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FLUIDS, LUBRICANTS, FUELS AND RELATED MATERIALS

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FOREWORD

This report was prepared by the Petroleum Refining Laboratory of the College of Chemistry and Physics at The Pennsylvania State University under Air Force Contract No. AF33(616)-5460. This contract was initiated under Project No. 8128, "Transmission Technology," Task No. 73313, "Power System Fluids," and Project No. 3044, "Aviation Lubricants," Task No. 73314, "Liquid and Solid Lubricants Development." This work was administered under the direction of the Fluids and Lubricants Branch, Nonmetallic Materials Laboratory, Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, with Mr. Harold W. Adams as project engineer.

This report covers work conducted from January through December 1959.

ABSTRACT

This report describes work carried out on a continuing program to characterize the capabilities of various base stocks and fluid formulations for application as hydraulic fluids and/or jet engine lubricants under a wide variety of conditions. An antiwear or chemical polishing mechanism similar to that suggested for tricresyl phosphate is shown for silicon-containing fluids with ferrous bearing surfaces. Variables designed to improve yield, efficiency, and fluid properties are discussed for low temperature solvent dewaxing. In many cases, the viscosity-temperature characteristics of the oil and wax fractions are both better than those of the original oil prior to separation. Formulation, distribution, and hardware testing of several mineral oil fluids for use over the range of -65° to >700°F. are noted. Results obtained in a 550°F. Vickers pump test program are discussed. The basic trends in thermal degradation with mineral oils have been studied in a pressure cylinder. Quantitative evaluation of the gaseous and liquid reaction products suggest different mechanisms for the gas and liquid phase reactions. The effectiveness of inhibitor combinations as antioxidants versus a single inhibitor is illustrated at temperatures of 347°, 400°, and 500°F. The use of a small volume test to evaluate materials available in limited quantities is discussed. A series of samples which have been in storage for periods of 2 to 17 years are being revaluated for changes in properties due to storage. An insight into the mechanism of oxidation on or in the vicinity of hot metal surfaces is provided by quantitative oxidation studies in the controlled atmosphere panel coker. A series of successive tests in the panel cokers has been used to explore further the mechanism of coking and the variables governing the deposit. Deposition type tests in a single-pass lube rig are also discussed.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

R. L. Adamczak

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SUMMARY

High Temperature Hydraulic Fluids and Jet Engine Lubricants. Work under this contract is concerned with the development and evaluation of improved fluids and lubricants for use under a variety of conditions over a wide temperature range. In general, no distinction as to end use is made in the various studies. Rather, current emphasis is placed on a better understanding of the capabilities of a given fluid under a wide variety of practical conditions.

Generally, the studies included in this report relate to the following topics.

(1) A better understanding of the lubricity behavior of silicon-containing fluids.
(2) Improvement in the capabilities of mineral oils.
(3) A cooperative effort to evaluate fluid and lubricant formulations.
(4) A critical evaluation of thermal stability.
(5) The determination of fluid capabilities.
(6) The quantitative evaluation of oxidation, corrosion, and deposition characteristics.

A survey of lubricity data experimentally determined by this Laboratory over a period of years is presented to point out a potential explanation of lubrication difficulties experienced with the silicones and silicates in ferrous bearing systems. Data presented indicate that the fluids may preferentially react with the ferrous bearing surface to form a soft but inert compound or alloy involving iron and silicon. This mechanism is similar to the mechanism which has been proposed for the antiwear reaction of materials such as tricresyl phosphate. The data shown have been obtained using a gear pump, a vane pump, and/or the Shell four-ball wear tester. The experimental data shown appear to support and to be consistent with this theory of silicone and silicate lubricity action with bearing surfaces.

Studies to optimize the viscosity-volatility-low temperature fluidity properties of mineral oils and hydrocarbons have been continued. The effect of viscosity level or boiling point on wax yield is evaluated by the deep dewaxing (-65°F) of a series of paraffinic mineral oil fractions. This series of narrow boiling fractions covers a viscosity range of 15 to 83 centistokes at 100°F and normal boiling points over the range of 750° to 920°F. The effect of several dispersant Acryloid polymers on the deep dewaxed oils is shown. In all cases, the amount of thickening caused by the polymer is less, percentage-wise, at -40° than at 210°F. This is in contrast to conventional military hydraulic fluids such as Spec. MIL-H-5606 which have about the same or a higher percentage viscosity due to the polymer at low temperature than at high temperature.

Data are shown for various properties of the charging stock, the oil fraction, and the wax fraction for dewaxings involving paraffinic and naphthenic mineral oils and aromatic and polyolefin hydrocarbons. Sufficiently severe dewaxings (-65° to -80°F) produce an oil phase exhibiting extrapolated viscosity values at the pour point in the range of 200,000 to 500,000 centistokes. A two-stage dewaxing procedure indicates that a wax-oil separation approaching the theoretical yield of each component can be obtained using simple dewaxing techniques. Changes in viscosity level and viscosity- temperature characteristics for both the oil fraction and the wax fraction are noted. In many cases the viscosity-temperature characteristics of the oil and wax fractions are both better than those of the original oil prior to separation.

The effect of pour depressants on filtration time and on the amount of oil occluded with the wax cake has been determined. Some studies to determine the most efficient solvent for use in low-temperature dewaxings are outlined. These studies include the evaluation of various solvent to oil ratios employing a single solvent as well as advantages and disadvantages encountered using a mixture of solvents. The effect of cooling rate and dewaxing temperature has been evaluated by using dry ice (-110°F) as a coolant as well as the conventional cold box (-65° to -80°F).

Several types of research and development programs in which experimental high temperature fluids are being evaluated by various organizations are listed. Results obtained by various organizations in development studies indicate excellent agreement with laboratory studies conducted by this Laboratory.

Results obtained in a Vickers pump test program with a prototype of a mineral oil fluid designed to be operational over a temperature range of -65° to +700°F are discussed. The fluid (MLO 7460) used in this program exhibits the same general high temperature lubricity and stability characteristics as the low temperature fluid (MLO 7485). However, MLO 7460 has not been dewaxed and, therefore, does not have the low temperature properties shown by MLO 7485. A precipitate was noted during the course of one of the pump tests. An examination of the precipitate indicates that it could not have been formed from any of the constituents of MLO 7460, but that it is probably the result of contamination of the hydraulic system from previous tests.

A number of fluids have been stored in an unheated storage building for periods of 2 to 17 years. Preliminary evaluation of about 60 of these fluids has been carried out. These samples include esters, mineral oils, hydrocarbons, and silicones as well as complete formulations using these materials as base stocks. This preliminary examination includes changes in such properties as viscosity, neutralization number, lubricity level, low temperature fluidity, homogeneity, and oxidative stability. Evidence is presented to show that the additive package may adversely affect storage stability in some cases.

A series of thermal stability tests have been conducted to determine the basic trends in thermal behavior of fluids in a semi-quantitative manner. The fluids used in these studies include paraffinic and naphthenic mineral oils and aromatic and polyolefin hydrocarbons. A modification of the liquid seal for the glass thermal stability apparatus is described. The modified seal allows gas leakage from the test unit at a pressure drop greater than 0.3 inch of mercury but prevents the leakage of air into the unit at a pressure drop of less than 24 inches of mercury.

The thermal degradation reactions occurring have been studied by determining the rate of gas formation; by the analysis of the gaseous product which is non-condensable at room temperature; and by a more rigorous examination of the liquid product. These studies have been carried out with the products from thermal stability tests conducted in a stainless steel pressure cylinder. The rate of gas formation has been measured as a function of pressure build-up with test time. The effect of variables such as heated gas space and test temperature on reaction rate has been investigated. The gas phase of the thermal degradation products has been analyzed quantitatively using a Perkin-Elmer Single-Stage Vapor Fractometer, Model 154C after careful calibration.

Changes in viscosity and neutralization number and degree of unsaturation have, in the past, been used to characterize the liquid product from thermal stability tests. In the present work, a small scale vacuum fractionation has been used to evaluate further the liquid product from the thermal stability tests. Boiling ranges of the liquid products are compared to that of the original test fluid. The data show that the degradation product contains a fraction boiling below the charging stock, a fraction boiling in the same range as the charging stock, and a fraction boiling higher than the original test fluid.

Data are presented which suggest the establishment of an equilibrium between degradation products and reactants in the thermal behavior of the mineral oils tested.

Recent research and development work at the Wright Air Development Division has suggested the use of 5-ethyl-10,10-diphenylphenazasiline (5-10-10) alone and in combination with other inhibitors as an antioxidant for Spec. MIL-L-9236 ester type lubricants. The combination of 5-10-10 and phenyl-alpha-naphthylamine (PAN) in a trimethylol propane ester has shown up well in bench tests, mock-up tests, and in a 400°F test in the J-57 engine. The initiation of a program to determine quantitatively the effect of 5-10-10 alone and in combination with PAN on oxidative stable life, oxidation rate, and oxygen tolerance is presented in this report. Various types of esters are being used in this study. In addition, other additives such as phenothiazine and Primene-81R (a primary aliphatic amine) are being evaluated alone and in combinations.

It has not been possible, in many cases, to evaluate completely the oxidative behavior of some materials available for use as high temperature fluid and lubricant components because of the limited sample size. The Spec. MIL-L-7808 type test used by this Laboratory has been modified to allow evaluation at 347° or at 500°F using a charge of 25 milliliters instead of the 100 milliliters normally required by a Spec. MIL-L-7808 or Federal Spec. VV-L-791e type test. Test geometry is kept the same for the two tests. Data comparing the small volume tests with the Spec. MIL-L-7808 type tests at 347° or at 500°F are presented.

A series of 13 experimental neopentyl type esters obtained from the Food Machinery and Chemical Corporation is discussed in WADC TR 55-30 Pt VII. Using the small volume oxidation procedure discussed above, it has been possible to evaluate the oxidative behavior of these materials at 347° and at 500°F. Stable life type tests have been conducted at 347°F At 500°F , oxidation rate and oxygen tolerance are emphasized.

A series of oxidation tests at 400°F with several esters is presented. The effectiveness of additives and additive combinations at this intermediate temperature is discussed. The data obtained at 400°F provide a link between the stable life studies at 347°F and oxidation rate and oxygen tolerance studies at 500°F. These studies, along with studies at 347° and 500°F. discussed in this report and earlier reports, provide a better understanding of the capability of the various ester fluids and formulations. Oxygen assimilation data show a definite absorption rate during the so-called stable life period. This rate is affected by the use of additive combinations rather than a single antioxidant.

A modification of the Spec. MIL-L-7808 type oxidation test in which samples of the fluid are taken at 72 and at 120 hours and the total test time is 168 hours has been used to evaluate this series of fluids at 400°F. This test procedure has been used previously at 347° and at 500°F. Magnesium corrosion is encountered in these 400°F tests. The effect of the magnesium on oxidation behavior is shown. In general, the additive combinations are more effective than phenothiazine alone in these fluids. The effect of a dispersant Acryloid and of a dialkyl acid phosphite lubricity additive on fluid dirtiness has been determined.

A series of deposition tests has been conducted in the controlled atmosphere (C.A.) panel coker. An insight into the mechanism of oxidation on or in the vicinity of hot metal surfaces is provided by quantitative oxidation studies in the C.A. coker. A comparison of paraffinic and naphthenic mineral oil formulations in the C.A. coker is presented. Decreased coking tendencies with increasing boiling point is illustrated for a series of narrow boiling mineral oil fractions. For the fluids used in these studies, oxygen assimilation is lower for the higher volatility fluids which show excessive coking.

The increased coke deposit caused by the presence of a dithiocarbamate additive in the test fluid is shown to be materially reduced by the addition of a dispersant Acryloid to the formulation. The effect of additives on the amount of oxygen assimilated in the C.A. panel coker is demonstrated.

A series of successive tests in the panel cokers has been used to explore further the mechanism of coking and the variables governing the deposit. The successive tests are conducted in eight-hour increments with the panel being replaced at the beginning of each increment. The same fluid is used throughout the series of tests.

Additional deposition type tests have been conducted in the single-pass high temperature lube rig. In this lube rig, deposit forming tendencies on a hot metal surface under severe oxidation conditions are measured. The effect of such variables as storage time of the test fluid, acid phosphite additives, fluid volatility, test time, and the type of metal deposition surface has been determined.

Miscellaneous. The preparation and distribution of a number of samples of experimental high temperature hydraulic fluids is noted.

The preparation of additional fluids for evaluation in the Universal gear and spline tester by the Western Gear Corporation is listed.

The distribution of a number of miscellaneous samples is discussed. These samples have been distributed for evaluation as high temperature fluids, for use as base stocks in additive studies, and for the determination of resistance to radiation.

Organizations to which samples of low temperature viscosity standard PRL 2815 and standard fluids PRL 3207 and PRL 3462 for interlaboratory calibration of the Shell four-ball wear tester are listed.

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I. HIGH TEMPERATURE HYDRAULIC FLUID AND JET ENGINE LUBRICANT STUDIES

A. GENERAL. Studies during this period have been directed toward the formulation and evaluation of improved hydraulic fluids and lubricants and the determination of the capabilities of various fluids and lubricants over a wide performance and temperature spectrum.

Points particularly emphasized include: (1) a mechanism for the antiwear action of silicon-containing fluids; (2) extending the temperature range of mineral oils by super-refining and low temperature dewaxing; (3) a more critical evaluation of the thermal degradation products of mineral oils and hydrocarbons; (4) an improved understanding of fluid capabilities through observation of samples stored for relatively long periods of time as well as through specially designed accelerated tests; (5) a cooperative effort with various organizations to evaluate fluids and lubricants formulated as a result of extensive laboratory testing; and (6) the quantitative evaluation of oxidation, corrosion, and deposition characteristics of various fluids.

Primary emphasis in this report is placed on mineral oils, hydrocarbons and esters as base stocks. Previous fluid and lubricant studies conducted by this Laboratory have been presented in detail in Annual Reports WADC TR 55-30 Parts I through VII. These reports were prepared under Contracts AF33(038)-18193, AF33(616)-2851, and AF33(616)-5460.

These background data in the fields of hydraulic fluids and lubricants encompass a large number of chemical classes of liquids. Essentially all of the evaluation and test techniques utilized in this work were also developed as a part of work performed under these contracts and are described in the previous Annual Reports mentioned above.

Studies presented in this report are applicable to the fields of hydraulic and functional fluids as well as to lubricants for primary, secondary, and auxiliary power plants. Severity and type of thermal stress, oxidative environment, and lubricity may vary with the application. Stress is placed on the evaluation of various liquids so that the capabilities of a particular fluid may be assayed in terms of the requirements of a given application.

B. SILICONES AND SILICATES AS LUBRICANTS. The properties of silicones and silicates have been evaluated by this Laboratory for the last 15 years as hydraulic fluids and lubricants. On the basis of viscosity and overall stability characteristics, these fluid types show an excellent potential for such applications. The silicon-containing fluids do, however, exhibit consistently poor lubricity characteristics for steel-on-steel bearing surfaces. These inadequacies in lubricity for ferrous systems have been attributed to several of the unique properties of some of the silicone type fluids such as: (1) the extreme stability of this type of molecular

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structure to deterioration by thermal and oxidizing environments; (2) the non-wetting characteristics of these materials on metal surfaces; and (3) the unusually high compressibility and viscosity-pressure coefficients of the silicones as these factors affect the hydrodynamic component of quasi-hydrodynamic lubrication.

A survey of experimentally determined lubricity data obtained by this Laboratory points to still another potential explanation of lubrication difficulties experienced with the silicones and silicates in ferrous bearing systems. These data indicate that the fluids may preferentially react with the ferrous bearing surface to form a relatively soft but inert compound or alloy involving iron and silicon. The formation of a relatively low melting soft or ductile compound parallels the behavior of the phosphorous-containing antiwear additives in providing antiwear or chemical polishing and surface mating for low bearing loads.

