94. Ruf, H. Methods of Estimation of Storage Stability of Fuels in Laboratory and Behavior in Bulk Storage in Practice. Schweiz. Archiv. angew. Wiss., Vol. 29, 1963, pp. 428-444. Abs. in J. Inst. Petrol., Vol. 50, No. 487, July 1964, p. 136A.

> Results of rapid and more moderately accelerated tests for assessing storage stability of aviation gasoline and jet fuel, auto gasoline, and diesel fuel were compared with the condition after actual bulk storage. Deterioration of these fuels, including leaded and unleaded gasolines, over periods of 2 to 14 years in both under- and aboveground storage is discussed with some comparative results of lab tests. The influence of long storage on heat stability of jet fuel is difficult to predict, but the other tests correlated satisfactorily with actual storage results.

95. Sauer, R. W., A. F. Weed, and C. E. Headington. A Mechanism for Organic Sediment Formation in Heating Oils. Am. Chem. Soc., Div. Petrol. Chem., Preprints, Vol. 3, No. 3, August 1958, pp. 95-113.

> Two stability tests for fuel oils were studied. The first was an accelerated test in which one liter of oil was heated to 180° C (212° F) in an atmosphere of oxygen for 24 hours. In the other test, 0.9 liter of oil was stored for one year at 29.4° C (85° F) in an atmosphere of air. For both tests, the samples were stored in glass bottles containing iron strips and were kept in darkness. At the end of the storage period, sediment and color were measured.
>
> Catalytically cracked distillates formed much more sediment than straight-run distillates. After the catalytically cracked distillates had been washed with caustic to remove aromatic thiols the stability was greatly improved. Addition of toluenethiol labeled with sulfur-35 to thiol-free oil increased sediment formation, and the sulfur in the sediment was derived from the added toluenethiol. The authors concluded that aromatic thiols were the primary cause of instability. They found that phenols inhibited sediment formation.
>
> Sediment from fuel oil which had been stored at ambient conditions in steel tanks was analyzed. The analyses indicated that the sediment was a heterogeneous condensate of hydrocarbons, nitrogen compounds, and sulfur compounds. Oxygen was present in ester type linkages; the oxygen was believed to originate from oxidation by air.
>
> See Tables 127 and 128.

96. Schwartz, F. G., C. S. Allbright, and C. C. Ward. Fundamentals of Fuel Stability. Tech. Report No. 18, Department of the Army Project 1A024401A106, Bureau of Mines, Bartlesville, OK, January 1967, 38 pp.

The stabilities of several additive-free gasolines of different compositions and stabilities were determined in both sealed storage and aerated storage at 43.3° C (110° F) in glass bottles and at 93.3° C (200° F) in stainless steel bombs. Additives were then blended with the samples and the stabilities redetermined by 43.3° C storage and by rapid aging at 93.3° C. Correlations were developed by which gum and residue formation in 43.3° C storage could be predicted from the results of 93.3° C tests. The tests on the additive-free gasoline indicated that formation of gum in unstable gasoline is retarded because of oxygen depletion unless the air in the sample containers is replenished periodically. Additions of an antioxidant improved the stability of the unstable fuels, but had little effect on the stable fuels. Addition of tetraethyl lead decreased the stability of all the fuels. An inorganic precipitate formed in the fuels containing lead.

See Tables 26 through 31.

97. Schwartz, F. G., C. S. Allbright, and C. C. Ward. Fundamentals of Fuel Stability. Tech. Report No. 19, Department of the Army Project 1A024401A106, Bureau of Mines, Bartlesville, OK, May 1968, 57 pp.

An accelerated test was developed in which the gasoline sample was placed in a 16-ounce glass bottle and heated in an oven at 93.3° C (200° F) for 16 hours. The amount of gum and insoluble residue and the oxygen content of the bottle outage at the end of the 16-hour oven test was used to predict the amount of gum and residue that would be formed in 43.3° C storage for any period up to 32 weeks. Since 32 weeks at 43.3° C is equivalent to over 5 years storage at 26.7° C (80° F), this prediction method was judged to be adequate to predict stability of motor gasoline in any practical storage.

98. Schwartz, F. G., C. S. Allbright, and C. C. Ward. Predicting Gasoline Storage Stability. Oil and Gas J., Vol. 66, No. 47, November 18, 1968, pp. 150-153.

An accelerated test for determining storage stability of gasoline is described. The gasoline, in a glass bottle, was heated to 93.3° C (200° F) for 16 hours. The amount of gum formed and the oxygen consumed in the 16 hour test was correlated with the amount of gum formed at 43.3° C (110° F) for various storage periods. Application of a modified Arrhenius equation permitted estimation and prediction of fuel stability characteristics for storage of periods over 5 years at 26.7° C (80° F).

99. Schwartz, F. G., C. S. Allbright, and C. C. Ward. Storage Stability of Gasoline: Oven Test for Prediction of Gasoline Storage Stability. BuMines RI 7197, December 1968, 28 pp., NTIS No. AD-683 748.

A rapid test for predicting gasoline storage stability is described. A gasoline sample, in a sealed glass bottle, was heated in an oven at 93.3° C (200° F) for 16 hours. The amounts of gum and inorganic residue formed, with the amount of oxygen consumed by the gasoline, could be used to predict the amount of gum and inorganic residue that would form in 43.3° C (110° F) storage for periods as long as 32 weeks. By use of a modified Arrhenius equation, the 43.3° C storage time could be extrapolated to equivalent time at any temperature below 43.3° C. By combining the stability prediction method with the mathematical extrapolation, the storage performance of motor gasoline for extended periods could be estimated at any temperature up to 43.3° C.

See Tables 32 and 33.

100. Schwartz, F. G., and C. C. Ward. Fundamentals of Fuel Stability. Tech. Report No. 15, Department of the Army Project 1A024401A106. Bureau of Mines, Bartlesville, OK, March 1965, 29 pp.

Storage tests at 43.3° C (110° F) were done with mixtures of sulfur compounds and reactive hydrocarbons in n-heptane. In this series of tests the bottles were opened and the air replenished periodically during storage, instead of leaving the bottles sealed the entire time as in previous work. Periodic air replenishment resulted in formation of larger amounts of gum than was formed in sealed storage.

