74. Melent'eva, N. I., I. V. Malysheva, N. N. Kalitina, and L. N. Savin. Accelerated Method for Evaluating Chemical Stability of Fuels During Long-Term Storage. Khimiya i Tekhnologiya Topliv i Masel, No. 11, November 1979, pp. 50-52. English Translation in Chemistry and Technology of Fuels and Oils, Plenum Publishing Corp., 1980. pp. 843-846.

    An accelerated oxidation test was developed in which the fuel was placed in a 200-ml beaker fitted with a reflux condenser and heated to 95° C for 8 hours a day for 5 days (total time at 95° C was 40 hours). Deterioration of the fuel was measured by changes in acidity, light absorbance, UV absorption, and thermal stability. This accelerated test was used to predict changes that would occur in fuels during five years of storage in large tanks.

The test was applied to both jet fuels and to diesel fuels. Jet fuel TS-1 was very stable; five years of storage produced only slight changes in acidity, gum content, and light absorbance. However, the accelerated test was sensitive enough to predict these small changes.

75. Milsom, D., and A. R. Rescorla. Determination of Fuel Oil Storage Stability. Am. Chem. Soc., Div. Petrol. Chem., Preprints, Vol. 1, No. 3, August 1956, pp. 239-247.

Several fuel oils were stored in glass bottles at four different temperatures--43.3° C (110° F), 65.6° C (150° F), 82.2° C (180° F), and 100° C (212° F). Each day the bottles were opened and aerated. At the end of each storage period, the amount of insolubles that had formed in the fuel was measured. An insolubles content of 2 mg per 100 ml of fuel was considered to be the maximum amount acceptable.

From the amount of insolubles formed during different storage times, a graphical method was developed for accurately determining the storage time to reach 2 mg of insolubles per 100 ml of fuel for each storage temperature. Correlations and equations were developed by which time of storage at temperatures up to 100° C could be converted to equivalent time of storage at any other temperature.

See Tables 120 and 121.

76. Nelson, F. L., D. P. Osterhout, and W. R. Schwindeman. Evaluating Additives for Distillate Fuels--Stability Tests. Ind. and Eng. Chem., Vol. 48, No. 10, October 1956, pp. 1892-1898.

A general discussion of storage stability testing is presented. The authors recommended storing fuel in vented glass bottles or in beakers covered with watch glasses, at a temperature of either 26.7° C (80° F) or 43.3° C (110° F). Storage at 26.7° C was considered to be about 1.5 times as severe as ambient storage, while storage at 43.3° C was considered to be about four times as severe as ambient storage. Storage at 26.7° C required a storage time of 3 to 6 months for reliable results. Fuel deterioration was determined from the amount of insoluble sediment formed. Soluble gum was not considered to be significant, other than the possibility that it was a precursor to the formation of insoluble sediment.

77. Nixon, A. C. Autoxidation and Antioxidants of Petroleum. Ch. 17 in Autoxidation and Antioxidants, Vol. II, W. O. Lundberg, Ed., Interscience, New York, NY, 1962, pp. 695-856.

Oxidation of petroleum products is discussed, including reaction mechanisms, methods and antioxidants for preventing oxidation, mechanism of antioxidant action, and effects of oxidation on the properties of petroleum products. Storage stability is discussed briefly in the context of oxidation during storage.

78. Nixon, A. C., C. A. Cole, and H. B. Minor. Effect of Composition and Storage on the Properties of Jet Fuels. J. Chem. and Eng. Data, Vol. 4, No. 2, April 1959, pp. 187-196.

Total and insoluble gum were measured in four jet fuels which had been in desert storage in steel drums for four years. A straight run fuel was the most stable, thermally cracked fuel was the least stable, and catalytically cracked fuel was intermediate in stability.

In a laboratory study of stability, gas oils were treated in various ways, including hydrogenation, acid or caustic washing, and redistillation, then blended with a stable gasoline to make a simulated jet fuel and stored at 43.3° C (110° F) for six months in the presence of excess air. While all the treatments improved the stability, acid treatment and hydrogenation gave the most improvement. Increasing the amount of oxygen over the fuel during storage increased the amount of gum formed.