The mechanism of the antiwear action of materials such as tricresyl phosphate has been shown to comprise the formation at the bearing surface of an iron-phosphorus alloy of relatively low melting point and good ductility so that larger bearing areas are formed, which in turn lower bearing loads per unit contact area and temperatures. The low threshold of seizure and welding may be an indication of the extreme inertness of the surface film formed on the bearing surface which effectively prevents the chemical erosion that typifies the action of extreme-pressure (E.P.) and mild E.P. lubricity additives. This theory of silicone and silicate lubricity action with ferrous bearing surfaces appears to be consistent with and supported by the experimental data which are presented here.

A series of lubricity tests were conducted with a Pesco gear pump under 2500 p.s.i. load for 100 hours at 200°F and 3600 r.p.m. These are severe conditions used for the evaluation of Spec. MIL-H-5606 fluids during the early developmental stages. A series of pump test results are shown on Table 1. Gear testing has shown a substantial hydrodynamic component (viscosity) of lubricity as well as boundary component (chemical activity) of lubricity. The data sequence with PRL 1912, which is a Spec. MIL-H-5606 fluid without tricresyl phosphate shows the boundary lubricity sensitivity of the Pesco gear pump. The addition, stepwise, of tricresyl phosphate and ester plus tricresyl phosphate shows substantial steel-on-steel lubricity improvement in terms of antiwear properties.

The dimethyl silicone (PRL 1836) fluid shown on Table 1 was used for a total of 700 hours in seven tests of 100 hours duration. The temperature for these tests was 100° and 200°F ; the pump speed was 1800 and 3600 r.p.m.; and the system pressure 1000 and 3000 p.s.i. The conditions shown on the table are for the last 100-hour test which was conducted under the most severe conditions. The wear on the pump is for a total of 700 hours of running. The total gear wear in the 700 hours of silicone testing is as low as the best mineral oil-base fluid in a severe 100-hour test.

Several observations appear pertinent in this series of tests. The silicone fluid has a viscosity of 16 centistokes at 200°F. compared with a base stock of 1.3 and an overall viscosity of 5.0 centistokes at 200°F. for the mineral oil-base fluid. The silicone, then, has a substantially higher viscosity and hydrodynamic component of lubricity. Observation of the used gears in the case of the silicone indicates a substantial amount of surface distortion on the gears. That is, the final appearance of the gears from the silicone runs shows a surface appearance generally encountered with poor lubricity, high wear fluids. This appearance coupled with the low weight loss suggests a boundary component of lubricity giving gross plastic deformation of the metal surface. These data suggest strongly the formation of a lower melting and/or more ductile layer of material on the gear surface than the original hardened steel surface.

In general, there is good agreement between 1 and 10 kilogram load wear values in the Shell four-ball wear tester and the behavior of lubricants in gear and vane type hydraulic pumps. The four-ball wear and E.P. data for the dimethyl silicone and several mineral oil formulations are shown on Tables 2 and 3. These data show the continued improvement of phosphorous type lubricity additives in the antiwear area and of acid phosphites in both wear and antiseize properties. The silicone shows relatively good antiwear properties at 1 and 10 kilograms but poor antiseize properties in the wear tester at 40 kilograms and in the E.P. tester. The silicone also shows a lack of improvement in wear and seizure properties with the addition of polar and effective phosphorous type lubricity additives. Again close evaluation of the wear surface in the four-ball may be helpful in establishing a mechanism for the silicone. The wear scar of the silicone fluid at low loadings contains, randomly located throughout the mated surface between the rubbing surfaces, pock marks indicative of spot welding, despite a generally well mated or worn-in surface. At high loadings, the evidence of seizure and welding dominates the picture.

The basic behavior of the methyl silicone discussed, thus far, suggests the positive action or reaction of this material with the steel surface to form a soft, ductile, but extremely unreactive surface film. Such a film lends itself to surface mating in much the same fashion as the film formed by mineral oils containing phosphorous type lubricity additives. The lack of antiseize or antiweld properties suggests the inertness of such a film to further chemical reaction. In general, E.P. properties are achieved by materials which react readily with the bearing surface to form a chemical compound which in turn is easily wiped from the bearing surface. This mechanism results in a continuous chemical erosion at the bearing surface. The inability of normally reactive antiwear or E.P. additives to function adequately in the silicones also suggests that the silicones have a high order of affinity for the metal surface (polarity). To become involved in the wear or lubricity process it is estimated that the molecules involved must be within a few molecular layers of the actual metal surface. Low melting chemically inert alloys of silicon and iron which are suggested by these studies are known in the field of metal alloys.

This Laboratory has conducted an extensive test program in the area of high temperature lubricity. These studies include both the four-ball wear testers and the Vickers vane pumps. The silicones and silicate fluids, as a general class, have shown relatively poor high temperature lubricity. In general, it appears that these silicon-containing materials show a poorer temperature coefficient of lubricity than do the mineral oils or esters.

These data are illustrated on Table 4 for the vane pump and on Table 5 for the four-ball wear tester. These data indicate tha the increase in bulk system temperature accelerates lubricant failures by the seizure and welding mechanism for the silicones and silicates, in general, to a greater extent than in the case of mineral oils and esters. The suggested formation of a lower melting inert surface layer where sufficient heat from the environment plus friction leads to seizure and welding type failures is consistent with the experimentally determined trends in the case of the silicates and silicones. In the case of the esters and mineral oils, however, increased temperature increases reactivity with the metal surface to form an easily sheared film which tends to counteract the trend of increased heat from environment plus friction that would be expected to lower the lubricity failure point with increasing temperature.

Another series of tests has been used to confirm further the polarity of the silicones and silicates and their participation in the lubricity reaction. This series of studies was carried out in the Shell four-ball wear and E.P. testers. These testers, by virtue of their configuration, have essentially no component of hydrodynamic lubrication. Boundary or chemical lubricity action is emphasized in this tester. The two base stocks used for this series of tests are: a highly refined naphthenic mineral white oil, and di-2-ethylhexyl sebacate. Wear data in the Shell four-ball wear tester are shown on Table 6 and E.P. tester data are shown on Table 7. The effect of 1.0 weight per cent tricresyl phosphate in each base stock is shown as a reference point. The silicon-containing materials used as additives in this study include a methyl silicone (D.C. type 200), methylphenyl silicone (D.C. type 500), improved lubricity chlorinated silicone (G.E. Versilube F-50), tetra-2-ethylhexyl silicate, and a compounded silicate fluid Oronite 8200. In all cases in both solvents, these silicon-containing materials show antiwear effectiveness. The antiwear properties are more effective at 1 and 10 kilogram loads than at 40 kilograms.

The silicones and silicates show little or no improvement in the seizure and weld points of the base fluids in the E.P. lubricity testers. In general, the silicones and silicates behave as additives in mineral oils and esters in essentially the same fashion as when evaluated neat. That is, in both cases, the silicones and silicates act as chemical polishing antiwear additives at low bearing loadings but show little or no effectiveness in preventing seizure and welding. In this respect, they show a close analogy to the behavior of the phosphorous type antiwear additives such as tricresyl phosphate.

The phosphorous type antiwear additive mechanism as a chemical polishing agent can be adequately demonstrated by a sequence of tests in the Shell four-ball wear tester. In this sequence type evaluation, two successive one-hour tests in the four-ball wear tester are conducted with the same set of test balls on the same wearing surfaces. The first step is a conventional one-hour test. Following this test, the balls and ball pot are thoroughly cleaned with a solvent without removing the balls from the ball pot or rotating chuck. The apparatus is then reassembled and a second one-hour test is conducted with a new charge of test fluid. Using this technique, the test fluid may be the same for both tests, or a different test fluid may be used in the second portion of the test.

A series of double runs illustrating the "run-in" properties of various additive types in a mineral oil base stock are shown on Table 8. These data show that in the case of the non-additive fluid and all of the antifriction and E.P. type additives, wear continues at a substantial rate for the second incremental test using the same fluid in both tests. For the same series of test fluids, the wear continues for the second incremental test if a non-additive mineral oil is used for this second test. However, if a phosphorous type antiwear additive such as tricresyl phosphate, triphenyl thiophosphate, or diisopropyl acid phosphite is used in the first test, a second test with the same fluid or with a non-additive fluid can be conducted with essentially no increase in the wear scar. In general, these double runs adequately illustrate the mechanical erosion of non-additive mineral oils, the chemical erosion of antifriction and E.P. additives, and the chemical polishing (surface mating) of the phosphorous-containing antiwear additives.

A series of double runs have been made with the silicones and silicates as antiwear additives in mineral oil and ester base stocks (Table 9). The second run of the series was made, in each case, with the non-additive base stock. At one kilogram, all of the double runs with silicones show the same kind of chemical polishing or antiwear effect as has been demonstrated for the phosphorous type antiwear additive. At loads of 10 and 40 kilograms, the silicones are not completely effective in providing a well "run-in" surface. The tricresyl phosphate additive provides a well "run-in" surface for 1 and 10 kilogram loads in this test sequence, but is not always effective at 40 kilograms. In view of the relative merits of silicone and tricresyl phosphate in preventing seizure and welding, the comparison between their behavior as antiwear or chemical polishing agents appears to be of the right order of magnitude. The silicate does not appear to be as effective as the silicone as a chemical polishing agent. The Oronite 8200 is more effective than the tetra-2-ethylhexyl silicate. Oronite 8200 is a finished formulation which probably contains, in addition to a silicate type base stock, a silicone thickener and lubricity additives.

The silicones in this double run sequence in the four-ball wear tester do illustrate antiwear behavior consistent with the data obtained in hydraulic pumps and other four-ball wear tester studies.

Thus far, all data point to the similar behavior of the silicones and phosphorous-containing antiwear additives. An additional series of four-ball studies have been carried out to explore further the nature of these two types of antiwear effects and the competition for the preferential position on the bearing surface between the silicon type and the phosphorous type additives. Tricresyl phosphate and phosphoric acid are the two phosphorous type additives used in this comparison. These materials differ in polarity and, therefore, in minimum concentration to provide good antiwear properties.

Data obtained with several phosphorous-containing materials having different degrees of polarity are shown on Table 10. These data illustrate the use of a trialkyl phosphate, a dialkyl acid phosphate, and phosphoric acid as antiwear additives in di-3-methylbutyl adipate. In this diester, three to five weight per cent of tricresyl phosphate is required to give antiwear improvement. In contrast, a concentration of 0.05 weight per cent of dilauryl acid phosphate or 0.01 weight per cent of phosphoric acid gives optimum antiwear behavior.

The phosphoric acid may be considered a bifunctional additive in mineral oils and esters. At low concentrations of less than 0.1 weight per cent, this material provides antiwear properties with a minimum effect on E.P. properties. This behavior is typical of tricresyl phosphate at concentrations of 1 to 5 per cent. At concentrations of 0.5 weight per cent and higher, the phosphoric acid provides E.P. properties as well as antiwear properties. In the four-ball tester, the highest concentration of the phosphoric acid additive used (1.0 weight per cent) shows indications of the chemically erosive E.P. properties characteristic of the acid group rather than the antiwear properties of the phosphorus portion of the molecule. Diisopropyl acid phosphite behaves in a manner similar to that shown for the dilauryl acid phosphate. At high concentrations of diisopropyl acid phosphite, the chemically erosive nature of the acid grouping begins to be evident in the lubricity reaction.

The E.P. effect of the diisopropyl acid phosphite on the mineral oil and ester base stocks is illustrated on Table 11. The same concentration of this additive has also been evaluated in the silicone and silicate fluids. The lack of effectiveness of the acid phosphite in these silicon-containing materials is also shown on Table 11.

Shell four-ball wear and E.P. tester results with the diisopropyl acid phosphite and silicone or silicate additives tested separately and in combination are shown on Table 12 and 13. The base stocks for these additive tests are a diester (Table 12) and a highly refined naphthenic white oil (Table 13). In both base stocks, the 0.5 weight per cent diisopropyl acid phosphite provides good antiwear, antiseize, and antiweld properties. In both base stocks, the two silicones and silicate antiwear additives at 5.0 weight per cent concentration provide antiwear properties but do not alter significantly the antiseize and antiweld properties of the base stock. The combination of phosphorous- and silicon-containing additives in all cases shows some or all of the E.P. effects of the diisopropyl acid phosphite. In both base stocks, however, there is a general trend indicating an interference in lubricity action between the two additive types. This interference is best illustrated by the consistent trend toward higher wear for the combined additives at the 10 kilogram load than for either additive alone; and a general trend for a reduction in seizure and weld point for the combination of additives over that obtained from the acid phosphite alone.

To summarize, the silicates and silicones show antiwear characteristics under low bearing loadings in boundary conditions coupled with consistently poor antiseize and antiweld properties under more severe boundary conditions. This behavior of the silicones and silicates can be consistently demonstrated to be a function of chemical reactivity with the bearing surface when these materials are tested neat or as an additive in mineral oils and esters. The data indicate that the antiwear behavior of these silicon-containing materials parallels closely the mechanism of the phosphorous type antiwear additives. This parallel suggests the reaction of the iron and silicon to form a lower melting ductile surface film that is more inert toward further chemical reaction than the original steel surface.

C. LOW TEMPERATURE MINERAL OIL PROGRAM. Preliminary studies designed to optimize the properties of mineral oils and hydrocarbons were reported in WADC TR 55-30 Pt VII. These studies comprise three separate areas of investigation. Super-refining studies are designed to produce a base stock free of polar impurities which exhibits inhibitor susceptibility comparable with the synthetics. Vacuum fractionation of mineral oils and hydrocarbons has been used to optimize the viscosity-volatility properties to afford improved high temperature properties for a given viscosity grade. Deep dewaxing has been applied to mineral oils and hydrocarbons to extend the liquid range of the narrow boiling fractions prepared by vacuum fractionation. Preliminary deep dewaxing studies already reported have shown that with adequate techniques, paraffinic and naphthenic mineral oils and aromatic hydrocarbons can be dewaxed to a pour point equivalent to a viscosity level of 200,000 to 500,000 centistokes. Measured low temperature viscosities on these deep dewaxed paraffinic and naphthenic mineral oils show a lower viscosity value than that predicted from a straight line on the ASTM viscosity-temperature chart in the range of 0° to -40°F. The deep dewaxing operations with the narrow boiling fractions of the paraffinic mineral oils were accomplished with very good oil yield. The wide boiling range paraffinic bright stock gave relatively low oil yields.

To determine the effect of viscosity level or boiling point on wax yield from paraffinic mineral oil fractions, a series of narrow boiling fractions covering a viscosity range of 15 to 83 centistokes at 100°F were dewaxed at -65°F according to the procedure outlined in WADC TR 55-30 Pt VII. The 83-centistoke fraction represents the highest boiling range (920°F normal boiling point) overhead product from the fractional distillations. The 15-centistoke fraction has a normal boiling point of about 750°F A total of three different crude sources and six different commercial neutral mineral oil products are represented in the dewaxing data shown on Table 14.

Table 1

LUBRICITY TESTS CONDUCTED IN A PESCO MODEL 349 GEAR PUMP

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 200°F.; TEST TIME = 100 HOURS; TEST SPEED = 3600 R.P.M.; AND PRESSURE RELIEF PROVIDED BY A VICKERS MODEL C-167 VALVE.