Elemental analysis of the gums formed in these simple mixtures of a reactive hydrocarbon and a sulfur compound in n-heptane showed that the gums were similar to those from full-boiling range fuels. In an experiment to determine if the n-heptane entered into the gum-forming reaction, a blend prepared with carbon-14 labeled n-heptane and thiophenol and stored at 43.3° C showed no reaction.

See Tables 22, 212, 213, 214, and 215.

101. Schwartz, F. G., and C. C. Ward. Fundamentals of Fuel Stability. Tech. Report No. 16, Department of the Army Project 1A024401A106, Bureau of Mines, Bartlesville, OK, June 1965, 31 pp.

An attempt was made to develop a gas-liquid chromatographic technique for analysis of gasolines before and after storage. This method was not successful for measurement of gum content; however, small quantities of high boiling materials could be obtained from gasoline samples by using a backflush technique.

An accelerated aging test using metal bombs and 100 ml samples was developed. By making a correction based on percent light transmission and using the amounts of gum formed in the bomb at 121.1° C (250° F), an excellent correlation of bomb aging with 43.3° C (110° F) storage results was achieved for six of the seven fuels tested. The bomb results and the correction curve could be used to predict the amount of gum formed for any period up to 40 weeks at 43.3° C storage.

See Table 23.

102. Schwartz, F. G., and C. C. Ward. Fundamentals of Fuel Stability. Tech. Report No. 17, Department of the Army Project 1A024401A106, Bureau of Mines, Bartlesville, OK, June 1966, 33 pp.

A series of gasolines and gasoline blending stocks, with and without additives, were aged at 43.3° C (110° F) in sealed glass bottles and in glass bottles which were aerated periodically. Samples of the same gasolines were also aged at 93.3° C (200° F) or at 121.1° C (250° F) in stainless steel bombs. At the end of each aging period, the oxygen in the vapor space of the aging container was measured and the gum and inorganic sediment were determined. The results from the different aging methods were compared. It was found that maintaining an excess of oxygen over the fuels in storage resulted in increased gum formation compared to sealed storage, but the relative stability of the series of fuels remained the same. The bomb tests at 93.3° C or 121.1° C correlated with 43.3° C storage through 16-weeks of storage.

See Table 25.

103. Schwartz, F. G., and C. C. Ward. Storage Stability. Oil and Gas J., Vol. 55, 1957.
Part 1. A Study of Blended-Fuel Deterioration. June 3, p. 121.
Part 2. How Liquids Were Tested by W.P.R.A. June 24, p. 176.
Part 3. Comparison of Distillate Fuel in Storage. July 8, p. 144.
Part 4. How Storage Affects Blended Fuels. July 22, p. 111.
Part 5. Blending Effects Bring Up Specific Questions. August 5, p. 98.
Part 6. Does Thermal Cracking Affect Stability? October 7, p. 177.
Part 7. More on Fuel Blends. October 21, p. 139.
Part 8. How Insoluble Gum Values Vary. December 2, p. 116.
Part 9. Temperature Important in Storage. December 16, p. 129.

This series of brief one-page reports summarizes a cooperative program between the Bureau of Mines and the Western Petroleum Refiners Association (W.P.R.A.) to obtain storage stability data on distillate fuels that were representative of crude oil sources from major producing areas of the world. A total of 34 distillate fuels and 250 blends of these fuels were stored under several conditions -- at 37.8° C (100° F) in glass bottles with contaminants (copper or iron, with or without water), at 43.3° C (110° F) in vented glass bottles with no contaminant, or at ambient temperature in 55-gallon vented steel drums. The fuels and blends in glass bottles were stored for periods of 6, 13, 26, or 39 weeks, while those in the drums remained in storage for one year. At the end of each storage period, a sample was removed for determination of light transmission, insoluble gum, and soluble gum.

Straight-run fuels were found to be the most stable, catalytically cracked fuels were intermediate in stability, and thermally cracked fuels were the least stable. Oxidation appeared to be a major factor in gum formation. Copper catalyzed gum formation; storage of a fuel in contact with copper and sea water was the most severe storage condition studied. Iron had no effect on gum formation; however, some of the fuels were degraded by contact with galvanized iron and sea water.

See Table 125.

104. Schwartz, F. G., M. L. Whisman, C. S. Allbright, and C. C. Ward. Storage Stability of Gasoline. Development of a Stability Prediction Method and Studies of Gasoline Composition and Component Reactivity. BuMines Bull. 660, September 1972, 60 pp., NTIS No. PB-212 555.

The first section of this Bulletin describes the development of the 16-hour, 93.3° C (200° F) oven test as a rapid and precise method for predicting the storage stability of motor gasoline. Equations were derived that related the amount of gum formed and amount of oxygen consumed in the 16-hour oven test to the amount of gum that would form in 43.3° C (110° F) storage. Nomographs are shown with which the amount of gum that would form in gasoline stored at 110° F for periods as long as 32 weeks could be predicted from the results of the 16-hour oven test.

The second section discusses studies of fuel composition, component reactivity, and lead alkyl reactions. A radiotracer technique was used to obtain a quantitative measurement of the gum-forming reactions of certain sulfur compounds and selected hydrocarbons in

43.3° C storage. Thiols were the most reactive sulfur compounds studied. Investigation of the reaction of tetraethyllead with hydrocarbons to form precipitates showed that the structure of the lead precipitates was a function of the storage temperature.

See Tables 25, 26, 27, and 36.