A small laboratory apparatus for measuring filterability of jet fuels was developed. There was no correlation between filter-plugging tendency and insoluble gum content of a fuel. The insoluble gums were examined with an electron microscope, and it was found that filterability behavior was related to the character of the deposit. An amorphous type deposit rapidly plugged the filter, while a crystalline type deposit did not.

79. Nixon, A. C., and H. B. Minor. Effect of Additives on Jet Fuel Stability and Filterability. Ind. and Eng. Chem., Vol. 48, No. 10, October 1956, pp. 1909-1916.

The effects of several additives on storage stability of jet fuel were investigated. The fuel-additive blends were aged under four different sets of conditions: at 100° C and 100 psi oxygen in steel bombs, at 70° C in glass bottles, at 43.3° C in glass bottles, and desert storage in steel cans or drums. Fuel deterioration was determined by the amount of soluble and insoluble gum formed and by filterability of the fuel after aging.

Three oxidation inhibitors were tested: 2,6-di-t-butyl-4-methylphenol; 2,4-dimethyl-6-t-butylphenol; and N,N'-di-sec-butyl-p-phenylenediamine. None of these inhibitors had a significant effect on the amount of gum formed in the accelerated aging tests.

Nearly 250 organic compounds of various types were tested in jet fuels for antioxidant activity. A few of these appeared to reduce gum formation during storage. None of the compounds were identified.

The metal deactivator N,N'-disalicylidene-1,2-propanediamine was effective in counteracting the catalytic effect of soluble copper on jet fuel deterioration, but it had little effect on gum formation during storage of copper-free fuel.

See Tables 88, 89, and 90.

80. Nixon, A. C., H. B. Minor, and G. M. Calhoun. Effect of Alkyl Phenols on Storage and Manifold Stability of Gasolines. Ind. and Eng. Chem., Vol. 48, No. 10, October 1956, pp. 1874-1880.

The effects of a number of different alkyl phenols on various gasoline properties were investigated. One of the properties investigated was storage stability. Gasoline-additive blends were aged in amber glass bottles at either 60° C or 70° C in an atmosphere of oxygen, or at 43° C (110° F) in an atmosphere of air. Deterioration of the gasoline was estimated from the increase in air jet gum and from changes in other properties. Few data on the results of the storage tests are included.

81. Nixon, A. C., and R. E. Thorpe. The Effect of Composition on the Stability and Inhibitor Response of Jet Fuels. Am. Chem. Soc., Div. Petrol. Chem., Preprints, Vol. 1, No. 3, August 1956, pp. 265-279.

The gas oil portion of jet fuels (that part boiling above 177° C (350° F)) was separated into compound type fractions by distillation followed by chromatography on silica gel and alumina. The separated fractions were analyzed chemically, by ultraviolet and infrared spectroscopy, and by mass spectrometry. The storage stability of the fractions were determined by aging them at 43° C, 70° C, or 100° C, followed by measurement of the soluble and insoluble gum. The stability of each fraction was then related to the composition of that fraction. The saturate fractions were very stable and did not form gum. The aromatics fractions were fairly stable. Olefins, particularly conjugated diolefins, gave high soluble gum values but formed relatively little insoluble gum. Aromatic olefins were very reactive and produced large amounts of both soluble and insoluble gum. Thiophenes were very unstable toward formation of both soluble and insoluble gum.

Nitrogen compounds isolated from the cracked gas oils were mainly nitrogen bases and pyrroles. When the nitrogen bases were blended with a saturate fraction, they had no effect on the stability of the saturates. However, pyrroles were very unstable; addition of pyrroles to a saturate fraction caused formation of large quantities of soluble and insoluble gum.

82. Nowack, C. J. Analysis and Testing of JP-5 Fuel Derived from Coal. Report No. NAPTC-PE-99, Naval Air Propulsion Test Center, Trenton, NJ, January 1977, 59 pp. NTIS No. AD A036073.

This report includes a section on storage stability of four coal-derived jet fuels. The fuels were stored for 26 weeks at 43.3° C (110° F) in steel cans lined with an inert resin coating. Every two weeks the cans were cooled and opened to replenish the air in the vapor space.

JFTOT thermal stability tests conducted before and after the storage period indicated that there was no degradation of the thermal oxidation stability characteristics of these fuels during storage.