TEST FLUID		TEST PRESSURE, P.S.I.	RATE OF FLOW, G.P.M.	CENTISTOKE VISCOSITY AT 200°F.	LOSS IN WEIGHT OF PUMP PARTS, GRAMS		
DESIGNATION	DESCRIPTION				DRIVE GEAR	IDLER GEAR	BUSHINGS(1)
PRL 1912	SPEC. MIL-H-5606 TYPE FLUID WITHOUT TRICRESYL PHOSPHATE (MINERAL OIL-BASE FLUID).	2500	3.43	5.5	0.104	0.090	0.167
PRL 2724	PRL 1912 + 1.0 WEIGHT PER CENT TRICRESYL PHOSPHATE.	2500	3.26	5.5	0.026	0.018	0.130
PRL 2026	PRL 1912 + 20 WEIGHT PER CENT DI-2-ETHYLHEXYL SEBACATE + 1.0 WEIGHT PER CENT TRICRESYL PHOSPHATE.	2500	2.65	5.3	0.005	0.006	0.530
PRL 1836	DIMETHYL SILICONE OIL (2)	3000	3.28	16	0.010(2)	0.000(2)	0.105(2)

(1) VALUE SHOWN IS THAT FOR THE TOTAL LOSS ENCOUNTERED BY THE FOUR BUSHINGS IN THE PUMP.

(2) A SERIES OF SEVEN 100-HOUR TESTS WERE CONDUCTED ON THIS FLUID (USING ONE SET OF PUMP PARTS THROUGHOUT) AT PRESSURES RANGING FROM 1000 TO 3000 P.S.I., AT PUMP SPEEDS OF 1800 OR 3600 R.P.M., AND AT A TEST TEMPERATURE OF 100°F. WEAR VALUES SHOWN ARE THE TOTALS FOR THE ENTIRE 700 HOURS OF TEST.

Table 2

WEAR CHARACTERISTICS OF SEVERAL FLUIDS

TESTS CONDUCTED IN THE SHELL FOUR-BALL WEAR TESTER

TEST CONDITIONS INCLUDE: TEST TIME = 1 HOUR; TEST TEMPERATURE = 75°C.; TEST SPEED = 620 R.P.M.; STEEL BALLS = SKF INDUSTRIES GRADE NO. 1 (0.5 INCH DIAMETER) STEEL BALL BEARINGS.

TEST FLUID		AVERAGE WEAR SCAR DIAMETER, MM.		
DESIGNATION	DESCRIPTION	1 KG.	10 KG.	40 KG.
PRL 1912	SPEC. MIL-H-5606 TYPE FLUID WITHOUT TRICRESYL PHOSPHATE (MINERAL OIL BASE FLUID)	0.34	0.54	1.04
PRL 2724	PRL 1912 + 1.0 WEIGHT PER CENT TRICRESYL PHOSPHATE	0.14 0.14	0.23 0.25	0.47 0.46
PRL 2026	PRL 1912 + 20 WEIGHT PER CENT DI-2-ETHYLHEXYL SEBACATE + 1.0 WEIGHT PERCENT TRICRESYL PHOSPHATE	0.16	0.22	0.51
MLO 7021	NAPHTHENIC WHITE OIL (3 CS. AT 100°F.)	0.46	0.71	0.89
-	1.0 WT.% TRICRESYL PHOSPHATE IN MLO 7021	0.15	0.23	0.44
	0.5 WT.% DIISOPROPYL ACID PHOSPHITE IN MLO 7021	0.27	0.36	-
MLO 7144	NAPHTHENIC WHITE OIL (80 CS. AT 100°F.)	0.22	0.47	0.61
-	1.0 WT.% TRICRESYL PHOSPHATE IN MLO 7144	0.14	0.22	0.39
-	0.5 WT.% DIISOPROPYL ACID PHOSPHITE IN MLO 7144	0.18	0.30	0.46
MLO 7071	PARAFFINIC NEUTRAL (100 CS. AT 100°F.)	0.20	0.43	0.59
-	1.0 WT.% TRICRESYL PHOSPHATE IN MLO 7071	0.15	0.26	0.41
-	0.5 WT.% DIISOPROPYL ACID PHOSPHITE IN MLO 7071	0.19	0.32	0.45
PRL 1836	DIMETHYL SILICONE OIL	0.32	0.39	1.40
PRL 2094	DIMETHYL SILICONE OIL	0.35	0.48	1.75
-	0.5 DIISOPROPYL ACID PHOSPHITE IN PRL 2094	0.39	0.56	1.17

Table 3

LUBRICITY CHARACTERISTICS OF SEVERAL FLUIDS

TESTS CONDUCTED IN SHELL FOUR-BALL EXTREME-PRESSURE LUBRICANT TESTER

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = ROOM TEMPERATURE (70°-80°F.); TEST TIME = 1 MINUTE; AND TEST SPEED = 1750 R.P.M.
STEEL BALLS = SKF INDUSTRIES GRADE NO. 1 (0.5 INCH DIAMETER) 52-100 STEEL BALL BEARINGS

DESIGNATION	TEST FLUID DESCRIPTION	APPROXIMATE LOAD FOR INCIPIENT SEIZURE, KG.	APPROXIMATE LOAD FOR PERMANENT WELDING, KG.	AVERAGE WEAR SCAR DIAMETER, MM. 40 KG.	60 KG.	80 KG.	100 KG.	120 KG.	140 KG.
MLO 7021	A NAPHTHENIC WHITE OIL (3 CS. AT 100°F.)	<40	100	1.78	1.97	2.62	WELDED		
-	MLO 7021 + 1.0 WT.% TRICRESYL PHOSPHATE	40	100	0.45	2.18	2.40	WELDED		
-	MLO 7021 + 0.5 WT.% DISOPROPYL ACID PHOSPHITE	130	140	-	0.43	-	0.49	0.54	WELDED
PRL 1836	A DIMETHYL SILICONE OIL	<40	120	1.36	-	2.34	-	WELDED	
-	PRL 1836 + 0.5 WT.% DIISOPROPYL ACID PHOSPHITE	<40	120	1.56	2.25	-	2.66	WELDED	
PRL 3076	ESTER-BASE FORMULATION WITHOUT A LUBRICITY ADDITIVE	50	100	0.42	2.42	2.66	WELDED		
PRL 3161	5.0 WT.% TRICRESYL PHOSPHATE IN PRL 3076	70	140	0.32	0.35	2.29	-	2.98	WELDED
PRL 3514	0.5 WT.% DIISOPROPYL ACID PHOSPHITE IN PRL 3076	190	200 *	-	-	-	-	-	- *

* 160 KG. = 0.52; 180 KG. = 0.55; 200 KG. = WELDED.

Table 4

LUBRICITY TESTS IN THE VICKERS VANE PUMP

TESTS CONDUCTED IN THE PRL HIGH TEMPERATURE PUMP TEST UNIT.
TEST PRESSURE = 700 P.S.I. UNLESS OTHERWISE INDICATED.

TEST FLUID	TEST TEMP., °F.	TEST TIME, HRS.	FLOW RATE, G.P.M. INITIAL	FLOW RATE, G.P.M. FINAL	FLUID VISCOSITY AT TEST TEMP., C'STOKES	AV. WT. LOSS PER VANE, MG.
SILICATE HYDRAULIC FLUID	300	4	4.9	4.9	1.9	0.7
	400	4	4.3	2.8	1.2	1.5(1)
	500	0.5(2)	1.8	1.2	0.9	1.3(2)
DI-2-ETHYLHEXYL SEBACATE + 0.5 WT. % PHENOTHIAZINE	300	4	5.4	5.4	1.8	0.4
	400	4	4.9	4.6	1.0	+0.3
	500	4	3.4	2.7	0.8	2.3
HIGH TEMPERATURE HYDRAULIC FLUID 8515	400	4	3.8	3.3	3.0	1.9(1)
	500	4	2.1	<1.0(3)	2.1	2.2(3)
CHLORINE-CONTAINING SILICONE (81406)	100	4	5.4	5.4	44.6	0.0
	400(4)	4(4)	<1.0(4)	<1.0	3.9	1.3
NAPHTHENIC NEUTRAL + 0.5 PHENYL-ALPHA-NAPHTHYLAMINE	500	4	1.8	1.8	0.9	0.0
NAPHTHENIC NEUTRAL + 1.0 WT. % PARANOX 441 + 5.0 WT.% TRICRESYL PHOSPHATE	600	4	2.3	1.2	0.6	18.0

(1) EXCESSIVE CAM RING AND VALVE PLATE WEAR NOTED AFTER COMPLETION OF TEST. A SMALL AMOUNT OF COLLOIDAL METAL WAS OBSERVED IN RESERVOIR DURING OPERATION.

(2) OPERATION AT 500°F. AND 700 P.S.I. WAS TERMINATED AFTER 0.5 HOURS BECAUSE STEADY OPERATION COULD NOT BE MAINTAINED. COLLOIDAL METAL APPEARED IN RESERVOIR DURING TEST. EXCESSIVE VALVE PLATE WEAR WAS NOTED AFTER COMPLETION OF TEST.

(3) DURING OPERATION AT 500°F. COLLOIDAL METAL WAS OBSERVED IN THE RESERVOIR. THE FLOW RATE DROPPED STEADILY FROM 2.1 TO LESS THAN 1.0 G.P.M. AS A RESULT, THE SYSTEM PRESSURE COULD NOT BE MAINTAINED AT 700 P.S.I. AND DROPPED STEADILY TO 450 P.S.I. DURING THE COURSE OF THE RUN.

(4) PUMP WAS OPERATED AT 400°F. FOR 4 HOURS. UNDER THESE CONDITIONS, THE FLOW RATE WAS TOO LOW TO MEASURE WITH THE CALIBRATED ORIFICE USED TO DETERMINE FLOW RATE. SEVERE CAM RING AND VALVE PLATE WEAR WERE OBSERVED AFTER THE COMPLETION OF THE TEST.

Table 5

EFFECT OF TEMPERATURE ON THE WEAR CHARACTERISTICS OF SEVERAL FLUIDS

TEST CONDITIONS INCLUDE: TEST TEMPERATURE AS INDICATED; TEST TIME = 1 HOUR; TEST SPEED = 620 R.P.M.; BEARINGS = 52-100 STEEL BEARINGS (0.5-INCH DIAMETER) SKF INDUSTRIES GRADE NO. 1, PRL BATCH NO. 12.

TESTS AT 500° AND 600°F. WERE CONDUCTED UNDER A CONTROLLED ATMOSPHERE. THIS WAS ACCOMPLISHED BY INTRODUCING DRY AIR AT A RATE OF 0.7 LITERS PER HOUR INTO THE GAS SPACE OVER THE BALL POT.

TEST FLUID	TEST TEMP., °F.	AVERAGE WEAR SCAR DIAMETER, MM.		
		1 KG.	10 KG.	40 KG.
SILICATE FLUID O.S. 45 (PRL 3505)	167	0.21	0.44	0.63
	500	0.35	0.72	1.43
SILICATE FLUID O.S. 45-1 (MLO 7037)	500	0.72	1.04	1.62
	600	0.78	1.17	1.19
SILICATE FLUID 8200 (PRL 3506)	167	0.35	0.64	0.89
	500	0.28	0.81	1.62
	600	0.29	1.38	1.30
IMPROVED SILICONE FLUID 81406 (MLO 7016)	167	0.18	0.31	0.67
	500	0.39	0.77	1.56
	600	0.29	1.38	1.30
IMPROVED SILICONE FLUID F-4050 (MLO 7012)	167	0.36	0.67	0.83
	500	0.67	0.77	1.04
DI-2-ETHYLHEXYL SEBACATE (PRL 3509)	167	0.34	0.56	0.69
	500	0.48	0.80	0.96
	600	0.22	0.63	1.10
A NAPHTHENIC NEUTRAL (PRL 3457)	167	0.28	0.42	0.60
	500	0.31	0.47	1.38
	600	0.20	0.57	1.71
A POLYOLEFIN (MLO 7014)	500	0.21	0.32	1.08
	600	0.29	0.86	1.69

Table 6

EFFECT OF SILICONES AND SILICATES AS ANTIWEAR ADDITIVES

ALL TESTS CONDUCTED IN THE SHELL FOUR-BALL WEAR TESTER.
TEST CONDITIONS INCLUDE: TEST TIME = 1 HOUR; TEST TEMPERATURE = 75°C. (167°F.); TEST SPEED = 620 R.P.M.
STEEL BALLS = SKF INDUSTRIES GRADE NO. 1 (0.5 INCH DIAMETER) 52-100 STEEL BALL BEARINGS, PRL BATCH NO. 12.

TEST FLUID (COMPOSITIONS IN WT. %)	AVERAGE WEAR SCAR DIAMETER, MM. 1 KG.	10 KG.	40 KG.
DI-2-ETHYLHEXYL SEBACATE (MLO 7038)	0.36	0.52	0.70
MLO 7038 + 0.5 PHENOTHIAZINE	0.43	0.56	0.80
+ 1.0 TRICRESYL PHOSPHATE	0.14	0.26	0.37
+ 5.0 DOW CORNING NO. 200 SILICONE (PRL 2094)	0.15	0.25	0.62
+ 5.0 DOW CORNING NO. 500 SILICONE (PRL 2091)	0.18	0.25	0.50
+ 1.0 TETRA-2-ETHYLHEXYL SILICATE (PRL 3455)	0.39	0.54	0.78
+ 5.0 TETRA-2-ETHYLHEXYL SILICATE (PRL 3455)	0.15	0.25	0.60
+ 5.0 ORONITE 8200 SILICATE FLUID (PRL 3506)	0.16	0.25	0.46
+ 5.0 VERSILUBE F-50 (MLO 7017)	0.17	0.29	0.50
A WELL-REFINED NAPHTHENIC MINERAL OIL (PRL 2964)	0.49	0.62	0.99
+ 1.0 TRICRESYL PHOSPHATE	0.15	0.23	0.44
+ 5.0 DOW CORNING NO. 200 SILICONE (PRL 2094)	0.22	0.37	0.84
+ 5.0 DOW CORNING NO. 500 SILICONE (PRL 2091)	0.25	0.40	1.06
+ 5.0 TETRA-2-ETHYLHEXYL SILICATE (PRL 3455)	0.36	0.56	1.04
+ 5.0 ORONITE 8200 SILICATE FLUID (PRL 3506)	0.26	0.58	0.79
+ 5.0 VERSILUBE F-50 (MLO 7017)	0.41	0.41	0.64

Table 7

EFFECT OF SILICONES AND SILICATES AS LUBRICITY ADDITIVES

ALL TESTS CONDUCTED IN THE SHELL FOUR-BALL EXTREME-PRESSURE LUBRICANT TESTER.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = ROOM TEMPERATURE (70° TO 80°F.); TEST TIME = 1 MINUTE; AND TEST SPEED = 1750 R.P.M.
STEEL BALLS = SKF INDUSTRIES GRADE NO. 1 (0.5 INCH DIAMETER) 52-100 STEEL BALL BEARINGS, PRL BATCH NO. 12.

TEST FLUID (COMPOSITIONS IN WT.%)	APPROX. LOAD FOR INCIPIENT SEIZURE, KG.	APPROX. LOAD FOR PERMANENT WELDING, KG.	AVERAGE WEAR SCAR DIAMETER, MM. 40 KG.	60 KG.	80 KG.	100 KG.	120 KG.
DI-2-ETHYLHEXYL SEBACATE (MLO 7038)	<60	100	-	2.38	2.51	WELDED	
MLO 7038 + 0.5 PHENOTHIAZINE	-	100	-	-	2.49	WELDED	
+ 5.0 TRICRESYL PHOSPHATE	90	100	-	0.36	0.43	WELDED	
+ 5.0 DOW CORNING NO. 200 SILICONE (PRL 2094)	<60	100	-	1.88	2.47	WELDED	
+ 5.0 DOW CORNING NO. 500 SILICONE (PRL 2091)	90	100	-	0.39	0.42 *	WELDED	
+ 1.0 TETRA-2-ETHYLHEXYL SILICATE (PRL 3455)	<60	100	-	2.21	2.47	WELDED	
+ 5.0 TETRA-2-ETHYLHEXYL SILICATE (PRL 3455)	70	100	-	0.42	2.47	WELDED	
+ 5.0 ORONITE 8200 SILICATE FLUID (PRL 3506)	70	120	-	0.39	2.40	2.34	WELDED
+ 5.0 VERSILUBE F-50 (MLO 7017)	70	100	0.39	0.46	2.62	WELDED	
A WELL REFINED NAPHTHENIC MINERAL OIL (PRL 2964)	<40	100	1.78	1.97	2.62	WELDED	
+ 5.0 DOW CORNING NO. 200 SILICONE (PRL 2094)	<40	100	1.56	-	3.31	WELDED	
+ 5.0 DOW CORNING NO. 500 SILICONE (PRL 2091)	<40	100	1.15	2.97	-	WELDED	
+ 5.0 TETRA-2-ETHYLHEXYL SILICATE (PRL 3455)	70	100	-	0.42	2.47	WELDED	
+ 5.0 ORONITE 8200 SILICATE FLUID (PRL 3506)	40	100	0.93	2.03	1.95	WELDED	
+ 5.0 VERSILUBE F-50 (MLO 7017)	<40	80	1.86	2.43	WELDED	-	

* CHECK RUN VALUE = 0.44.