105. Schwartz, F. G., M. L. Whisman, C. S. Allbright, and C. C. Ward. Storage Stability of Gasoline. Fundamentals of Gum Formation, Including a Discussion of Radiotracer Techniques. BuMines Bull. 626, 1964, 44 pp. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

Variables of composition and environment affecting storage stability of gasoline were studied, utilizing radioactive tracers and other analytical techniques. Changes in gasoline composition brought about by aging at 43.3° C (110° F) were determined and correlated with gum formation. Rapid aging with UV light was compared to storage at 43.3° C. The amounts of reaction of selected gasoline components, labeled with radioactive tracers, were determined in a gasoline and in a mixture of 17 selected pure gasoline components. Sulfur compounds, nitrogen compounds, polycyclic aromatics, and olefins entered into gum-forming reactions. The aromatic constituents of gasolines contributed substantially to gum formation. A mixture of tetralin- and indan-type compounds was reactive, and this mixture appeared to be the main aromatic portion entering into gum formation. A significant amount of naphthalenes also appeared to have reacted in the gum-forming process. Analyses of the sulfur compounds in a fresh and an aged fuel indicated that elemental sulfur, hydrogen sulfide, thiols, sulfides, and disulfides were depleted during aging, but thiophenes and residual sulfur compounds were not depleted by fuel deterioration.

See Tables 2, 3, 6, 7, 8, 9, 15, 17, 19, 20, and 21.

106. Solvent Refined Coal International, Inc. SRC-II Fuel Oil Stability, Compatibility Studies. SRC-II Update, Vol. 1, No. 1, January 1981, 2 pp. Published by Solvent Refined Coal International, Inc., Englewood, CO.

The properties of SRC-II fuel oil are discussed. In a storage stability test, SRC-II Fuel Oil and blends of SRC-II fuel oil with petroleum-derived fuel oil were satisfactorily stable in five months of storage at 47.8° C (118° F), showing no appreciable changes in viscosity, resins, or asphaltene content.

See Table 157.

107. Stavinoha, L. L., J. N. Bowden, S. R. Westbrook, and H. N. Giles. Final Report on Assessment of Crude Oil and Refined Petroleum Product Quality During Long-Term Storage. AFLRL Report No. 121, Contract No. DAAK70-80-C-0001, U.S. Army Fuels and Lubricants Research Lab., Southwest Research Inst., San Antonio, TX, December 1979, 63 pp., NTIS No. AD A082365.

A 4-task program was undertaken to assist in ensuring that products being considered for long-term storage in the Strategic Petroleum Reserve would remain of a quality immediately usable and to identify likely quality assurance procedures. The first task was assessment of current state-of-the-art in underground storage of petroleum and refined products. Underground storage has been practiced primarily in Europe and South Africa, and in a few instances in the U.S. There have been no reports of serious deterioration of the stored materials. In some cases, additives have been used to improve the stability.

The second task was a study of the effects of storage on the quality of the stored fuel. No storage tests are reported. The tests that were selected to evaluate characteristics of heavy fuel oils that could affect their performance during storage were sedimentation tendencies, water-shedding characteristics, and wax content.

The third task was development of a SPRO crude oil Search File, based on the BETC Crude Oil Data Bank, and the fourth task was an overall assessment. The authors concluded that strategic storage of crude oil and refined products can be successfully accomplished if sites are properly chosen and crudes and products to be stored are selected properly, with additives possibly being necessary in the refined products.

108. Stavinoha, L. L., and M. E. LePera. A Review of Diesel Fuel Deterioration and Related Problems. Interim Report AFLRL No. 88, Contract No. DAAG53-76-C-0003, U. S. Army Fuels and Lubricants Research Lab., Southwest Research Inst., San Antonio, TX, May 1977, 25 pp., NTIS No. AD A043566.

This report reviews the general topic of fuel deterioration with primary emphasis on diesel or distillate fuels used in compression ignition engines which power the majority of Army tactical and combat vehicles. Selected field problems regarding fuel stability and related problems are presented and the status of on-going research and development programs are outlined. This information places in perspective the background and field problems which have prompted current research activities to detect, predict, and prevent fuel stability associated equipment failures. A selected bibliography used as the basis for the review portion of this report and as a source for additional fuel stability information is included.

109. Stavinoha, L. L., and S. R. Westbrook. Accelerated Stability Test Techniques for Diesel Fuels. DOE/BC/10043-12, Southwest Research Inst., San Antonio, TX, October 1980, 137 pp. NTIS No. DOE/BC/10043-12.

An extensive literature search was conducted to provide a list of stability test techniques and their interpretations. A table lists 55 accelerated stability test techniques, with a brief description of each.

Seven accelerated stability tests were evaluated using a set of six test fuels. The test techniques represented a wide variety of test conditions including temperature, aging time, and oxygen availability. The six test fuels were diesel or middle distillate fuels chosen to represent a wide range of stabilities. Correlations of the accelerated stability test results were then related to test results obtained at a storage temperature of 43° C, which has generally been regarded as showing good correlation with long-term ambient storage. The stability data from the 43° C storage did not follow a trend which was directly predictable by any one of the other test methods; however, the data from an 80° C test gave the best predictions.

This report includes an annotated bibliography with 116 references.

110. Stavinoha, L. L., and S. R. Westbrook. Accelerated Stability Test Techniques for Middle Distillate Fuels. *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. 3-21.

Seven accelerated stability tests were evaluated, and the results compared to data from 43° C storage tests. The stability data from 43° C storage were not directly predictable by any of the accelerated test methods. This material has been covered in more detail in Reference 109.

111. Stavinoha, L. L, and S. R. Westbrook. Optimization of Accelerated Stability Test Techniques for Diesel Fuels. DOE/BC/10043-25. Southwest Research Inst., San Antonio, TX, June 1981, 64 pp. NTIS No. DOE/BC/10043-25.

The report discusses the second year's work on a two year project. The first year's work was covered in Reference 109. Four test methods for determining storage stability were investigated more intensively in this second year. These were: storage at 43° C in vented and nonvented borosilicate glass bottles for periods up to 24 weeks; storage at 80° C in vented borosilicate glass bottles for 3,7, or 14 days; aging at 150° C in open borosilicate glass tubes for 1.5 or 3 hours; and aging at 95° C for 16 hours with oxygen bubbling through the fuel.