The gum content of the fuels was also determined before and after storage. For three of the fuels, there was only a very slight increase in gum content with storage, which was considered insignificant. The fourth fuel showed a significant increase in gum content as a result of storage; however, addition of the oxidation inhibitor 2,4-dimethyl-6-t-butylphenol eliminated any gum increase during storage in this fuel.

See Tables 145 and 146.

83. Nowack, C. J., and R. J. Delfosse. Thermal Oxidative Stability of Synthetic Jet Fuels. 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. 127-148. In NTIS No. AD A060081.

This paper is primarily concerned with thermal stability, but it includes a brief discussion of storage stability of jet fuels derived from oil shale. The fuel samples were prepared by first extracting them with dilute acid to remove basic nitrogen compounds, followed by percolation through silica gel to remove the remaining nitrogen compounds. The fuel samples were then doped with the acid extracted nitrogen compounds to a concentration range of 8 to 125 ppm basic nitrogen. Phenylenediamine oxidation inhibitor was also added to some samples.

Stability was determined in an accelerated test in which the fuel samples plus one percent water were stored in glass bottles, covered with aluminum foil, at 60° C for four weeks. Thermal stability analyses of the samples before and after storage showed that small quantities of basic nitrogen compounds caused the fuel to become unstable. A high level of peroxidation had also occurred during storage. There was a correlation between the peroxide content and the thermal oxidation stability of the samples. Addition of oxidation inhibitor retarded deterioration of the fuel. A petroleum-derived JP-5 fuel remained stable during this accelerated storage period.

84. Nowack, C. J., R. J. Delfosse, G. Speck, J. Solash, and R. N. Hazlett. Relation Between Fuel Properties and Chemical Composition. Stability of Oil Shale-Derived Jet Fuel. Oil Shale, Tar Sands, and Related Materials, H. C. Stauffer, Ed., ACS Symposium Series No. 163, American Chemical Society, 1981, pp. 267-283.

Storage stability of shale oil derived jet fuel was studied. The fuels were placed in 1 liter dark borosilicate glass bottles which were loosely covered to keep out dust but still permit air diffusion into the bottle. Water and iron filings were added to simulate actual storage tank conditions. The samples were stored at 60° C for four weeks. Deterioration during storage was determined by measuring gum, contamination and high temperature stability (JFTOT) before and after storage.

Nitrogen compounds were removed from the fuel by acid extraction and silica gel chromatography. In a storage test of the nitrogen-free fuel some peroxide formed but no appreciable gum formed and the JFTOT stability remained acceptable. As the extracted basic nitrogen compounds were reintroduced into the fuel, the gum and peroxide levels after storage increased and then decreased as the concentration of nitrogen extract increased. Mass spectral analysis of the acid-extracted nitrogen containing material indicated the presence of major amounts of pyridine compounds with lesser quantities of quinoline and tetrahydroquinoline types. Pyrroles and carbazoles were not extracted.

Pure nitrogen compounds were added to both petroleum jet fuel and nitrogen-free shale oil jet fuels, and the storage stability of the blends determined. It was found that pyridines and pyrroles contributed to fuel instability during storage.

See Table 156.

85. Offenhauer, R. D., J. A. Brennan, and R. C. Miller. Sediment Formation in Catalytically Cracked Distillate Fuel Oils. Ind. and Eng. Chem., Vol. 49, No. 8, August 1957, pp. 1265-1266.

The effect of sulfur and nitrogen compounds on the stability of distillate fuel oils was studied. Samples were stored for 12 weeks at 43.3° C (110° F), and the amount of sediment formed was determined by weighing.

Untreated and uninhibited catalytically cracked distillate fuels were usually unstable when stored in the presence of air. When aromatic thiols were removed by caustic washing, the stability was improved. Reblending aromatic thiols with caustic-washed oil caused sediment formation in storage, and the content of thiol decreased to zero during storage. Aliphatic thiols and diaryl disulfides did not increase sediment formation.

Pyrroles had been reported to increase sediment formation when added to a whole oil, but it was found that pyrroles were relatively harmless in a thiol-free oil. Indole caused sediment formation in oil containing aromatic thiols, but other basic nitrogen heterocyclics had little effect. 1-Naphthol caused formation of sediment during storage in the absence of both pyrroles and aromatic thiols. Sulfonic acids caused rapid formation of sediment in the presence of oxygen, but not when oxygen was excluded.