Table 8

EFFECT OF "RUN-IN" ON THE SHELL FOUR-BALL WEAR TESTER

TEST CONDITIONS INCLUDE: TEST TIME = 1 HOUR; TEST SPEED = 620 R.P.M.: TEST TEMPERATURE = 75°C.· BEARINGS = SKF INDUSTRIES GRADE NO. 1 (0.5-INCH DIAMETER) 52-100 STEEL BALL BEARINGS, PRL BATCH NO. 9

TEST FLUIDS INCLUDE:
PRL 2574 = A TYPICAL HYDROCARBON-BASE HYDRAULIC FLUID WITH NO LUBRICITY ADDITIVE.
PRL 3078 = 1.0 WT.% TRICRESYL PHOSPHATE IN PRL 2574
PRL 3105 = 1.0 WT.% TRIPHENYL THIOPHOSPHATE IN PRL 2574
PRL 3711 = 0.5 WT.% DIISOPROPYL ACID PHOSPHITE IN PRL 2574
PRL 3145 = 1.0 WT.% ORTHOLEUM 162(1) IN PRL 2574
PRL 3146 = 1.0 WT.% STEARIC ACID IN PRL 2574
PRL 3139 = 1.0 WT.% SANTOPOID S(2) IN PRL 2574

TEST FLUID DESIGNATION		AVERAGE WEAR SCAR DIAMETER, MILLIMETERS					
		1 KILOGRAM LOAD		10 KILOGRAM LOAD		40 KILOGRAM LOAD	
1ST TEST(3)	2ND TEST(4)	1ST TEST(3)	2ND TEST(4)	1ST TEST(3)	2ND TEST(4)	1ST TEST(3)	2ND TEST(4)
PRL 2574	PRL 2574	0.40	0.48	0.56	0.68	0.66	0.76
PRL 3078	PRL 3078	0.18	0.18	0.23	0.24	0.54	0.63
PRL 3105	PRL 3105	0.19	0.20	0.22	0.23	0.42	0.46
PRL 3711	PRL 3711	-	-	0.44	0.45	-	-
PRL 3146(5)	PRL 3146(5)	-	-	0.35	0.47	0.42	0.58
PRL 3139	PRL 3139	-	-	0.61	0.73	0.84	0.95
PRL 3078	PRL 2574	0.16	0.16	0.23	0.23	0.56	0.57
PRL 3105	PRL 2574	0.19	0.20	0.22	0.22	0.38	0.40
PRL 3711	PRL 2574	0.27	0.28	0.36	0.37	0.45	0.46
PRL 3145	PRL 2574	-	-	0.35	0.54	0.45	0.68
PRL 3146(5)	PRL 2574	0.30	0.40	0.35	0.54	0.42	0.62
PRL 3139	PRL 2574	0.43	0.45	0.61	0.72	0.84	0.91

(1) ORTHOLEUM 162 IS BELIEVED TO BE ESSENTIALLY DILAURYL ACID PHOSPHATE.
(2) SANTOPOID S IS A CHLORONAPHTHA XANTHATE CONTAINING 10-15 WT.% S AND 30-35 WT.% CL.
(3) TEST CONDUCTED WITH THE INDICATED FLUID AND A NEW SET OF BALL BEARINGS IN CONVENTIONAL FASHION.
(4) BALLS FROM THE FIRST TEST WERE USED IN THE SAME POSITION FOR THE SECOND TEST. BETWEEN TESTS THE BALL POT AND BALLS WERE THOROUGHLY WASHED AND DRIED AND THE SECOND FLUID CHARGED. THE SECOND TEST SCAR IS THE TOTAL SCAR SIZE RESULTING FROM TWO HOURS RUNNING.
(5) BLEND WAS SLIGHTLY CLOUDY INDICATING INCOMPLETE SOLUBILITY.

Table 9

EFFECT OF "RUN-IN" ON THE SHELL FOUR-BALL WEAR TESTER USING SILICONES AND SILICATES AS LUBRICITY ADDITIVES

TEST CONDITIONS INCLUDE: TEST TIME = 1 HOUR; TEST SPEED = 620 R.P.M.; TEST TEMPERATURE = 75°C.; BEARINGS = SKF INDUSTRIES GRADE #1 (0.5-INCH DIAMETER) STEEL BALL BEARINGS, PRL BATCH NO. 12.

TEST FLUID = DI-2-ETHYLHEXYL SEBACATE + 0.5 WT.% PHENOTHIAZINE		AVERAGE WEAR SCAR DIAMETER, MILLIMETERS					
		1 KILOGRAM LOAD		10 KILOGRAM LOAD		40 KILOGRAM LOAD	
1ST TEST(1) ADDITIVE, WT.%	2ND. TEST(2) ADDITIVE, WT.%	1ST. TEST(1)	2ND. TEST(2)	1ST. TEST(1)	2ND. TEST(2)	1ST. TEST(1)	2ND. TEST(2)
NONE	NONE	0.44	0.48	0.56	0.64	0.85	1.04
5.0 ORONITE 8200 SILICATE FLUID (PRL 3506)	NONE	0.16	0.17	0.28	0.44	0.69	0.86
5.0 TETRA-2-ETHYLHEXYL SILICATE (PRL 3455)	NONE	0.16	0.35	0.24	0.57	0.66	0.93
5.0 DOW CORNING NO. 500 SILICONE (PRL 2091)(3)	NONE	0.21	0.22	0.36	0.45	0.57	0.63
2.0 DOW CORNING NO. 500 SILICONE (PRL 2091)(3)	NONE	0.16	0.33	0.28	0.46	0.69	0.86
5.0 VERSILUBE F-50 (MLO 7017)	NONE	0.17	0.23	0.29	0.48	0.50	0.68
TEST FLUID = A NAPHTHENIC WHITE MINERAL OIL (MLO 7021)							
NONE	NONE	0.46	0.58	0.71	0.86	0.89	1.06
5.0 ORONITE 8200 SILICATE FLUID (PRL 3506)	NONE	0.24	0.25	0.56	0.71	0.82	1.17
5.0 TETRA-2-ETHYLHEXYL SILICATE (PRL 3455)	NONE	0.22	0.26	0.42	0.47	1.00	1.12
5.0 DOW CORNING NO. 500 SILICONE (PRL 2091)	NONE	0.29	0.31	0.42	0.49	0.89	1.11
5.0 DOW CORNING NO. 200 SILICONE (PRL 2094)	NONE	0.30	0.32	0.50	0.56	0.96	0.99
5.0 VERSILUBE F-50 (MLO 7017)	NONE	0.41	0.41	0.41	0.51	0.64	0.93

(1) TEST CONDUCTED WITH THE INDICATED FLUID AND A NEW SET OF BALL BEARINGS IN CONVENTIONAL FASHION.

(2) BALLS FROM THE FIRST TEST WERE USED IN THE SAME POSITION FOR THE SECOND TEST. BETWEEN TESTS THE BALL POT AND BALLS WERE THOROUGHLY WASHED AND DRIED AND THE SECOND FLUID CHARGED. THE SECOND TEST SCAR IS THE TOTAL SCAR SIZE RESULTING FROM TWO HOURS RUNNING.

(3) THE BLEND IS SLIGHTLY CLOUDY INDICATING INCOMPLETE SOLUBILITY.

Table 10

EFFECT OF CONCENTRATION ON ANTIWEAR PROPERTIES OF PHOSPHOROUS-CONTAINING ADDITIVES

Tests Conducted in the Shell Four-Ball Wear Tester
Test Conditions Include: Test Temperature = 75°C.; Test Speed = 620r.p.m; Test Time = 1 Hour; Steel Balls = SKF Industries Grade No. 1 (0.5-inch Diameter) 52-100 Steel Ball Bearings.

Test Fluid (Conc. in Wt.%)	Average Wear Scar Diameter, mm. 1 Kg.	10 Kg.	40 Kg.
Di-3-Methylbutyl Adipate	0.39	0.71	0.91
+ 1.0 Tricresyl Phosphate	0.38	0.71	0.97
+ 3.0 Tricresyl Phosphate	0.40	0.64	0.97
+ 5.0 Tricresyl Phosphate	0.23	0.25	0.78
+ 0.01 Dilauryl Acid Phosphate	0.21	0.41	0.84
+ 0.05 Dilauryl Acid Phosphate	0.19	0.28	0.43
+ 1.0 Dilauryl Acid Phosphate	0.17	0.28	0.42
+ 0.001 Phosphoric Acid	0.41	0.69	0.90
+ 0.01 Phosphoric Acid	0.16	0.37	0.50
+ 1.0 Phosphoric Acid	0.38	0.60	0.78

Table 11

EFFECT OF AN ACID PHOSPHITE ADDITIVE ON THE LUBRICANT BEHAVIOR OF SOME FLUIDS

TEST CONDITIONS INCLUDE: WEAR TESTER – TEST TEMPERATURE = 75°C.; TEST SPEED = 620 R.P.M.; TEST TIME = 1 HOUR.

E.P. TESTER – TEST TEMPERATURE = ROOM TEMPERATURE (70°–80°F.); TEST TIME = 1 MINUTE; AND TEST SPEED = 1750 R.P.M.

STEEL BALLS = SKF INDUSTRIES GRADE NO. 1 (0.5–INCH DIAMETER) 52–100 STEEL BALL BEARINGS, PRL BATCH NO. 12.

TEST FLUID (CONC. IN WT.%)	WEAR TESTER AVERAGE WEAR SCAR DIAM., MM.			<– – – – – – – – – – – – EXTREME – PRESSURE LUBRICITY TESTER – – – – – – – – – – – – –>								
				APPROX. LOAD FOR		AVERAGE WEAR SCAR DIAMETER, MM.						
	1 KG.	10 KG.	40 KG.	INCIPIENT SEIZURE, KG.	PERMANENT WELDING, KG.	40 KG.	60 KG.	80 KG.	100 KG.	120 KG.	140 KG.	160 KG.
A NAPHTHENIC MINERAL OIL (MLO 7021)	0.46	0.71	0.89	<40	100	1.78	1.97	2.62	WELDED			
+ 0.5 DIISOPROPYL ACID PHOSPHITE	0.27	0.36	–	130	140	–	0.43	–	0.49	0.54	WELDED	
DI–2–ETHYLHEXYL SEBACATE + 0.5 PHENOTHIAZINE	0.43	0.56	0.80	50	100	0.42	2.38	2.51	WELDED			
+ 0.5 DIISOPROPYL ACID PHOSPHITE	0.15	0.24	0.40	190	200 *	–	–	–	–	–	–	0.52 *
TETRA–2–ETHYLHEXYL SILICATE (PRL 3455)	0.27	0.41	0.74	40	100	0.74	–	3.90	WELDED			
+ 0.5 DIISOPROPYL ACID PHOSPHITE	0.26	0.54	0.51	60	100	0.38	–	2.34	WELDED			
DIMETHYL SILICONE (PRL 2094)	0.35	0.48	1.75	–	–							
+ 0.5 DIISOPROPYL ACID PHOSPHITE	0.39	0.56	1.17	<40	120	1.56	2.25	–	2.66	WELDED		
VERSILUBE F–50 (MLO 7017)	0.18	0.31	0.67	40	100	–	0.93	1.86	WELDED			
+ 0.5 DIISOPROPYL ACID PHOSPHITE	0.21	0.41	0.80	40	100	0.74	–	2.19	WELDED			

* SCAR AT 180 KG. = 0.55; WELDS AT 200 KG.

Table 12

EFFECT OF PHOSPHOROUS - AND/OR SILICON-CONTAINING ADDITIVES ON THE LUBRICITY CHARACTERISTICS OF A DIESTER

TEST CONDITIONS INCLUDE: WEAR TESTER – TEST TEMPERATURE = 75°C., TEST SPEED = 620 R.P.M.; AND TEST TIME = 1 HOUR.
E. P. TESTER – TEST TEMPERATURE = ROOM TEMPERATURE (70°-80°F.); TEST TIME = 1 MINUTE; AND TEST SPEED = 1750 R.P.M.

STEEL BALLS = SKF INDUSTRIES GRADE NO. 1 (0.5-INCH DIAMETER) 52-100 STEEL BALL BEARINGS, PRL BATCH NO. 12.

TEST FLUID (CONC. IN WT.%)	WEAR TESTER AVERAGE WEAR SCAR DIAM., MM.			← EXTREME-PRESSURE LUBRICITY TESTER →								
				APPROX. LOAD FOR		AVERAGE WEAR SCAR DIAMETER, MM.						
	1 KG.	10 KG.	40 KG.	INCIPIENT SEIZURE, KG.	PERMANENT WELDING, KG.	60 KG.	80 KG.	100 KG.	120 KG.	140 KG.	160 KG.	180 KG.
DI-2-ETHYLHEXYL SEBACATE + 0.5 PHENOTHIAZINE	0.43	0.56	0.80	<60	100	2.38	2.51	WELDED				
+0.5 DIISOPROPYL ACID PHOSPHITE	0.15	0.24	0.40	190	200	-	-	-	-	-	0.52	0.55*
+5.0 TETRA-2-ETHYLHEXYL SILICATE	0.16	0.24	0.66	70	100	0.42	2.47	WELDED				
+5.0 TETRA-2-ETHYLHEXYL SILICATE AND 0.5 DIISOPROPYL ACID PHOSPHITE	0.47	0.54	0.63	190	200	-	-	0.47	0.49	-	0.51	0.57*
+5.0 DOW CORNING NO. 500 SILICONE (1)	0.21	0.36	0.57	90	100	0.39	0.42	WELDED				
+5.0 DOW CORNING NO. 500 SILICONE AND 0.5 DIISOPROPYL ACID PHOSPHITE(1)	0.19	0.47	0.53	150	160	-	-	-	-	0.49	WELDED	
+5.0 VERSILUBE F-50	0.17	0.29	0.50	70	100	0.46	2.62	WELDED				
+5.0 VERSILUBE F-50 AND 0.5 DIISOPROPYL ACID PHOSPHITE	0.19	0.44	0.53	190	200	-	-	0.44	-	0.50	-	0.56*

* WELDS AT THE 200 KILOGRAM LOAD.

(1) BLEND WAS CLOUDY INDICATING INCOMPLETE SOLUBILITY.

Table 13

EFFECT OF PHOSPHOROUS- AND/OR SILICON-CONTAINING ADDITIVES ON THE LUBRICITY CHARACTERISTICS OF A MINERAL OIL

TEST CONDITIONS INCLUDE: WEAR TESTER – TEST TEMPERATURE = 75°C.; TEST SPEED = 620 R.P.M.; AND TEST TIME = 1 HOUR.
E. P. TESTER – TEST TEMPERATURE = ROOM TEMPERATURE (70°–80°F.); TEST TIME = 1 MINUTE; AND TEST SPEED = 1750 R.P.M.