Eight different diesel fuels were tested. At the end of the storage period, the filterable and adherent insolubles, steam jet gum (soluble gum), light absorbance, and color were measured. The results of the four tests were compared, and the rapid aging tests were correlated with the 43° C storage. Total insolubles (filterable plus adherent) gave the best data correlation. Soluble gum was not acceptable for correlation because the soluble gum values could not be reliably corrected for initial gum values. All four methods tended to rank the eight test fuels in the same order in terms of storage stability.

See Tables 54 through 65.

112. Stavinoha, L. L., S. R. Westbrook, and M. E. LePera. Army Needs for Diesel Fuel Stability and Cleanliness. 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. 103-125.

This paper reviews the general topic of fuel deterioration. Field problems regarding fuel stability and related problems are summarized. Some research on tests for predicting long-term storage is discussed in very general terms.

113. Taylor, W. F., and J. W. Frankenfeld. Development of High Stability Fuel. Final Report for Phase III, Report No. EXXON/GRU.17GAHF.76, Department of the Navy Naval Air Propulsion Test Center, Contract N00140-74-C-0618, Exxon Research and Engineering Company, Linden, NJ, December 1976, 82 pp. NTIS No. AD A038977.

A JP-5 type jet fuel was developed which had the high thermal stability required for high speed aircraft. This "High Stability JP-5" had essentially the same hydrocarbon composition as standard JP-5; the high thermal stability was achieved by removal and exclusion of molecular oxygen and by control of the type and level of sulfur, nitrogen, and oxygen compounds and olefins.

The base fuel had good storage stability. It did not produce any sediment when stored for periods up to 160 days at room temperature. Addition of 2,5-dimethylpyrrole (DMP) caused formation of sediment. Addition of both DMP and n-decanoic acid accelerated the rate of sediment formation over that with DMP alone, indicating that there was an interaction between DMP and decanoic acid. In a fuel which had not been deoxygenated, the rate of sediment formation was faster than in the deoxygenated fuel. Light also increased the rate of sediment formation. Although DMP affected the storage stability, it did not appear to be deleterious to the high temperature stability of deoxygenated JP-5.

See Table III.

114. Thompson, N. E. S., and B. A. Oude Alink. Process of Preparing Hexahydropyrimidines. U.S. Pat. 4,311,841, January 19, 1982.

A hexahydropyrimidine was reacted with an aldehyde to yield a second hexahydropyrimidine in which a portion of the first hexahydropyrimidine molecule was replaced with a substituted group from the aldehyde. It was claimed that the product hexahydropyrimidine could be used as an additive in fuel oils to prevent deterioration of the oil, including sludge formation and discoloration, during storage.

115. Thompson, R. B., J. A. Chenicek, L. W. Druge, and T. Symon. Stability of Fuel Oils in Storage. Effect of Some Nitrogen Compounds. Ind. and Eng. Chem., Vol. 43, No. 4, April 1951, pp. 935-939.

Storage tests are described in which fuel oil samples containing a small amount of added nitrogen compound were stored at 37.8° C (100° F) for periods up to 10 months, followed by determination of the amount of gum formed. Addition of 2,5-dimethylpyrrole greatly increased the quantity of insoluble gum formed compared to the amount formed in additive-free oil. Pyrrole and indole also increased the formation of insoluble gum, although much less than 2,5-dimethylpyrrole. Isoquinoline and 2-aminopyridine caused a slight increase in gum formation, while quinoline, lutidine, and N-ethylcarbazole had no effect on gum formation.

116. Thompson, R. B., L. W. Druge, and J. A. Chenicek. Stability of Fuel Oils in Storage: Effect of Sulfur Compounds. Ind. and Eng. Chem., Vol. 41, No. 12, December 1949, pp. 2715-2721.

The effect of sulfur compounds on the storage stability of fuel oil was investigated. A number of different sulfur compounds, of the type that may be present in oil, were added to fuel oil and the blends were stored in vented brown glass bottles at 37.8° C (100° F). Samples were withdrawn once a month for determination of insoluble sediment and soluble gum. Thiophenes, aliphatic mercaptans, and aliphatic sulfides had little effect on formation of either insoluble sediment or soluble gum. Primary aliphatic mercaptans appeared to have a small inhibiting effect on sediment formation. Free sulfur, disulfides, and polysulfides all increased sediment formation, and thiophenol greatly increased sediment formation. The effect of added sulfur compounds varied from oil to oil; the increase in sediment formation was generally greater in unstable oils than in stable oils.

117. Vamos, A., and E. Pataki. Storage Stability of Fuel Oils. Energiagazdalkodas, Vol. 12, No. 7-8, 1971, pp. 295-301. (In Hungarian.) Chem. Abs., Vol. 75, 1971, Abs. No. 153559n.

The physical properties and storage stability of different-origin petroleum middle distillates and residual fuel oils were determined. The precipitate on storage consisted of water, inorganic dust and rust particles, waxes, and aging products (mainly asphaltenes). The thermal stability of the fuel oils was determined by the Shell Hot Filtration Test, both for existing and potential sludge. Other testing methods are also described. An experimental procedure for accelerated deposit formation consisted of pumping fuel oil at 93° C through a pipe for 20 hours at constant rate and subsequent visual inspection of the pipe surface. The accumulated deposit was dissolved in different organic solvents. Viscosity, Conradson carbon residue, pour and flash points of the samples were determined prior to and after the stability tests.

118. Walker, A. C., and J. P. Stanton. Examine Fuel Oils with Microscope. Petrol. Refiner, Vol. 33, No. 11, November 1954, pp. 187-191.

Microscopic examination of oil was used to estimate storage stability of the oil. The number and size of particles in liquid oil and in the film left after evaporation of the oil were measured with a light microscope and also with an electron microscope. Both fresh oils and oils which had been stored for up to 14 weeks at room temperature were examined. The increase in the number of particles in the oil during storage was correlated with the storage stability of the oil.

See Table 119.

119. Ward, C. C., and F. G. Schwartz. Incompatibility of Distillate Fuels. Symposium on Stability of Distillate Fuel Oils, ASTM STP 244, American Society for Testing and Materials, Philadelphia, PA, 1958, pp. 41-46.