The authors believed that the sediment formed from sulfur and nitrogen compounds was composed of sulfonic acids formed through oxidation of aromatic thiols plus a basic condensate formed by action of oxygen and acids on pyrroles and indoles.

See Tables 122 and 123.

86. Oswald, A. A. Organic Sulfur Compounds. I. Hydroperoxide Intermediates in the Co-oxidation of Mercaptans and Olefins. J. Org. Chem., Vol. 24, March 1959, pp. 443-444.

Intermediates of high hydroperoxide content were obtained as viscous liquids when air was introduced into hydrocarbon solutions of aromatic mercaptans and reactive olefins at 0° C or lower temperature. At room temperature, hydroperoxides containing sulfur rearranged to hydroxylethyl sulfoxides. Rearrangement was accompanied by loss of peroxide content, stronger absorption in the IR, and solidification.

The author proposed that the co-oxidation of olefins and mercaptans which results in the formation of hydroperoxide intermediates is largely responsible for the peroxidation and subsequent color, gum, and sediment formation in untreated petroleum distillates.

87. Oswald, A. A., and F. Noel. Role of Pyrroles in Fuel Instability. J. Chem. and Eng. Data, Vol. 6, No. 2, April 1961, pp. 294-301.

The chemical reactions involved in color and sediment formation by pyrroles were investigated. Experiments were carried out in pure hydrocarbon solutions containing pyrroles and other color and sediment precursors. The pure hydrocarbons used as solvents were cetane, xylene, or tetrahydronaphthalene. The pyrroles included pyrrole, indole, and their alkyl derivatives. The solutions were stored in borosilicate glass flasks at 43.3° C (110° F) or 98.9° C (210° F) for periods up to four weeks.

Pyrrole alone did not form any sediment in the hydrocarbon solvents. Addition of mercaptans to the pyrrole-hydrocarbon blend produced color and sediment formation. Olefins and mercaptans were found to co-oxidize in hydrocarbon solutions in the presence of air to form substituted mercaptoethyl hydroperoxides, which then reacted with pyrrole to form sediment. Peroxides and hydroperoxides also reacted with pyrrole to form sediment.

2,5-Dimethylpyrrole and 2,3-dimethylindole produced some sediment in hydrocarbon solvents without any other compounds present. Addition of hydroperoxides and mercaptans greatly increased sediment formation. N-substituted pyrroles were relatively unreactive toward sediment formation.

See Tables 207 and 208.

88. Oswald, A. A., and C. B. Ruper. Co-oxidation of Mercaptans and Olefins. Am. Chem. Soc., Div. Petrol. Chem., Preprints, Vol. 4, No. 1, March 1959, pp. 27-36.

Blends of a mercaptan and an olefin in cetane were stored in open flasks at 43.3° C (110° F) for periods up to one month. The amount of sediment formed was determined by weight. The mercaptans studied included thiophenol, p-toluene thiol, 2-naphthalene thiol, n-dodecyl mercaptan, t-dodecyl mercaptan, and 4-chlorothiophenol. The olefins included octene, dodecene, octadecene, indene, and styrene.

Indene alone, blended with cetane, produced some sediment. The other olefins studied did not produce sediment in cetane by themselves; however, an olefin and mercaptan together in cetane caused formation of sediment. An aromatic mercaptan plus an olefin generally produced more sediment than an aliphatic mercaptan plus olefin. The mechanism for the co-oxidation of mercaptans and olefins is discussed.

See Tables 203, 204, 205 and 206.

89. Oude Alink, B. A., and R. P. Hutton. Hexahydropyrimidines as Fuel Additives. U.S. Pat. 3,936,279, February 3, 1976.

Several methods for preparing hexahydropyrimidines are described. It was claimed that these hexahydropyrimidines could be used as additives in fuel oils, including diesel and jet fuel, to inhibit oil deterioration with the attendant formation of color and sludge. The additives of this invention not only inhibited deterioration in storage but could also be used to inhibit the formation of deposits on metal surfaces such as in tubes, evaporators, heat exchangers, distillation and cracking equipment, and the like.