STEEL BALLS = SKF INDUSTRIES GRADE NO. 1 (0.5-INCH DIAMETER) 52-100 STEEL BALL BEARINGS, PRL BATCH NO. 12.

TEST FLUID (CONC. IN WT.%)	WEAR TESTER AVERAGE WEAR SCAR DIAM., MM.			< EXTREME-PRESSURE LUBRICITY TESTER >							
				APPROX. LOAD FOR		AVERAGE WEAR SCAR DIAMETER, MM.					
	1 KG.	10 KG.	40 KG.	INCIPIENT SEIZURE, KG.	PERMANENT WELDING, KG.	40 KG.	60 KG.	80 KG.	100 KG.	120 KG.	140 KG.
NAPHTHENIC WHITE MINERAL OIL (MLO 7021)	0.46	0.71	0.89	<40	100	1.78	1.97	2.62	WELDED		
+ 0.5 DIISOPROPYL ACID PHOSPHITE	0.27	0.36	–	130	140	–	0.43	–	0.49	0.54	WELDED
+ 5.0 TETRA-2-ETHYLHEXYL SILICATE	0.22	0.42	1.00	<40	80	2.01	–	WELDED			
+ 5.0 TETRA-2-ETHYLHEXYL SILICATE AND 0.5 DIISOPROPYL ACID PHOSPHITE	0.36	0.56	1.04	90	100	–	–	0.48	WELDED		
+ 5.0 DOW CORNING NO. 500 SILICONE	0.29	0.42	0.89	<40	100	1.15	2.97	–	WELDED		
+ 5.0 DOW CORNING NO. 500 SILICONE AND 0.5 DIISOPROPYL ACID PHOSPHITE	0.30	0.38	0.61	60	100	0.36	–	2.79	WELDED		
+ 5.0 VERSILUBE F-50	0.41	0.41	0.64	<40	80	1.86	2.43	WELDED			
+ 5.0 VERSILUBE F-50 AND 0.5 DIISOPROPYL ACID PHOSPHITE	0.32	0.50	0.57	50	100	0.36	2.73	2.73	WELDED		
+ 1.0 TRICRESYL PHOSPHATE	0.15	0.23	0.44								
+ 5.0 DOW CORNING NO. 200 SILICONE	0.22	0.37	0.84								
+ 5.0 DOW CORNING NO. 200 SILICONE AND 1.0 TRICRESYL PHOSPHATE	0.21	0.36	0.56								

The dewaxings were carried out with a 6:1 solvent to oil ratio using methyl isobutyl ketone solvent. A Corning sintered glass filter of fine porosity was used in conjunction with a large suction flask to filter the wax cake. The entire filter setup is housed in a -65°F cold box. In all cases, satisfactory filtration was attained without the use of filter aids. No attempt was made to recover the oil occluded by, or held up in, the wax cake on the filter. The theoretical wax yield is determined by assuming the solvent to wax-free oil ratio in the recovered oil is the same as that in the oil occluded by or held up in the wax cake. Stripping the wax cake to remove the solvent allows for a quantitative measure of oil in the wax cake. The theoretical wax yield is then the wax fraction corrected in this fashion for the oil phase contamination.

The data on Table 14 show that the wax yield is essentially constant at 15 ± 5 per cent for all of the narrow boiling fractions studied. The more viscous fractions, in general, hold up and occlude more oil in the wax cake than do the lower viscosity fractions. With the refrigerator operating at -65°F for dewaxing, the minimum pour point obtained is in the range of -50° to -55°F. Hence, for the lighter fractions, the viscosity equivalent to the pour point is less than 200,000 centistokes. However, for the more viscous fractions, the extrapolated viscosity at the pour point equals the 200,000 to 500,000 centistoke value previously noted. The same value can be achieved for the lower viscosity fractions by dewaxing at a lower temperature. This has been illustrated previously by several dewaxings at -80°F.

Dewaxing, in all cases, with the paraffinic fractions causes an increase in 100°F viscosity level. The wax fraction (wax plus occluded oil) shows a drop in viscosity but an increase in viscosity index or an improvement (lowering) in ASTM slope. The oil fraction, based on 100° and 210°F viscosities, shows a decrease in viscosity index and an increase in ASTM slope. However, the measured viscosities at -40°F are considerably lower than the extrapolated viscosities from a straight line on the ASTM chart. If the viscosity index or ASTM slope is based on the 210° to -40°F viscosity properties, the viscosity index of the oil yield actually increases and the ASTM slope is improved. The wax fraction plus the occluded oil represents a high quality liquid product for high temperature uses which has a pour point on the order of 10° to 30°F higher than the original neutral from which it is derived.

The deep dewaxing of a paraffinic neutral, therefore, presents an unusual case wherein both products of the dewaxing are in fact upgraded as regards viscosity-temperature characteristics. Both products should also have the same high order of thermal stability. The oxidative stability of both fractions would again be essentially equal, and the level of inhibitor susceptibility dependent primarily on the degree of refining or super-refining of the oil prior to deep dewaxing.

1. The Effect of Two-Stage Dewaxing on Oil Yield. The actual oil yield from a severe dewaxing of a narrow boiling paraffinic mineral oil fraction is of the order of 50 to 70 per cent. That is, the actual wax yield exceeds the theoretical wax fraction by a factor of 2 to 3. The additional

volume of fluid in the wax fraction is occluded oil held in the wax structure and in the filter cake. The relative quantities of oil and wax in the wax fraction are determined by the amount of solvent in the wax fraction. It is assumed that the wax precipitate is solvent-free but that the occluded oil contains solvent in the same solvent to oil ratio that is present in the recovered oil phase. Therefore, stripping the solvent from the wax fraction will determine the quantity of occluded oil and the wax is determined by difference.

The validity of this approach has been evaluated by several experiments designed to recover the occluded oil from the wax fraction. It should be emphasized that, in the initial dewaxings, no attempts have been made to remove the occluded oil from the wax cake. The wax fractions from several initial dewaxings have been redissolved in methylisobutyl ketone in a 6 to 1 solvent to oil ratio. The cooling and filtration steps are repeated and the oil and wax fractions recovered as in the initial dewaxings. The results of these second dewaxings are shown on Table 15. These data show, in each case, that additional oil exhibiting low temperature properties comparable to those of the oil fraction from the initial dewaxing is obtained.

After this second stage dewaxing, the total actual oil yield is increased from an initial value of 50 to 70 per cent to a yield of about 80 per cent. The wax fraction is decreased from 30 to 50 per cent in the initial dewaxing to 20 per cent after the second dewaxing. This value of the wax fraction after the second dewaxing approaches the theoretical wax yield. Mechanical and handling losses in the dewaxing procedure are under three per cent for this series of dewaxings. Since these losses are low, they have been distributed over the oil and wax fractions so that the product recovery in all cases totals 100 per cent. These data indicate that simple dewaxing techniques used to rework the wax fraction are capable of giving a wax-oil separation approaching the theoretical yields of each component.

2. Properties of the Oil and Wax Fractions. The data presented on Tables 16 and 17 show the properties of the oil and wax fractions as well as the original charging stock for a number of experimental dewaxings involving paraffinic and naphthenic mineral oils and synthetic aromatic and polyolefin hydrocarbons. The paraffinic and naphthenic mineral oils all yield an oil phase of higher viscosity level and a wax phase of lower viscosity level than the charging stock. In all of these cases, the wax fraction shows a higher viscosity index (V.I.) and improved ASTM slope over that of the charging stock. In general, the increase in viscosity index and the improvement in ASTM slope is directly proportional to the concentration of the actual wax in the wax fraction and to the temperature of dewaxing. These trends are illustrated by the properties of the wax fractions from the secondary wax recovery and the properties of the wax fraction from a -20°F dewaxing.

In all cases, the oil fractions appear to have a larger ASTM slope and a lower viscosity index than the charging stock based on 210° to 100°F viscosity properties. However, in every case when measured data are available at -40°F , the oil fractions show an improvement in ASTM slope and viscosity index based on the viscosity-temperature characteristics over the temperature range of 210° to -40°F.

The polyolefin (MLO 7391) dewaxing yields a wax fraction of higher viscosity level and lower viscosity index than the oil fraction. These data suggest that molecular weight as well as molecular configuration may be involved in the wax-oil separation for the polyolefin.

The aromatic hydrocarbon separation follows the general trends indicated for the paraffinic and naphthenic mineral oils. The properties of the waxy fraction indicate the presence of highly aromatic constituents in both the oil and wax fractions.

The dewaxing data presented on Table 16 and 17 show that, as a general trend, both the oil and the wax fractions show improved viscosity-temperature characteristics. The improvements in low temperature fluidity for the oil fractions are of the order of a 35° to 85°F lowering in pour point. In all cases, the cloud point of the oil fractions is below the pour point. The wax fractions from the initial dewaxing exhibit an increase in pour point of the order of 10° to 25°F. In the case of the paraffins and naphthenes, the wax fraction is a high quality product comparable in overall stability with the initial charging stock and the oil fraction and differing only in low temperature capability.

3. Effect of Pour Depressants on Low Temperature Dewaxing. Several Acryloid types show pour depressant characteristics in waxy oils. To act as a pour depressant, a material is believed to alter the crystalline structure of the wax. The filtration time and the amount of oil occluded with the wax cake are the properties of specific interest in this study.

The properties of the oil-Acryloid blends and the resultant oil and wax fractions are shown on Table 18. The rate of filtration for the Acryloid blends is slower than for the oil without the Acryloid by a factor of 2 or 3 in all cases. The amount of oil occluded with the wax fraction is significantly lowered in the dewaxing of blends containing the Acryloid. It is interesting to note, however, that essentially all of the Acryloid is found in the wax fraction. These yield data indicate that the Acryloid pour depressant affects the wax structure or wax phase.

Included on Table 18 are data for the filtration of a wax-free blend containing the same Acryloid pour depressant. The pour depressant was blended with a mineral oil fraction previously dewaxed at -75°F. The blend was then filtered through a fine, sintered-glass filter at -65°F. Viscosity properties before and after the filtration indicate that essentially all of the pour depressant is removed by the filter.

4. Effect of Solvent on Dewaxing Efficiency. The solvent to oil ratios in the deep dewaxing studies were in the range of 6:1 to 8:1. This ratio is higher than that encountered in conventional dewaxing to a 0°F pour point. As indicated by the data already presented, the quantity of wax is of the order of 15 per cent in all cases for the paraffinic mineral oil. This quantity of wax is about twice the quantity of wax removed in conventional dewaxing to 0°F of a typical paraffinic stock. The lower temperature (-65° to -80°F) results in higher viscosity levels for the solvent, oil, and blends than those encountered in conventional dewaxing at 0°F.

The viscosity of a wax-oil-solvent slurry at the filtration temperature is difficult to measure. However, fuel dilution studies on wax-free oils at low temperatures have been made by this Laboratory and are reported in WADC TR 55-30 Part VII. These data indicate that methods for predicting blend viscosities using ASTM test method D341-43 do apply fairly well for components of widely different viscosities. If this calculation technique is applied to the viscosity of the wax-oil-solvent blend on a wax-free basis, the problems of -75° versus 0°F. dewaxing can be illustrated. For a viscous mineral oil fraction such as a heavy neutral or bright stock, the calculated blend viscosity at 3:1 solvent to oil ratio is of the order of 4 to 7 centistokes at 0°F. At -75°F., the viscosity of the pure solvent is 10 centistokes based on a straight line relationship on the ASTM viscosity-temperature chart. The predicted wax-free solvent-oil blend viscosity at 6:1 solvent to oil ratio is in the range of 20 to 50 centistokes at -75°F. It is believed that the increased wax concentration and the increased viscosity of the liquid phase at -75°F. adequately account for the increased difficulty in filtration at -75°F. over 0°F. The use of solvent to oil ratios in the range of 6:1 to 8:1 minimizes these increased difficulties.

A series of dewaxing tests were conducted using methylisobutyl ketone, methylethyl ketone, and blends of these two ketones with the same fraction of paraffinic mineral oil under the same temperature conditions. The data covering the oil yields and properties are shown on Table 19. Under comparable conditions, there is a consistent trend in yield of the oil fraction as a function of methylisobutyl ketone concentration in the blend. Most of the low temperature dewaxings to date have been conducted with methylisobutyl ketone solvent. In general, dewaxing with methylisobutyl ketone solvent at temperatures of -50° to -75°F results in an oil phase which exhibits a pour point from 5° to 15°F higher than the dewaxing temperature. Because of the difficulty of conducting low temperature filtrations and the refrigeration involved, it is desirable to obtain the optimum yield of oil with the best low temperature properties possible under a given set of low temperature dewaxing conditions. Methylethyl ketone has been evaluated as a solvent instead of methylisobutyl ketone. Solubility limitations of the paraffinic neutrals in methylethyl ketone at temperature of -40°F. and lower appear to be severe. The dewaxing shown on Table 19 using methylethyl ketone at -50°F shows an oil yield in the first operation of only 20 per cent. A second dewaxing of the partially dewaxed oil shows about the same oil yield as the first step. These data indicate that the limitation in this series of experiments is due to insolubility of the oil phase in the ketone solvent. In general, however, the oil phase obtained from the methylethyl ketone dewaxing exhibits a pour point below the dewaxing temperature.

Blends of methylethyl ketone and methylisobutyl ketone have been studied as indicated on Table 19. The use of methylethyl ketone in conjunction with methylisobutyl ketone tends to improve the pour point of the dewaxed oil over that obtained at the same dewaxing temperature with methylisobutyl ketone alone. These data show that, while the pour point tends to improve with increasing methylethyl ketone concentration, the yield of dewaxed oil decreases. A 3:1 methylisobutyl ketone to methylethyl ketone ratio provides a good yield coupled with a desirable relationship between pour point and dewaxing temperature.

5. Effect of Cooling Rate and Dewaxing Temperature. Several preliminary experiments have been conducted to show the effect of cooling rate and dewaxing temperature on wax filtration and yield. The conventional dewaxing procedure used in these studies comprises cooling of a solvent-oil blend in a conventional cold box set to operate at -75°F. Containers having capacities of a quart to a gallon of the solvent-oil blend exhibit a cooling rate of approximately one degree per minute over the critical range of +30° to -75°F. The sample is allowed to soak at -75°F. for at least one hour, although in many cases 16 to 20 hour soak periods were used for convenience. There is no evidence that the additional soak time at -75°F affects either yield or ease of filtration.

The wax is filtered through a medium porosity sintered glass Pyrex filter with 15 millimeters mercury pressure in the filter flask and atmospheric pressure above. There is no attempt to press the filter cake. Variation in filtering time is indicative of the difficulty of filtration. In general, filtration time is increased by lowering filtration temperature, or by using shock cooling techniques. However, variation of wax structure and type among the range of paraffinic materials dewaxed at -75°F causes more variation in filtering time than the variation between the normal cooling rate of about one degree per minute and the shock cooling rate of five degrees per minute. The yield of oil and the resultant pour point of the oil phase is not materially altered by cooling rate over the range of cooling at one degree F. per minute to shock cooling (5°F per minute) rates.

The effect of temperature on yield and pour point for a paraffinic neutral is illustrated on Table 20. Dewaxing of MLO 7433-4-10 was conducted at -110°F. (dry ice temperature) at an 8:1 methylisobutyl ketone to oil ratio. Filtration technique in this study is the same as that employed at -75°F. The yield of oil phase from this dewaxing was 26.2 per cent and the pour point of the oil phase was less than -85°F. The wax phase from the -110°F dewaxing was allowed to warm to -75°F and after a 16-hour soak at this temperature was refiltered. An additional yield of 28.6 per cent of the original charge was recovered as oil yield. This fraction had a -85°F pour point. The total yield of oil from the two filtrations at -110° and -75°F respectively is then 54.8 per cent of the original charge. A second charge of the same stock, MLO 7433-4-10, was shock cooled to -110°F and held there for three hours. The fluid was then allowed to warm to -75°F. and filtered. The resultant oil phase is 64.3 per cent of the charge and exhibits a -80°F. pour point. It is interesting to note that cooling to -110°F and warming to -75°F did not adversely affect the yield, but did improve the pour point of the oil phase over simple dewaxings at -75°F with the same methylisobutyl ketone solvent.