Blending of straight-run and cracked fuels to provide burner fuels showed that some blends of fuels were incompatible and formed gum deposits. The Bureau of Mines conducted a research program which included storage of several hundred blends of distillate fuels and determination of the amounts of gum formed. Incompatible blends formed more gum in storage than would be anticipated based on the amounts of gum formed in the component fuels when they were stored separately. Some blends formed less gum than the components stored separately. Blends of straight-run and catalytically cracked fuels showed the highest frequency of incompatibility The storage stability of a blend could not be predicted from the storage stability of its components.

120. Ward, C. C., and F. G. Schwartz. Motor Gasoline Stability. Tech. Report No. 1, Ordnance Project TB5-0010C, Department of the Army Project 5-B51-01-010, Bureau of Mines, Bartlesville, OK, December 1955, 49 pp.

This is the first of a series of reports covering research on gasoline storage stability which the Bureau of Mines conducted for the Army. Several gasoline samples were procured, analytical methods were developed, and a storage procedure was selected.

121. Ward, C. C., and F. G. Schwartz. Motor Gasoline Stability. Tech. Report No. 2, Ordnance Project TB5-0010C, Department of the Army Project 5-B51-01-010, Bureau of Mines, Bartlesville, OK, June 1956, 39 pp.

Three gasoline samples were stored at 43.3° C (110° F) in both the unleaded and leaded condition. The samples were analyzed for gum and other properties before and after storage.

See Table 2.

122. Ward, C. C., and F. G. Schwartz. Motor Gasoline Stability. Tech. Report No. 3, Ordnance Project TB5-0010C, Department of the Army Project 5-B51-01-010, Bureau of Mines, Bartlesville, OK, February 1957, 53 pp.

The original three test gasolines were separated into hydrocarbon-type fractions by column chromatography on silica gel, then these hydrocarbon-type fractions were further separated into boiling ranges by low-pressure distillation.

Three groups of samples were placed in 43.3° C (110° F) storage; the initial three test gasolines in both the unleaded and leaded state, 16 supplemental samples as both the whole fuel and silica gel depolarized fuel, and fractions from the chromatographic separation and distillation of the initial three test samples. It was found that removal of polar compounds decreased the stability of the fuel. The depolarized fuels had much more gum initially than the whole fuels, and after 20 weeks storage at 43.3° C the amount of gum was greatly increased.

Rapid aging with X-ray irradiation and UV irradiation was investigated. It was concluded that the effect was similar for both methods; since UV irradiation was simpler, work with X-ray irradiation was discontinued.

See Tables 2 and 3.

123. Ward, C. C., and F. G. Schwartz. Motor Gasoline Stability. Tech. Report No. 4, Ordnance Project TB5-0010C, Department of the Army Project 5-B51-01-010, Bureau of Mines, Bartlesville, OK, July 1957, 44 pp.

Several analytical methods were developed for studying gasolines before and after storage, including a polarographic method for measuring the hydroperoxide content, a spectrophotometric method for comparing the light transmittance of fresh and aged fuel, and a micro air-jet gum apparatus for determining gum in small volumes of gasoline. Induction system deposits were determined before and after storage as another measure of storage stability.

124. Ward, C. C., and F. G. Schwartz. Motor Gasoline Stability. Tech. Report No. 5, Ordnance Project TB5-0010C, Department of the Army Project 5-B51-01-010, Bureau of Mines, Bartlesville, OK, January 1958, 28 pp.

Storage tests of three unleaded gasolines indicated that platformate gasoline was very stable, catalytically-cracked gasoline was very unstable, and hydrogenated catalytically-cracked gasoline was moderately stable. Addition of tetraethyllead to these three gasolines reduced their storage stability and resulted in lead precipitation during storage. Several additional gasoline samples were also tested for stability. A study of UV irradiation as a means of accelerating gum formation showed that if the irradiation was continued for a relatively long period of time as much as eight percent of the gasoline could be converted to gum. Aromatic, olefinic, and paraffin-naphthene portions were separated by silica gel chromatography from each of the fuels and distilled to produce several distillation fractions of each silica gel portion. The gum content before and after storage of each fraction was determined. The fractions were much more unstable than the whole fuel and the most unstable fractions were included in the olefinic and aromatic portions.

See Table 4.

125. Ward, C. C., and F. G. Schwartz. Fundamentals of Fuel Stability. Tech. Report No. 6, Ordnance Project TB5-0010C, Department of the Army Project 5-B51-01-010, Bureau of Mines, Bartlesville, OK, October 1958, 32 pp.

Gasoline samples were aged by irradiation with ultraviolet light. Both heptane-soluble and heptane-insoluble gums were formed at constant rates during UV irradiation. The samples were analyzed before and after aging to determine the changes in aromatics content and in the concentration of sulfur and nitrogen compounds. The types of aromatics that reacted to form gum, in decreasing order of reactivity, were: alkyl benzenes, tetralins and indans, and naphthalenes. In the study of sulfur compounds, it was found that elemental sulfur, hydrogen sulfide, mercaptans, sulfides and disulfides reacted in gasoline aged by UV irradiation. Other types of sulfur compounds did not react. Sulfur compounds were not essential for gum formation. Nitrogen compounds were also reactive in gum formation. The main nitrogen compounds involved in gum formation were the basic compounds, such as pyridines, quinolines, anilines, and amines. Nitrogen compounds were not essential for gum formation.

See Tables 5, 6, 7, 8, and 9.

126. Ward, C. C., and F. G. Schwartz. Fundamentals of Fuel Stability. Tech. Report No. 7, Ordnance Project TB5-0010C, Department of the Army Project 5-B51-01-010, Bureau of Mines, Bartlesville, OK, March 1959, 25 pp.

A number of organic compounds were labeled with tritium, and these labeled compounds were added to gasoline samples to trace formation of gum in 43.3° C (110° F) storage. Measurement of radioactivity in the gum by liquid scintillation counting indicated whether or not the added compound had entered into the gum-forming reaction.

The results with radioactively labeled toluene showed that toluene had not entered into gum formation at all. Results from samples tagged with labeled indan and 1,3,5-trimethylbenzene were inconclusive. The activity in the gums was measurable but at such a low level that these compounds did not appear to be major reactants in gum formation. In the sample containing labeled thiophenol, radioactivity measurements indicated that more than 25 percent of the thiophenol present reacted and entered the gum.