90. Powers, E. J., and W. T. Wotring. Stabilization of No. 2 Fuel Oils with Caustic Treating and Additives. 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. 92-102.

    Caustic treating of distillate fuels as a means of increasing the stability was investigated. Caustic treating of the fuel reduced the amount of gum that was formed in 16 weeks of storage at 43° C. However, if the fuel contained a large percentage of cracked components, caustic treating by itself, while it reduced gum formation, did not always reduce it to the desired value of 2 mg gum per 100 ml of fuel or less for 16 weeks of storage at 43° C. In those cases, additives were used to reduce the gum formation during storage to the desired level.

91. Rescorla, A. R., J. H. Cromwell, and D. Milsom. Laboratory Evaluation of Fuel Oil Stability. Anal. Chem., Vol. 24, No. 12, December 1952, pp. 1959-1964.

    Two accelerated aging methods were developed for evaluating the storage stability of fuel oil. In one method, the oil was heated to 73.9° C (165° F) and circulated through a length of copper tubing. In the other method the oil was heated to 82.2° C (180° F) in a glass tube with air bubbling through the oil. Every 24 hours an aliquot of the oil was cooled and filtered and the amount of sediment on the filter was estimated simply from the color of the filter.

    The results of the two accelerated tests were correlated with the weight of insolubles formed in the same oil in actual storage. Samples were stored under two conditions--in 15-gallon steel drums at ambient temperature for periods up to 52 weeks, and in vented glass bottles in an oven at 43.3° C (110° F) for periods up to 13 weeks. The authors found excellent correlation between the oven storage at 43.3° C (110° F) and ambient storage, and they claimed that the results of the accelerated tests could be used to predict deterioration of the fuel in drum storage.

92. Ritchie, J. A Study of the Stability of Some Distillate Diesel Fuels. J. Inst. Petrol., Vol. 51, No. 501, September 1965, pp. 296-307.

Diesel fuels were stored in steel tanks for six years at ambient conditions. The fuels studied were selected to cover a wide range of stability characteristics, and included two straight-run products from different crudes, a blend containing hydrofined catalytically cracked constituents, a blend containing caustic washed catalytically cracked constituents, a raw catalytically cracked fuel, and a blend of this raw stock with one of the straight-run fuels. In order to measure the amount of sediment formed in storage, glass bottles with open tops were placed on the bottom of the storage tanks. The bottles were withdrawn periodically and the amount of sediment in them weighed. Straight-run and hydrofined fuels deposited very little sediment, while catalytically cracked fuels deposited a relatively large amount of sediment.

These same fuels were also tested in two accelerated aging tests, and the results of the accelerated tests were compared with the 6-year storage. In the accelerated tests the fuel was aged in borosilicate glass bottles at 48.9° C (120° F) for 4 weeks or at 98.9° C (210° F) for 16 hours, and filterable and adherent sediment were determined by weighing. The results of both accelerated tests corresponded roughly with the weight of sediment deposited in long-term storage.

See Tables 42 and 43.

93. Robinson, E. T. Refining of Paraho Shale Oil into Military Specification Fuels. U.S. Navy Contract No. N00014-77-C-0750. Presented at the 108th AIME Annual Meeting, New Orleans, LA, February 18-22, 1979.

A section on stability of jet fuel and marine diesel fuel produced from shale oil is included in this report on the refining of Paraho Shale Oil. The criteria adopted for acceptable storage stability of jet fuel was that the fuel pass the JFTOT test after being stored for one month at 60° C (140° F) in a vented actinic glass bottle. Fuel which had been acid treated to reduce the nitrogen content to less than 20 ppm passed the JFTOT test at 500° F and at 550° F, both before and after aging, indicating that it was a very stable fuel. Fuel which had not been acid treated and contained 189 ppm nitrogen passed the JFTOT test at 500° F both before and after aging, but the aged fuel failed the JFTOT test at 550° F. This indicates that the high nitrogen fuel was less stable than the acid-treated, low nitrogen fuel.

Stability of the diesel fuel was determined by heating the fuel to 98.9° C (210° F) for 16 hours with oxygen bubbling through it, and measuring the amount of gum formed. Acid treating to reduce the nitrogen content was required to produce a fuel which had acceptable stability.