6. Effect of a Polymeric Dispersant on Dewaxed Mineral Oils. A polymeric dispersant has been found to be an effective portion of the additive package for high temperature lubricant applications for mineral oils. The polymeric dispersants also improve the viscosity-temperature characteristics of the mineral oil base stock. The effect of several Acryloid polymers on deep dewaxed mineral oils is shown on Table 21. The -40°F viscosity values are measured properties in all cases. In all cases the dewaxed mineral oil

with and without the Acryloid polymer is clear at -40°F. in the viscometer. That is, there is no visual evidence of insoluble material. In all cases the amount of thickening caused by the Acryloid is less, percentage-wise, at -40° than at 210°F. In every case, the minimum effect on low temperature viscosity for a given increase in high temperature viscosity is shown by the Acryloid 966. This material has been used in an ester solvent to avoid difficulties from wax in the carrier oil.

Conventional military hydraulic fluids such as Spec. MIL-H-5606, Spec. MIL-F-17111, and Spec. MIL-L-6387 show about the same or a higher percentage of the viscosity due to the polymer at low temperatures than at high temperatures.

The Acryloid blends of MLO 7344 fractions all exhibit a tendency to change in -40°F. viscosity with time in the viscosity bath. In all cases the variation shown represents about two to three hours soak time at -40°F in the viscometer. The -40°F viscosity values of the MLO 7344 fractions without Acryloid give a constant viscosity value over the same soak period. The polymer solutions show no visual evidence of insolubility in the viscometers at -40°F.

The Acryloid blends of MLO 7358, MLO 7374, and MLO 7376 fractions, however, do exhibit stable -40°F viscosity values. With these fractions, high temperature thickening of 50 to 80 per cent can be achieved with Acryloid 966 with less than 10 per cent thickening at -40°F. These polymer-thickened deep dewaxed paraffinic mineral oil blends exhibit unique viscosity properties for the mineral oil class.

7. Deep Dewaxed Mineral Oils as Base Stocks for Formulations. The deep dewaxed paraffinic mineral oils offer a promising base stock for both hydraulic fluids and lubricants over the range of -40° to +700°F. The paraffinic mineral oils have been shown to be equivalent in thermal stability to the naphthenic mineral oils which have been extensively tested in the laboratory, in mock-up equipment, and in actual hydraulic pumps in the high temperature range of 500° to 700°F.

Data are presented on Table 22 to compare the viscosity properties of the fluids of suitable volatility to meet the 700°F high temperature requirements. Based on pour point, the lower limit of operation is 0°F for the aromatic hydrocarbon, -30°F for the naphthenic mineral oil, and -65°F. for the paraffinic mineral oil.

Based on a value of 13,000 centistokes limiting viscosity, the aromatic hydrocarbon is a +25°F fluid, the naphthenic mineral oil a 0°F fluid, and the deep dewaxed paraffinic mineral oil a -40°F. fluid. Based on thermal stability studies, the aromatic hydrocarbon has a life of the order of 20 hours or more at 750°F while the naphthenic and paraffinic mineral oils achieve this life at 700°F.

A comparison of lubricant properties are shown on Table 23. Spec. MIL-L-7808 and the more viscous ester-based fluid used in the turbo-prop engines are shown as reference points. Based on a Spec. MIL-L-7808 volatility level, the deep dewaxed paraffinic mineral oil can be used to formulate a fluid of about the same viscosity and low temperature properties as the turbo-prop engine oil. This means that, based on the Spec. MIL-L-7808 fluid, the present paraffinic mineral oil would have a -40°F capability compared with the -65°F capability of the current ester-base fluids. Again, as in the case of the hydraulic fluids, these paraffinic mineral oils have a capability of operation for reasonable times at 700°F even in an oxidizing environment. Operation at temperatures above 700°F would appear feasible on the basis of a one-pass or limited-pass lubricant system.

D. EXPERIMENTAL HIGH TEMPERATURE HYDRAULIC FLUIDS. Three types of mineral oil-base high temperature hydraulic fluids have been formulated as a result of the research effort on super-refined mineral oils. The aromatic hydrocarbon-base fluid (MLO 7244-type) appears to be suitable for the temperature range of +30° to 750°F. The potential commercial availability of this material is good, but current availability is very limited. Only small experimental samples of this material have been distributed for test purposes. The advantages of MLO 7244-type fluids over the naphthenic and paraffinic mineral oil formulations appears to be limited to applications in which temperatures of 700°F and above are encountered, or where radiation dosages are severe.

The naphthenic super-refined formulation MLO 7243 or MLO 7277 (both designations refer to the same fluid) is formulated from commercially available stocks. This material has a useful temperature range of 0° to 700°F and comprises a highly refined naphthenic white oil base stock, an oxidation inhibitor, an antiwear additive and an antifoam additive. Chemical and physical properties of this fluid are summarized on Tables 24, 25, 26, and 27.

This formulation has been supplied in 1-gallon to 50-gallon lots for research and development programs in the areas of seals, hydraulic pumps, hydraulic systems, servo-valves, accessory lubricants, etc.

A total of 340 gallons representing 22 specific samples of MLO 7277 have been prepared by this Laboratory and supplied to 15 different organizations. All of the data and comments received thus far from development studies with this fluid indicate excellent agreement with the laboratory studies conducted by this Laboratory.

These data include 50-hour tests in a high temperature hydraulic test stand conducted by Vickers Incorporated at a pump temperature of 550°F. All of these data continue to emphasize the 700°F potential of this fluid as a good lubricant and a stable fluid in a closed or airless system.

The third fluid is a paraffinic mineral oil-base fluid. The capability of a deep-dewaxed super-refined paraffinic mineral oil fluid MLO 7485 is illustrated on Table 28. This composition has been prepared in the laboratory and, therefore, is not available in large quantity for test

Table 14

DEEP DEWAXING OF PARAFFINIC MINERAL OILS

DEWAXINGS WERE CARRIED OUT AT -65°F. WITH A 6:1 SOLVENT TO OIL RATIO USING METHYL-ISOBUTYL KETONE.

TEST FLUIDS: MLO 7344 = A PARAFFINIC NEUTRAL OBTAINED FROM ESSO RESEARCH AND ENGINEERING COMPANY
MLO 7358 = A PARAFFINIC NEUTRAL OBTAINED FROM WOLFS HEAD OIL REFINING COMPANY
MLO 7363, MLO 7374, MLO 7375, AND MLO 7376 = PARAFFINIC NEUTRALS OBTAINED FROM THE KENDALL REFINING COMPANY

TEST FLUID MLO NO.	FRACT. NO.	CENTISTOKES VISC. AT 100°F. BEFORE	AFTER	ASTM SLOPE BEFORE (210 TO 100°F.)	AFTER (210 TO -40°F.)	THEOR. WAX YIELD, %	OIL OCCLUDED IN WAX, %	OIL SEP. FROM WAX, %	POUR POINT, °F. BEFORE	AFTER	EXTRAPOLATED CS. VISC. AT POUR POINT
7344	7	15.0	16.9	0.772	-	14	7.5	75	0	-50	15,000
	10	19.9	22.4	0.756	0.752	16	27	53	+15	-55	77,000
	11	22.3	26.0	0.753	0.750	18	16	62	+10	-55	100,000
	12	25.0	28.7	0.751	0.750	15	12	71	+10	-55	145,000
	13	28.0	33.1	0.747	0.746	15	27	57	+15	-55	180,000
	14	32.5	38.3	0.750	-	14	16	70	+20	-50	220,000
	14	32.5	38.2	0.750	0.744	14	38	46	+20	-55	355,000
7358	3	14.4	15.9	0.790	-	11	7.5	81	+5	-50	18,000
	7	20.6	23.3	0.773	0.768	12	17	70	+15	-55	108,000
	11	29.8	35.3	0.757	0.753	15	31	54	+25	-55	205,000
	20	83.2	114	0.712	-	17	20	63	+25	-40	500,000
7363	9	30.8	36.0	0.769	-	11	20	69	+10	-50	200,000
	20	70.3	90.6	0.729	-	16	22	62	+10	-40	640,000
7374	17	23.3	26.9	0.754	0.747	15	30	55	+10	-50	69,000
7375	8	31.4	37.7	0.755	-	14	32	51	+15	-55	370,000
	17	80.3	103	0.716	-	17	37	45	+5	-40	690,000
7376	2	23.0	26.0	0.774	-	11	17	71	+15	-50	80,000
	2	23.0	25.7	0.774	0.774	9	20	71	+15	-55	140,000

Table 15

EFFECT OF TWO-STAGE DEEP-DEWAXING ON YIELD

DEWAXINGS CARRIED OUT AT -65°F. USING METHYLISOBUTYL KETONE SOLVENT. SOLVENT TO OIL RATIO FOR INITIAL DEWAXINGS = 6:1. FOR THE SECOND DEWAXINGS, THE SOLVENT TO OIL RATIO = 8:1.

TEST FLUID	C'STOKE VISC. AT 100°F.	POUR POINT, °F.	YIELD, % OF CHARGE (2) WAX FRACTION	OIL FRACTION	TOTAL YIELD OF (1) DEWAXED OIL, % OF CHARGE
PARAFFINIC MINERAL OIL FRACTIONS					
CHARGE (MLO 7376-2)	23.0	+15	-	-	-
INITIAL DEWAXING	-	-	28.2	71.8	-
OIL FRACTION	26.0	-50	-	-	-
WAX FRACTION FROM INITIAL DEWAXING	17.4	-	-	-	-
SECOND DEWAXING	-	-	17.4	10.8	-
OIL FRACTION	26.1	-55	-	-	82.6
WAX FRACTION	14.5	-	-	-	-
CHARGE (MLO 7433-5)	9.60	-	-	-	-
INITIAL DEWAXING	-	-	45.7	54.3	-
OIL FRACTION	11.6	-55	-	-	-
WAX FRACTION FROM INITIAL DEWAXING	8.16	-	-	-	-
SECOND DEWAXING	-	-	23.2	22.5	-
OIL FRACTION	10.8	-55	-	-	76.8
WAX FRACTION	6.81	-	-	-	-
CHARGE (MLO 7433-8)	13.1	-	-	-	-
INITIAL DEWAXING	-	-	24.8	75.2	-
OIL FRACTION	15.6	-50	-	-	-
WAX FRACTION FROM INITIAL DEWAXING	-	+65	-	-	-
SECOND DEWAXING	-	-	18.0	6.8	-
OIL FRACTION	15.2	-40	-	-	82.0
WAX FRACTION	11.4	-	-	-	-
CHARGE (MLO 7433-9)	14.2	-	-	-	-
INITIAL DEWAXING	-	-	24.0	76.0	-
OIL FRACTION	15.7	-50	-	-	-
WAX FRACTION FROM INITIAL DEWAXING		-	-	-	-
SECOND DEWAXING	-	-	16.4	7.6	83.6
OIL FRACTION	17.2	-55	-	-	-
WAX FRACTION	9.65	-	-	-	-

(1) PER CENT YIELD OF OIL FRACTION FROM SECOND DEWAXING, AND THEREFORE THE TOTAL YIELD, ARE CALCULATED ON THE BASIS OF THE AMOUNT OF OIL CHARGED FOR THE INITIAL DEWAXING. MECHANICAL LOSSES ARE LESS THAN THREE PER CENT ARE DISTRIBUTED BETWEEN THE OIL AND WAX FRACTIONS.

Table 16

PROPERTIES OF DEEP DEWAXED PARAFFINIC MINERAL OILS

DEWAXINGS WERE CARRIED OUT AT INDICATED TEMPERATURES WITH A 6:1 SOLVENT TO OIL RATIO USING METHYLISOBUTYL KETONE.

TEST FLUID	C'STOKE VISCOSITY AT			ASTM SLOPE		VISCOSITY INDEX		EXTRAPOLATED(2) VISC. AT POUR PT. TEMP., CS.	CLOUD PT., °F.	POUR PT., °F.	YIELD, % OF CHARGE		
											WAX FRACTION		
	210°F.	100°F.	-40°F.	210° TO 100°F.	210° TO -40°F.	NORMAL	EXT. TEMP. RANGE (1)				THEOR. WAX	OCCLUDED OIL	OIL FRACTION
PARAFFINIC MINERAL OIL FRACTIONS													
CHARGE (MLO 7358-3)	3.16	14.4	-	0.790	-	86	-	393	+28	+5	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	10.9	7.6	81.2
OIL FRACTION	3.26	15.9	-	0.806	-	69	-	22,000	-58	-50	-	-	-
CHARGE (MLO 7344-7)	3.32	15.0	-	0.771	-	102	-	532	+36	0	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	13.8	7.5	75.1
OIL FRACTION	3.48	16.9	7,760	0.788	0.784	87	97	21,600	-54	-50	-	-	-
WAX FRACTION	2.86	10.5	-	0.730	-	136	-	-	-	-	-	-	-
CHARGE (MLO 7344-10)	3.98	19.9	-	0.756	-	108	-	287	+30	+15	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	16.1	26.9	53.1
OIL FRACTION	4.16	22.4	-	0.771	-	93	-	77,000	-60	-55	-	-	-
WAX FRACTION	3.69	16.7	-	0.742	-	122	-	-	-	-	-	-	-
CHARGE (MLO 7358-7)	3.95	20.6	-	0.773	-	92	-	333	+32	+15	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	11.9	17.4	69.7
OIL FRACTION	4.12	23.3	13,900	0.789	0.767	72	97	108,000	-62	-55	-	-	-
CHARGE (MLO 7344-11)	4.26	22.3	-	0.753	-	108	-	460	+28	+10	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	18.2	15.5	62.3
OIL FRACTION	4.55	26.0	15,800	0.765	0.750	95	108	120,000	-62	-55	-	-	-
CHARGE (MLO 7376-2)	4.19	23.0	-	0.774	-	88	-	408	+14	+15	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	10.5	17.4	71.2
OIL FRACTION	4.41	26.0	20,600	0.784	0.769	78	92	63,000	-56	-50	-	-	-
WAX FRACTION	3.74	17.4	-	0.747	-	118	-	-	-	-	-	-	-
CHARGE (MLO 7374-17)	4.37	23.3	-	0.753	-	107	-	512	+14	+10	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	15.1	29.8	54.5
OIL FRACTION	4.61	26.9	15,400	0.769	0.747	92	110	59,000	-56	-50	-	-	-
WAX FRACTION	4.07	19.8	-	0.741	-	121	-	-	-	-	-	-	-
CHARGE (MLO 7344-12)	4.56	25.0	-	0.749	-	107	-	560	+28	+10	-	-	-
DEWAXED AT -20°F.	-	-	-	-	-	-	-	-	-	-	6.6	3.5	88.0
OIL FRACTION	4.66	25.6	986*	0.758	0.748*	111	109*	2,900	-16	-15	-	-	-
WAX FRACTION	3.73	15.2	-	0.698	-	157	-	-	-	-	-	-	-
DEWAXED AT -40°F.	-	-	-	-	-	-	-	-	-	-	10.1	5.0	82.4
OIL FRACTION	4.61	26.8	5020**	0.760	0.753**	97	107**	6,300	-30	-25	-	-	-
WAX FRACTION	3.83	16.4	-	0.718	-	147	-	-	-	-	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	14.7	12.2	71.3
OIL FRACTION	4.79	28.7	20,200	0.767	0.751	94	106	145,000	-58	-55	-	-	-
WAX FRACTION	3.90	17.2	-	0.718	-	141	-	-	-	-	-	-	-
CHARGE (MLO 7344-13)	4.89	28.0	-	0.747	-	108	-	510	+26	+15	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	15.0	27.1	57.3
OIL FRACTION	5.23	33.1	29,000	0.763	0.747	96	107	180,000	<-55	-55	-	-	-
CHARGE (MLO 7358-11)	5.00	29.8	-	0.756	-	102	-	375	+28	+25	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	15.3	30.7	53.5
OIL FRACTION	5.33	35.3	37,600	0.772	0.753	89	103	205,000	<-55	-55	-	-	-
CHARGE (MLO 7363-9)	4.97	30.8	-	0.769	-	92	-	910	+6	+10	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	11.3	20.0	68.5
OIL FRACTION	5.29	36.0	-	0.782	-	81	-	185,000	-58	-50	-	-	-
WAX FRACTION	4.38	22.6	-	0.741	-	117	-	-	-	-	-	-	-

(CONCLUDED ON NEXT PAGE)

* CS. VISCOSITY AT 0°F.; ASTM SLOPE AND V.I. CALCULATED FOR TEMPERATURE RANGE OF 210° TO 0°F.
** CS. VISCOSITY AT -25°F.; ASTM SLOPE AND V.I. CALCULATED FOR TEMPERATURE RANGE OF 210° TO -25°F.