See Tables 10, 11, 12, and 13.

127. Ward, C. C., and F. G. Schwartz. Fundamentals of Fuel Stability. Tech. Report No. 8, Ordnance Project TB5-0010C, Department of the Army Project 5-B51-01-010, Bureau of Mines, Bartlesville, OK, October 1959, 32 pp.

Tritium labeling of selected organic compounds suspected of being gum formers is reported. The labeled materials included hydrocarbons, sulfur compounds, nitrogen compounds, and blends. These labeled materials were added to gasoline for storage testing. Conclusions were (1) that the quantities of labeled compounds added in preparing samples for storage tests did not appear to have any effect on the rate or amount of gum formation; and (2) that labeled alkyl benzenes, sulfur compounds, and nitrogen compounds appeared to contribute radioactivity to the gum and merited further study. Other types of compounds did not appear to enter into gum-forming reactions.

Several gasolines were distilled into different boiling range fractions. Storage tests conducted on the individual fractions showed that there was a concentration of unstable materials in the middle of the gasoline boiling range.

See Table 14.

128. Ward, C. C., and F. G. Schwartz. Fundamentals of Fuel Stability. Tech. Report No. 9, Ordnance Project TB5-0010C, Department of the Army Project 5-B51-01-010, Bureau of Mines, Bartlesvill, OK, April 1960, 10 pp.

This report summarizes a study of tritium migration from tritium labeled compounds to other components in a gasoline-type mixture. It was concluded from both theoretical considerations and experimental work that tritium migration from labeled compounds to other components of the gasoline mixture was negligible.

129. Ward, C. C., F. G. Schwartz, and M. L. Whisman. Fundamentals of Fuel Stability. Tech. Report No. 10, Ordnance Project TB5-0010C, Department of the Army Project 5-B51-01-010, Bureau of Mines, Bartlesville, OK, August 1960, 24 pp.

About 70 compounds, including hydrocarbons, sulfur compounds, nitrogen compounds, and oxygen compounds were labeled with tritium and added to gasoline for storage tests at 43.3° C (110° F). The amount of the compound which reacted in storage was measured by separating the aged gasoline from the gum, and radioassaying the gum and the gasoline to determine the radioactivity distribution. These storage tests with tritium-labeled compounds indicated that the following compounds appeared to be gum formers: alkylbenzenes, cycloolefins, sulfur compounds, polycyclic compounds, diolefins, and nitrogen compounds.

See Tables 15 and 16.

130. Ward, C. C., F. G. Schwartz, and M. L. Whisman. Fundamentals of Fuel Stability. Tech. Report No. 11, Ordnance Project TB5-0010C, Department of the Army Project 5-B51-01-010, Bureau of Mines, Bartlesville, OK, July 1961, 30 pp.

Additional studies of the reactivities of organic comcompounds toward gum formation using radiotracer techniques and accelerated storage were completed. Several pounds toward gum formation using radiotracer techniques and accelerated storage were completed. Several carbon-14 labeled compounds and sulfur-35 labeled compounds were included, in addition to the tritium labeled compounds.

As a result of this work, the list of compounds that contribute to gum formation was revised from that shown in Reference 129. The revised list of compounds that contribute to gum formation, listed in order of decreasing reactivity, was: cycloolefins, aliphatic olefins, sulfur compounds, polycyclic compounds, alkylbenzenes, diolefins, and nitrogen compounds.

Tentative conclusions were that the compounds which contribute to gum formation were sulfur compounds, nitrogen compounds, olefins, aromatics, and oxygen. Aromatic materials appeared to be essential for gum formation. There appeared to be both fast and slow reactions occuring in gum formation. Gum apparently resulted from an interaction of several of the fuel components and not from extensive polymerization.

See Tables 15, 17, 18, and 19.

131. Ward, C. C., and F. G. Schwartz. Fundamentals of Fuel Stability. Tech. Report No. 12, Ordnance Project TB5-0010C, Department of the Army Project 5-B51-01-010, Bureau of Mines, Bartlesville, OK, February 1962, 22 pp.

A synthetic gasoline-type mixture was prepared by blending together a number of organic compounds. Radioactive-labeled blend components were used to determine the contribution of each component to the gum formed during storage.

Conclusions from this work were that compounds contributing to gum formation were sulfur compounds, nitrogen compounds, olefins, polycyclic compounds, and oxygen. Gum formation appeared to be the result of chemical reaction of these compounds and not extensive polymerization. Sulfur compounds appeared to be essential to gum formation. Alkyl benzenes did not appear to contribute to the gum. It was also concluded that radioactive-tracer techniques were the only methods developed that would measure gum-forming reactions at the extremely low levels involved.

See Tables 20 and 21.

132. Ward, C. C., F. G. Schwartz, and B. H. Eccleston. Fundamentals of Fuel Stability. Tech. Report No. 13, Department of the Army Project 1A014401A106, Bureau of Mines, Bartlesville, OK, October 1963, 30 pp.

An investigation was conducted to evaluate some of the factors associated with the precision of measuring the quantity, and the radioactivity of, residues formed in binary mixtures of pure compounds during storage. The mixtures consisted of a sulfur compound and an unsaturated hydrocarbon blended with n-heptane as a diluent. The mixtures were stored in glass bottles at 43.3° C (110° F). It was found that the estimates of coefficient of variation of the analytical procedures were less than 12 percent, and for the entire procedure less than 15 percent. The authors concluded that the procedure used was satisfactory for comparison of relative reactivities of a group of compounds.

See Tables 209, 210, and 211.

133. Ward, C. C., and F. G. Schwartz. Fundamentals of Fuel Stability. Tech. Report No. 14, Department of the Army Project 1A024401A106, Bureau of Mines, Bartlesville, OK, September 1963, 71 pp.

Radioactive tracer techniques were used to determine the relative reactivities of a selected group of hydrocarbons and sulfur compounds toward gum formation in 43.3° C (110° F) storage. Each of the sulfur compounds, labeled with sulfur-35, was tested with each of the hydrocarbons, labeled with tritium, in a mixture with heptane as diluent. It was found that thiols were the most reactive of the sulfur compounds tested. Sulfur compounds other than thiols did not appear to make significant contribution to the gum but may initiate oxidation-type reactions when present with unstable hydrocarbons. Olefins were the most reactive hydrocarbons tested.

134. Westbrook, S. R., L. L. Stavinoha, and J. V. Mengenhauser. Final Report on Fully Fueled POMCUS Vehicle Storage Test Program. Interim Report AFLRL No. 139, Contract No. DAAK70-80-C-0001, U.S. Army Fuels and Lubricants Research Lab., Southwest Research Inst., San Antonio, TX, July 1981, 29 pp., NTIS No. AD A108231.

About 20 vehicles fully fueled with military diesel fuel were stored for 30 months in a humidity controlled warehouse. Selected vehicles contained additive-treated fuel, while the remaining vehicles contained untreated fuel for comparison purposes. The fuel additive included corrosion inhibitor, dispersant, metal deactivator, antioxidant, and biocide.

Samples of the fuel were taken initially and at 6-month intervals during the storage period. Laboratory analyses showed that the treated fuel was significantly more stable than the untreated fuel. However, the fuel in all the vehicles remained adequately clean and stable throughout the entire 30 months of storage. No fuel-related malfunctions occurred when the test was ended and the vehicles were driven.

135. Whisman, M. L., C. S. Allbright, and C. C. Ward. Fundamentals of Fuel Stability. Tech. Report No. 21, Department of the Army Project 1A024401A106, Bureau of Mines, Bartlesville, OK, February 1971, 42 pp.

The formation of insoluble precipitates in leaded gasoline was studied. A series of binary blends of a reactive hydrocarbon and tetraethyl lead in isooctane were aged at 82.2° C (180° F) for 40 hours to produce lead precipitates in a system less complex than gasoline. Elemental analysis of the lead precipitates indicated that they were a mixture of oxygenated materials, principally diethyl lead carbonate.

Nomographs based upon the 16-hour accelerated aging test were developed for the prediction of gasoline storage stability.

See Tables 216, 217, and 218.

136. Whisman, M. L., F. O. Cotton, J. W. Goetzinger, and C. C. Ward. Radiotracer Study of Turbine Aircraft Fuel Stability. BuMines RI-7493, March 1971, 30 pp. NTIS No. PB-198825.

A radiotracer method was developed for detecting the contribution of selected fuel components and additives to thermally induced deposits in turbine aircraft fuels before and after 52 weeks of storage at 54.4° C (130° F). Ninety-one blends were prepared from five different jet fuels and 14 carbon-14 labeled fuel components and additives. An aliquot of each blend was thermally stressed in a microfuel coker; a second aliquot of each blend was stored for 52 weeks at 54.4° C before thermal stressing in the microfuel coker. The contribution of each carbon-14 labeled compound to deposits formed during thermal stressing was determined by radioactive-counting techniques.

The carbon-14 labeled additives included two antioxidants, a metal deactivator, and a corrosion inhibitor. The labeled fuel components included 7 aromatic hydrocarbons, a diolefin, a paraffin, and an organic acid. Three of the additives degraded and reacted during storage and thermal stress; however, a phenol antioxidant barely contributed to deposit formation. Of the labeled hydrocarbons studied, the greatest reaction was observed in blends containing methyl- and ethyl-substituted indenes, while other aromatic types also showed some contribution to the deposits. Oleic acid and cadmium, which was added to simulate the cadmium in aircraft fuel systems, interacted during storage and produced deleterious effects upon the thermal-stability quality of the fuel.

See Tables 101 through 110.

137. Whisman, M. L., J. W. Goetzinger, and C. C. Ward. Storage Stability of Aviation Turbine Fuels: A Radiotracer Technique for Estimating Component Contribution to Thermally Induced Deposits. BuMines RI-7325, December 1969, 23 pp., NTIS No. AD-698 742.

A radiotracer technique was developed which extended to the parts-per-billion range the sensitivity for determining contributors to deposits formed in stored and thermally stressed jet fuels. The method depended upon measuring radioactivity associated with thermally induced deposits in a 5-ml test bomb from fuels containing a labeled compound. The technique was applied to 88 test blends, representing 12 different jet fuels and 8 carbon-14 labeled fuel components and additives, before and after 26 weeks of storage at 54.4° C (130° F). The labeled compounds included a phenol antioxidant, 5 aromatic hydrocarbons, an olefin, and a paraffin. The largest contribution to the thermally induced deposits was observed for the antioxidant, while the blends containing the labeled olefin or paraffin produced the least amount of deposits.

See Tables 92 through 99.

138. Whisman, M. L., and C. C. Ward. Storage Stability of High Temperature Fuels. BuMines-Tech. Report AFAPL-TR-65-13.
Part I. February 1965, 80 pp. NTIS No. AD-612468.
Part II. February 1966, 168 pp. NTIS No. AD-630768.
Part III. February 1967, 83 pp. NTIS No. AD-647787.

A radiotracer technique was developed to investigate the influence of fuel constituents on thermal stability during storage of jet fuels. The method utilized a 5-ml bomb in which blends of jet fuels and radioactively labeled fuel constituents were thermally stressed; the bomb was then converted to a proportional counter for measurement of the radioactivity in adherent deposits. Other test methods evaluated for the separation and measurement of radioactivity in deposits and gums included liquid-solid chromatography followed by liquid-scintillation counting, and gas-liquid chromatography combined with ionization chamber counters and liquid scintillation radioassay techniques; however, these methods lacked the resolution and sensitivity necessary for an acceptable test method.

Ninety-four test blends of 12 jet fuels and 9 carbon-14 labeled fuel constituents and additives were prepared and tested by the 5-ml bomb technique both before and after storage for 26 weeks at 54.4° C (130° F). The large volume of test data included in the three parts of this report is summarized in Reference 137.