Table 16 (Concluded)

PROPERTIES OF DEEP DEWAXED PARAFFINIC MINERAL OILS

TEST FLUID	C'STOKE VISCOSITY AT			ASTM SLOPE		VISCOSITY INDEX		EXTRAPOLATED(2) VISC. AT POUR PT. TEMP., CS.	CLOUD PT., °F.	POUR PT., °F.	YIELD, % OF CHARGE		
											WAX FRACTION		
	210°F.	100°F.	-40°F.	210° TO 100°F.	210° TO -40°F.	NORMAL	EXT. TEMP. RANGE (1)				THEOR. WAX	OCCLUDED OIL	OIL FRACTION
CHARGE (MLO 7375-8)	5.14	31.4	-	0.755	-	101	-	660	+16	+15	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	14.0	31.8	51.2
OIL FRACTION	5.51	37.7	-	0.773	-	87	-	300,000	<-55	-55	-	-	-
CHARGE (MLO 7344-14)	5.30	32.5	-	0.750	-	105	-	535	+26	+20	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	14.3	16.9	69.5
OIL FRACTION	5.69	38.2	43,100	0.762	0.744	96	106	355,000	-64	-55	-	-	-
CHARGE (MLO 7363-20)	8.41	70.3	-	0.729	-	98	-	3,410	+6	+10	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	15.5	22.9	61.6
OIL FRACTION	9.31	90.6	-	0.746	-	84	-	640,000	<-40	-40	-	-	-
WAX FRACTION	7.26	50.4	-	0.711	-	113	-	-	-	-	-	-	-
CHARGE (MLO 7375-17)	9.32	80.3	-	0.716	-	100	-	5,350	+4	+5	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	17.4	38.0	45.0
OIL FRACTION	10.3	103	-	0.732	-	88	-	690,000	<-40	-40	-	-	-
CHARGE (MLO 7358-20)	9.60	83.2	-	0.711	-	101	-	1,680	+32	+25	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	16.2	20.9	62.6
OIL FRACTION	10.9	114	-	0.731	-	86	-	500,000	<-40	-35	-	-	-
WAX FRACTION	-	-	-	-	-	-	-	-	+54	+50	-	-	-
PARAFFINIC MINERAL OILS													
CHARGE (MLO 7344)	3.65	17.3	-	0.760	-	107	-	124	+32	+30	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	13.3	24.6	59.6
OIL FRACTION	3.85	19.7	-	0.772	-	94	-	41,000	<-55	-55	-	-	-
WAX FRACTION	3.30	13.7	-	0.740	-	126	-	-	-	-	-	-	-
CHARGE (MLO 7358)	5.09	30.7	-	0.755	-	103	-	635	+30	+15	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	15.3	30.0	54.4
OIL FRACTION	5.37	35.6	-	0.771	-	90	-	250,000	<-55	-55	-	-	-
WAX FRACTION	4.83	26.1	-	0.731	-	120	-	-	+44	+35	-	-	-
CHARGE (MLO 7375)	5.92	39.1	-	0.744	-	104	-	715	+16	+20	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	15.6	33.2	50.5
OIL FRACTION	6.22	45.0	-	0.761	-	92	-	320,000	<-50	-50	-	-	-
WAX FRACTION	5.57	33.2	-	0.728	-	117	-	-	+32	+35	-	-	-
CHARGE (MLO 7376)	11.5	113	-	0.706	-	97	-	4,900	+10	+15	-	-	-
DEWAXED AT -65°F.	-	-	-	-	-	-	-	-	-	-	22.7	30.8	46.5
OIL FRACTION	12.6	144	-	0.723	-	83	-	750,000	<-35	-35	-	-	-

(1) VISCOSITY INDEX CALCULATED USING THE VISCOSITY-TEMPERATURE CHARACTERISTICS OVER THE TEMPERATURE RANGE OF 210° TO -40°F.

(2) CALCULATED USING "TABLES FOR DETERMINATION OF ASTM SLOPE AND PREDICTION OF VISCOSITIES" COMPILED BY LAWRENCE T. EBY, ESSO RESEARCH AND ENGINEERING COMPANY.

Table 17

PROPERTIES OF SEVERAL DEEP DEWAXED FLUIDS

DEWAXINGS WERE CARRIED OUT AT THE INDICATED TEMPERATURE WITH THE SOLVENT SHOWN. SOLVENT TO OIL RATIOS RANGE FROM 4:1 TO 6:1.

TEST FLUID	SOLVENT USED	C'STOKE VISCOSITY AT 210°F.	C'STOKE VISCOSITY AT 100°F.	C'STOKE VISCOSITY AT -40°F.	ASTM SLOPE 210° TO 100°F.	ASTM SLOPE 210° TO -40°F.	VISCOSITY INDEX NORMAL	VISCOSITY INDEX EXT. TEMP. RANGE (1)	EXTRAPOLATED(2) VISC. AT POUR PT. TEMP., CS.	CLOUD PT., °F.	POUR PT., °F.	YIELD, % OF CHARGE WAX FRACTION THEOR. WAX	YIELD, % OF CHARGE WAX FRACTION OCCLUDED OIL	YIELD, % OF CHARGE OIL FRACTION
NAPHTHENIC MINERAL OILS														
CHARGE (MLO 7343-14)		4.05	23.1	-	0.796	-	69	-	9,500	-14	-30	-	-	-
DEWAXED AT -65°F.	MIK*	-	-	-	-	-	-	-	-	-	-	0.4	0.0	96.0
OIL FRACTION		4.03	22.9	17,740	0.796	0.784	68	81	390,000	<-70	-65	-	-	-
WAX FRACTION		4.00	22.4	-	0.795	-	70	-	-	-	-	-	-	-
CHARGE (MLO 7345-8)		7.33	66.5	-	0.783	-	71	-	160,000	-38	-30	-	-	-
DEWAXED AT -80°F.	MIK*	-	-	-	-	-	-	-	-	-	-	1.4	8.9	87.4
OIL FRACTION		7.35	67.4	-	0.784	-	69	-	550,000	<-40	-40	-	-	-
AROMATIC HYDROCARBONS														
CHARGE (MLO 7225-8)		2.24	10.3	-	0.916	-	-15	-	8,500	<-40	-40	-	-	-
DEWAXED AT -65°F.	MEK*	-	-	-	-	-	-	-	-	-	-	3.9	19.6	74.0
OIL FRACTION		2.22	10.2	-	0.918	-	-144	-	14,500	<-45	-45	-	-	-
WAX FRACTION		2.34	10.8	-	0.900	-	0	-	-	-	-	-	-	-
CHARGE (MLO 7218-8)		2.82	18.8	-	0.972	-	-126	-	1,610	+6	+5	-	-	-
DEWAXED AT -65°F.	ACE*	-	-	-	-	-	-	-	-	-	-	17.1	9.6	71.9
OIL FRACTION		2.83	20.4	-	0.998	-	-69	-	17,400	<-15	-15	-	-	-
WAX FRACTION		2.81	16.3	-	0.921	-	-51	-	-	-	-	-	-	-
CHARGE (MLO 7218-9)		2.80	18.2	-	0.965	-	-111	-	1,410	+6	+5	-	-	-
DEWAXED AT -20°F.	ACE*	-	-	-	-	-	-	-	-	-	-	1.6	0.0	97.3
OIL FRACTION		2.82	18.8	-	0.972	-	-125	-	29,000	<-30	-25	-	-	-
CHARGE (MLO 7225-16)		3.84	34.0	-	0.955	-	-154	-	5,900	+4	+5	-	-	-
DEWAXED AT -65°F.	ACE*	-	-	-	-	-	-	-	-	-	-	58.2	3.0	38.8
OIL FRACTION		3.78	38.0	-	0.998	-	-241	-	32,000	<-5	-5	-	-	-
WAX FRACTION		3.91	33.1	-	0.936	-	-121	-	-	-	-	-	-	-
CHARGE (MLO 7218-12)		3.78	35.4	-	0.977	-	-194	-	1,460	+26	+25	-	-	-
DEWAXED AT -65°F.	ACE*	-	-	-	-	-	-	-	-	-	-	19.8	3.5	75.3
OIL FRACTION		-	-	-	-	-	-	-	-	<0	0	-	-	-
CHARGE (MLO 7218-14)		4.32	48.2	-	0.984	-	-223	-	1,310	+34	+35	-	-	-
DEWAXED AT -20°F.	ACE*	-	-	-	-	-	-	-	-	-	-	7.3	0.0	92.4
OIL FRACTION		4.48	56.9	-	1.007	-	-272	-	233,000	<-25	-10	-	-	-
CHARGE (MLO 7218-25)		13.5	1100	-	1.088	-	-606	-	9,200	>+75	+75	-	-	-
DEWAXED AT -20°F.	MIK*	-	-	-	-	-	-	-	-	-	-	3.2	0.0	96.7
OIL FRACTION		14.2	1440	-	1.095	-	-758	-	202,000	<+50	+50	-	-	-
CHARGE (MLO 7225-29)		25.7	3840	-	1.013	-	-584	-	-	>+70	>+70	-	-	-
DEWAXED AT -20°F.	MIK*	-	-	-	-	-	-	-	-	-	-	8.0	0.0	92.0
OIL FRACTION		32.5	12,200	-	1.087	-	-1320	-	315,000	<+65	+70	-	-	-
CHARGE (MLO 7218-29)		46.9	59,400	-	1.152	-	-3250	-	-	>+70	>+75	-	-	-
DEWAXED AT -20°F.	MIK*	-	-	-	-	-	-	-	-	-	-	2.4	0.0	93.6
OIL FRACTION		55.5	136,000	-	1.185	-	-5000	-	510,000	<+75	+90	-	-	-
HYDROGENATED POLYOLEFIN														
CHARGE (MLO 7391)		7.38	45.8	-	0.678	-	128	-	4,690	+20	-15	-	-	-
DEWAXED AT -65°F.	MIK*	-	-	-	-	-	-	-	-	-	-	55.1	2.1	39.8
OIL FRACTION		6.23	36.6	10,500	0.693	0.673	128	142	230,000	<-65	-65	-	-	-
WAX FRACTION		7.90	50.8	-	0.671	-	127	-	-	-	-	-	-	-

* MIK = METHYL ISOBUTYL KETONE; MEK = METHYLETHYL KETONE; ACE = ACETONE

(1) VISCOSITY INDEX CALCULATED USING THE VISCOSITY-TEMPERATURE CHARACTERISTICS OVER THE TEMPERATURE RANGE OF 210° TO -40°F.

(2) CALCULATED USING "TABLES FOR DETERMINATION OF ASTM SLOPE AND PREDICTION OF VISCOSITIES" COMPILED BY LAWRENCE T. EBY, ESSO RESEARCH AND ENGINEERING COMPANY.

Table 18

EFFECT OF POUR POINT DEPRESSANTS ON DEEP-DEWAXING BEHAVIOR

DEWAXINGS WERE CARRIED OUT AT THE INDICATED TEMPERATURE WITH A 6:1 SOLVENT TO OIL RATIO USING METHYLISOBUTYLKETONE.

POUR POINT DEPRESSANTS USED:

PRL Ac337 = A 917 TYPE ACRYLOID POLYMER CONCENTRATE COMPRISING ABOUT 30 WT.% POLYMER IN A MINERAL OIL.
PRL Ac345 = A 150 TYPE ACRYLOID POLYMER CONCENTRATE COMPRISING ABOUT 25 WT.% POLYMER IN A MINERAL OIL.

TEST FLUID	C'STOKE VISC. AT 100°F.	POUR POINT, °F.	YIELD, % OF CHARGE		
			WAX FRACTION THEORETICAL	WAX FRACTION OCCLUDED OIL	OIL FRACTION
PARAFFINIC MINERAL OIL FRACTIONS					
CHARGE (MLO 7358-6)	19.4	- 5	-	-	-
MLO 7358-6 + 1.5% PRL Ac337	-	-	-	-	-
DEWAXED AT -80°F.	-	-	13.1	9.9	76.1
OIL FRACTION	22.3	-65	-	-	-
CHARGE (MLO 7344-10)	19.9	+15	-	-	-
DEWAXED AT -65°F.	-	-	16.1	26.9	53.1
OIL FRACTION	22.4	-55	-	-	-
WAX FRACTION	16.7	-	-	-	-
MLO 7344-10 + 5.0% PRL Ac337	31.4	-	-	-	-
DEWAXED AT -65°F.	-	-	15.8	6.8	74.7
OIL FRACTION	22.9	-55	-	-	-
WAX FRACTION	52.8	-	-	-	-
MLO 7344-10 + 5.0% PRL Ac345	34.5	-	-	-	-
DEWAXED AT -65°F.	-	-	16.4	10.2	71.8
OIL FRACTION	22.6	-55	-	-	-
CHARGE (MLO 7358-7)	20.6	+15	-	-	-
DEWAXED AT -80°F.	-	-	14.0	21.6	64.6
OIL FRACTION	23.5	-60	-	-	-
MLO 7358-7 + 5.0% PRL Ac337	35.1	-	-	-	-
DEWAXED AT -80°F.	-	-	14.6	13.6	69.2
OIL FRACTION	24.2	-55	-	-	-
CHARGE (MLO 7344-14)	32.5	+20	-	-	-
DEWAXED AT -65°F.	-	-	14.2	37.8	46.2
OIL FRACTION	38.2	-55	-	-	-
MLO 7344-14 + 5.0% PRL Ac337	-	-	-	-	-
DEWAXED AT -65°F.	-	-	19.2	16.3	66.0
OIL FRACTION	39.4	-60	-	-	-
OIL DEWAXED AT -75°F.	15.6	-75	-	-	-
OIL DEWAXED AT -75°F. + 5.0 % PRL Ac337	28.3	-	-	-	-
FILTERED AT -65°F.	-	-	-	-	-
OIL FRACTION	16.8	-	-	-	-

Table 19

EFFECT OF SOLVENT COMPOSITION AND SOLVENT-TO-OIL RATIO ON DEEP-DEWAXING BEHAVIOR

TEST FLUID	SOLVENT COMPOSITION RATIO OF MIK*:MEK*	SOLVENT TO OIL RATIO	DEWAXING TEMP., °F.	POUR POINT, °F.	OIL YIELD % OF CHARGE
PARAFFINIC MINERAL OIL FRACTION					
MLO 7433-4-10	1:0	4:1	-75	-70	49.6
	1:0	6:1	-65	-55	53.1
	1:0	8:1	-74	-60	64.9
MLO 7433-4-7	0:1	7:1	-50	-65	19.8
WAX FRACTION FROM 1ST DEWAXING	0:1	7:1	-50	-60	26.5
MLO 7433-4-10	1:0	8:1	-74	-60	64.9
	3:1	8:1	-74	-75	65.5
	1:1	8:1	-74	-80	53.6
	1:3	8:1	-74	-85	32.7
	0:1	8:1	-74	-85	7.8

* MIK = METHYLISOBUTYL KETONE; MEK = METHYLETHYL KETONE.