139. Whisman, M. L., and C. C. Ward. Storage Stability of High Temperature Fuels. BuMines Tech. Report AFAPL-TR-68-32.
  Part I. Micro Fuel Coker Tests of Fuel-Radiotracer Blends Before Storage. May 1968, 103 pp. NTIS No. AD-667818.
  Part II. The Effect of Storage Upon Thermally Induced Deposition of Labeled Fuel Components. March 1969, 126 pp. NTIS No. AD-685201.
  Part III. The Effect of Storage Upon Thermally Induced Deposition of Selected Fuel Components and Additives. June 1970, 92 pp. NTIS No. AD-707524.

This report describes the experimental investigation of the influence of fuel constituents during storage on the thermal stability of high-temperature hydrocarbon jet fuels. A micro fuel coker test apparatus was used to measure the thermal stability of test fuel blends before and after storage for 52 weeks at 54.4° C (130° F). The contribution of selected fuel components and additives, labeled with carbon-14, to deposits formed in the thermal stability test was determined by radioactive counting techniques. Ninety-one blends of 5 test fuels and 14 ratioactively labeled fuel components or additives were tested for deposit-forming tendencies before and after storage. The test results showed changes in thermal stability quality during storage for many of the blends. The detailed experimental procedures and data which are included in the three parts of this report are summarized in Reference 136.

140. White, E. W. Storage Stability of Distillate Fuels for Ships. _Manual on Requirements, Handling, and Quality Control of Gas Turbine Fuels, ASTM STP 531_, American Society for Testing and Materials, Philadelphia, PA, 1973, pp. 143-166.

The basis of instability, the effect of temperature on sediment formation, and some of the tests for storage stability are discussed. In the experimental program, three types of long-term storage stability tests were used. Distillate fuels were stored at ambient conditions for 3 years in 3 different containers: 20-foot-long glass columns constructed of standard glass pipe with a steel wire suspended inside the columns, 1-gallon borosilicate glass bottles and 1-gallon tinned steel cans. The bottle samples were stored at three different locations--Annapolis, Maine, and Florida; the columns and cans were all stored at Annapolis. Samples were withdrawn periodically from all the containers for determination of gum and chemical and physical properties of the fuel.

Two accelerated tests--a 16-hour test at 95° C (203° F) and a 43.3° C (110° F) oven storage test--were also run on the same fuels and the results compared to the long-term storage tests. Although there was some scattering of data, the accelerated storage tests gave promise of correlating with the results of long-term storage. The amount of gum formed in the 1-gallon glass bottles increased as the storage location moved south to warmer climates, and the fuels stored in tin cans gave high gum values because of corrosion of the cans.

See Tables 139, 140, 141, 142, 143, and 144.

141. Wiland, S. Use of Mathematical Methods for Investigating the Stability of Residual Fuel. Gospodarka Paliwami i Energia, Vol. 21, No. 8-9, 1973, pp. 29-31 (in Polish). Chem. Abs., Vol. 82, 1975, Abs. No. 112893e.

A statistical evaluation was performed of fuel oil storage stability and sulfur content in relation to its composition; i.e. the relative concentrations of catalytic cracking oil, atmospheric distillation residue, and vacuum distillation residue. A concentration of less than 3 percent vacuum distillation residue did not increase the sulfur content or decrease the storage stability of the fuel oil; however, more than 3.5 percent atmospheric distillation residue increased the sulfur concentration of the fuel oil and decreased its storage stability. A blend of 93 percent catalytic cracking oil, 1.5 percent atmospheric distillation residue and 5.5 percent vacuum distillation residue contained 1.76 percent sulfur, was stable in storage, and could be used as fuel oil.

142. Worstell, J. H., and S. R. Daniel. Deposit Formation in Liquid Fuels. 2. The Effect of Selected Compounds on the Storage Stability of Jet A Turbine Fuel. Fuel, Vol. 60, June 1981, pp. 481-484.

The influence of nitrogen compounds on storage stability of jet fuels was evaluated using the microscope cover slip method. Four classes of heterocyclic nitrogen compounds were studied--pyrroles, indoles, pyridines, and quinolines. The nitrogen compounds were dissolved in THF and the volume of this solution which would give the desired nitrogen concentration was added to the fuel. The blends were stored in an oven at 120° C with a microscope cover slip in each bottle. After 168 hours in the oven, the bottles were taken out and the cover slips removed, dried, and weighed.

Pyrrole and indole, up to a maximum concentration equivalent to 30 ppm nitrogen, produced only a very slight increase in deposit formation compared to the jet fuel alone. Pyridine and quinoline produced a significant increase in deposit formation and the increase was strongly dependent on concentration, with the maximum concentration investigated equivalent to 30 ppm N.

Substituted compounds of all four classes were tested at a concentration equivalent to 5 ppm N. Within a compound class, the effectiveness in promoting deposit formation could be correlated with basicity. However, there was no correlation of basicity with effectiveness between compound classes. This indicated that parameters other than basicity influence deposit formation. Steric hindrance at the nitrogen atom reduced effectiveness in promoting deposit formation.

See Table 114.

143. Worstell, J. H., S. R. Daniel, and G. Frauenhoff. Deposit Formation in Liquid Fuels. 3. The Effect of Selected Nitrogen Compounds on Diesel Fuel. Fuel, Vol. 60, June 1981, pp. 485-487.

The effect of nitrogen compounds on deposit formation in diesel fuel was investigated by the microscope cover slip technique. Diesel fuel was spiked with the nitrogen compounds, and the spiked fuel was stored at 121° C for 168 hours with a microscope cover slip in each bottle. The amount of deposit was determined by weighing the cover slip.

The effects of nitrogen compounds on deposition were very similar in diesel fuel and jet fuel, although absolute deposition rates were significantly higher in diesel fuel. The influence of nitrogen compounds on deposit formation in diesel fuel could be correlated with basicity of the nitrogen compound within compound classes but not between classes.

Diesel fuel which had been treated with silica gel to remove polar constituents was more stable than untreated fuel. When the treated fuel was spiked with a nitrogen compound, the increase in deposit formation was much less than in the untreated fuel.

See Table 66.