Table 20

EFFECT OF TEMPERATURE ON DEEP-DEWAXING BEHAVIOR

DEWAXINGS WERE CARRIED OUT AT THE INDICATED TEMPERATURE WITH AN 8:1 SOLVENT TO OIL RATIO USING METHYLISOBUTYL KETONE.

TEST FLUID	CENTISTOKE VISC. AT 100°F.	POUR POINT, °F.	YIELD, % OF CHARGE	
			WAX FRACTION	OIL FRACTION
<u>PARAFFINIC MINERAL OIL FRACTIONS</u>				
CHARGE (MLO 7433-4-10)	14.9	–	–	–
DEWAXED AT –110°F. (NORMAL COOLING RATE)	–	–	–	26.2
OIL FRACTION	18.4	<–85	–	–
WAX FRACTION (WARMED TO –74°F.)	–	–	–	–
FILTERED AFTER 1 HR. AT TEMP.	–	–	–	28.6
OIL FRACTION	17.5	–85	–	–
CHARGE (MLO 7433-4-10)	14.9	–	–	–
COOLED TO –110°F. FOR 3 HRS. (NORMAL COOLING RATE)				
FILTERED AT –74°F. AFTER 1 HR. AT TEMP.	–	–	–	64.3
OIL FRACTION	17.8	–80	–	–
CHARGE (MLO 7458-4-10)	14.7	–	–	–
COOLED TO –110°F. FOR 1 HR. (NORMAL COOLING RATE)				
FILTERED AT –80°F. AFTER 1 HR. AT TEMP.	–	–	38.8	61.2
OIL FRACTION	18.0	–80	–	–
CHARGE (MLO 7433-4-10)	14.9	–	–	–
DEWAXED AT –72°F. (NORMAL COOLING RATE)	–	–	–	64.9
OIL FRACTION	17.5	–60	–	–
CHARGE (MLO 7433-4-10)	14.9	–	–	–
DEWAXED AT –80°F. (SHOCK COOLING RATE)	–	–	–	61.3
OIL FRACTION	–	–75	–	–

Table 21

LOW TEMPERATURE PROPERTIES OF ACRYLOID-DEWAXED OIL BLENDS

BASE STOCKS ARE NARROW BOILING FRACTIONS OF THE INDICATED PARAFFINIC (DEEP DEWAXED) STOCKS
TEST FLUIDS : MLO 7344 = A PARAFFINIC NEUTRAL OBTAINED FROM ESSO RESEARCH AND ENGINEERING COMPANY
MLO 7358 = A PARAFFINIC NEUTRAL OBTAINED FROM WOLFS HEAD OIL REFINING COMPANY
MLO 7475 AND MLO 7476 = PARAFFINIC NEUTRALS OBTAINED FROM KENDALL REFINING COMPANY

TEST FLUID		ACRYLOID		CENTISTOKES VISCOSITY AT			% VISC. INCR. DUE TO ACRYLOID AT	
MLO NO.	FRACT. NO.	TYPE	WT.%	210°F.	100°F.	-40°F.	210°F.	-40°F.
7344	10	-	-	4.16	22.4	(10,000)	-	-
	10	AC 917	5.0	7.28	36.6	13,600-15,700	75	36-57
	10	AC 966	5.0	6.48	30.7	11,400-12,300	56	14-23
	11	-	-	4.55	26.0	15,800	-	-
	11	AC 966	6.0	7.52	36.9	17,000-24,000	65	8-52
	12	-	-	4.79	28.7	20,200	-	-
	12	AC 966	5.5	7.67	40.5	22,500-34,400	60	11-70
	13	-	-	5.23	33.1	29,000	-	-
	13	AC 966	4.0	7.23	40.5	29,500-35,600	39	2-23
	14	-	-	5.69	38.2	43,100	-	-
	14	AC 966	3.5	7.64	45.9	41,700-44,000	34	-3-+2
7358	7	-	-	4.12	23.3	13,900	-	-
	7	AC 917	5.0	7.63	41.4	17,700	85	27
	7	AC 966	5.8	7.35	37.7	15,100	78	9
	7	AC 160	5.2	9.06	47.4	22,300	120	60
	11	-	-	5.33	35.3	37,600	-	-
	11	AC 966	3.9	7.52	46.1	35,700	41	-5
7374	17	-	-	4.61	26.9	15,400	-	-
	17	AC 966	5.8	7.74	40.7	16,000	68	4
7376	2	-	-	4.35	25.7	20,600	-	-
	2	AC 966	6.0	7.91	42.7	20,900	82	1

Table 22

PROPERTIES OF HIGH TEMPERATURE HYDRAULIC FLUID FORMULATIONS

EACH OF THE FORMULATIONS INCLUDES AN OXIDATION INHIBITOR, AN ANTIWEAR ADDITIVE, AND AN ANTIFOAM AGENT.

BASE STOCK TYPE	A SUPER-REFINED NAPHTHENIC MINERAL OIL	A SUPER-REFINED DEEP DEWAXED PARAFFINIC OIL	A SUPER-REFINED AROMATIC HYDROCARBON
CENTISTOKE VISCOSITY AT 700°F.	0.6	0.5	0.5
500°F.	1.1	0.8	0.9
210°F.	8.4	4.5	7.6
100°F.	79	25	116
30°F.	1500	220	6000
0°F.	10,000	1000	-
ASTM SLOPE (100° TO 210°F.)	0.759	0.759	0.900
C.O.C. FLASH POINT, °F.	445	400	430
C.O.C. FIRE POINT, °F.	495	450	460
ASTM POUR POINT, °F.	-30	-65	0
DENSITY, D_4^{20}	0.878	0.852	0.971

Table 23

PROPERTIES OF JET ENGINE LUBES FORMULATED FROM DEWAXED PARAFFINIC STOCK

FLUID TYPE	SPEC. MIL-L-7808	TURBO-PROP LUBE	DEWAXED PARAFFINIC-BASE FLUID	DEWAXED PARAFFINIC PLUS DISPERSANT ACRYLOID	
MEASURED CS. VISC. AT					
400°F.	1.2	2.1	1.25	2.0	2.0
210°F.	3.6	7.58	4.61	7.74	7.35
100°F.	14.0	36.3	26.9	40.7	37.7
-40°F.	1890	(12,000)	15,400	16,000	15,100
FLASH POINT, °F.	440	440	400	400	400
FIRE POINT, °F.	510	510	450	450	450
POUR POINT, °F.	<-75	<-65	-60	-60	-60
VISCOSITY INDEX	162	156	92(110)**	147	149
ASTM SLOPE 210° TO -40°F.	0.703	0.633	0.747	0.642	0.650
13,000 CS. ATTAINED AT TEMP., °F.	-65	(-40)	-37	-37	-37

** VISCOSITY INDEX CALCULATED FROM 210° AND -40°F. VISCOSITIES.

PETROLEUM REFINING LABORATORY
COLLEGE OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA
APRIL 23, 1959

purposes. However, a companion blend, MLO 7460, is also shown on Table 28. These two blends are super-refined and matched in high temperature and overall stability properties. They differ only in low temperature properties. MLO 7485 has been dewaxed while MLO 7460 has not. The three fluids MLO 7277, MLO 7485, and MLO 7460 all exhibit the same general high temperature lubricity and stability characteristics in applications involving closed or airless systems.

The major difference is the useful range of -65° to +700°F in the case of MLO 7485. Thus far, a total of eight samples of MLO 7460 have been formulated and distributed to four organizations. This represents a preparation of 73 gallons.

Part of the super-refining operation (distillation) in the preparation of these samples has been conducted in pilot plant equipment at this Laboratory. The distillation equipment used for this purpose has been described in WADC TR 55-30 Part VI.

1. Evaluation of MLO 7460 in Vickers High Temperature Pump Program. A total of 30 gallons of MLO 7460 fluid has been supplied to Vickers Incorporated for inclusion in a high temperature hydraulic system program. In this program, MLO 7460 has been tested at 550°F pump temperature for 32 hours in one test and for 50 hours in a second test. The property changes of the MLO 7460 test fluid in the Vickers tests are shown in Table 29. The viscosities and neutralization numbers from Test 2 indicate no change in the fluid during the 50-hour test at 550°F. Slight changes in neutralization number but no appreciable change in viscosity are noted in Test 1.

A flocculent precipitate which appeared to increase with test time is noted for Test 1. Samples of the used oils from Tests 1 and 2 have been returned to this Laboratory for evaluation. The viscosity and neutralization number values as indicated by Vickers have been confirmed. The presence of a flocculent precipitate in the sample from Test 1 was also confirmed. No precipitate is observed or was reported for Test 2.

A 250 milliliter representative sample of used oil from Test 1 has been centrifuged to separate the precipitate from the oil. A total of nine milliliters of sludge and occluded oil was obtained from the centrifuging. It was obvious from the flocculent nature of the sludge that this nine milliliters contained primarily occluded oil. The nine-milliliter slurry was washed thoroughly with 50 milliliters of petroleum naphtha and then centrifuged and the naphtha layer removed. This procedure was repeated with an additional 50 milliliters of naphtha to insure complete removal of the occluded oil. The sludge was dried in an oven at 100°C. The sludge represents 0.13 weight per cent of the original oil. Evaporation of the wash naphtha indicates that none of the sludge was naphtha soluble.

The sludge was insoluble in all common solvents. An ash determination showed the sludge to be 56.3 weight per cent ash with a gray-white color. The ash was insoluble in the common mineral acids. A test for SiO_2 was made with sulfuric and hydrofluoric acid in a platinum crucible. This test indicated the ash to be 86.9 weight per cent SiO_2. MLO 7460 contains 0.001 weight per cent silicone antifoam additive. This is not sufficient to account for any appreciable portion of the SiO_2 found. The precipitate could not have been formed from MLO 7460 constituents. The deposit probably came from the pump test system where it had collected from previous tests with silicon-containing fluids. This is a good illustration of the necessity of purging test systems thoroughly, so that carry-over of the previous test fluid is eliminated completely.

The used fluid from Test 1 also had a characteristic odor not encountered with thermally treated mineral oils. The odor did resemble a halogenated material such as trichloroethylene degreasing solvent. The presence of a contaminant such as trichloroethylene or the silicon-containing sludge may have been responsible for the slight neutralization number noted in the used samples of fluid from Test 1.

Formulations MLO 7277 and MLO 7460 both contain an amine type oxidation inhibitor. The finished formulation, because of the amine type inhibitor, will darken upon prolonged exposure to light at room temperature, or upon heating to elevated temperatures. The color change does not adversely alter the effectiveness of the inhibitor or the overall properties of the fluid.

E. LONG TIME STABILITY STUDIES. The useful fluid life at elevated temperatures is dependent on thermal and oxidative stability in most cases. These properties, in general, can be measured in the laboratory within convenient time intervals because of the increased reaction rate associated with the high temperatures. Studies of such limiting high temperature stable life are being measured for both oxidative and thermal environments as discussed in this report.

The stable life at room temperature, 70° to 80°F , or in unheated storage throughout the world (140° to -65°F) is a more elusive number to determine. In many cases, extrapolation of the high temperature stability using measured temperature coefficients of reaction rate predicts almost infinite stable life under these conventional storage conditions.

Often the long time storage of fluids and lubricants is affected by secondary reactions completely different from the reaction measured in the high temperature accelerated thermal and oxidative tests. The storage stability problem with Spec. MIL-L-7808 type fluids is an excellent example of this phenomenon. In the case of Spec. MIL-L-7808 fluids, a so-called low temperature oxidation (below 200°F) occurs at a rate not predicted from the high temperature (347°F) oxidation studies.

This Laboratory has shown that this low temperature storage problem is closely related to the purity of the phosphorous-containing antiwear additive and the water content of the fluid. The dependence of such a reaction on water content suggests an explanation for the discontinuity of the oxidation rate with temperature at about 212°F. Continuous operation above 212°F would tend to keep the water content low and minimize the rate of reactions

Table 24

TYPICAL PHYSICAL PROPERTIES OF MLO 7277 HYDRAULIC FLUID

Fluid Designation	MLO 7277
Centistoke Viscosity	
at 700°F.	0.6
at 500°F.	1.1
at 210°F.	8.4
at 100°F.	79
at 30°F.	1,500
at 0°F.	10,000
ASTM Slope (210° to 100°F.)	0.759
C.O.C. Flash Point, °F.	445
C.O.C. Fire Point, °F.	495
ASTM Pour Point, °F.	-30
Density, d_4^{20}	0.878

Table 25

PROPERTIES FOR MLO 7277

TEMPERATURE, °F.	0	100	200	300	400	500
COEFFICIENT OF EXPANSION (CC/CC/°F. X 10^4)*	4.4	4.8	5.4	5.5	6.4	
THERMAL CONDUCTIVITY [BTU/FT.^{2}/HR./(°F. PER FT.)]	0.0775	0.0732	0.0729	0.0705	0.0682	0.0659
SPECIFIC HEAT (BTU/LB. – °F.)	0.424	0.471	0.519	0.566	0.615	0.660
BULK MODULUS (P.S.I. X 10^{-5})						
AV. VALUE FOR 0-10,000 P.S.I.	3.2	2.7	2.2	1.7	1.2	0.7
DENSITY, (GMS./ML.)	0.908	0.873	0.838	0.802	0.768	0.732
VAPOR PRESSURE, (MM. HG)	–	–	–	< 0.1	2.0	17

* AVERAGE VALUES BETWEEN THE INDICATED TEMPERATURE AND THE NEXT HIGHER TEMPERATURE, E.G., 4.4 = AV. FOR 0° TO 100°F.

Table 26

THERMAL STABILITY CHARACTERISTICS OF A HIGH TEMPERATURE HYDRAULIC FLUID

TEST CONDUCTED IN GLASS TEST TUBE CONSISTS OF A FIFTY GRAM CHARGE OF TEST FLUID. CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM. THE TEST TUBE IS SEALED WITH A U-TUBE CONTAINING APPROXIMATELY 3 ML. OF TEST FLUID. THE SEAL ALLOWS THE PASSAGE OF GAS OUT OR AIR IN WITH PRESSURE CHANGES GREATER THAN 4 INCHES OF FLUID - APPROXIMATELY 0.25 LBS./SQ. IN.

TEST CONDUCTED IN STAINLESS STEEL PRESSURE CYLINDER CONSISTS OF A 20 ML. CHARGE. CATALYSTS = A 0.5 IN. DIAM. BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. THE TOTAL VOLUME OF THE STAINLESS STEEL CYLINDER IS 46 MLS. PRIOR TO THE START OF THE TEST THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. IN THE STAINLESS STEEL CYLINDER, THE NITROGEN PRESSURE AT 700°F. IS APPROXIMATELY 20 P.S.I.G.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 700 ± 10°F.; TEST TIME = 6 HOURS.

TEST FLUID	TYPE OF APPARATUS(1)	CENTISTOKE VISCOSITY AT 100°F. <- - - - - - - - - - -> ORIG.	FINAL	% CHANGE	CATALYST WT. LOSS (MG./SQ. CM.) <- - - - - - - - - - - - - - - - - - - -> COPPER	STEEL	ALUMINUM	52-100 STEEL	M-10 STEEL	NAVAL BRONZE	NEUT. NO. INCREASE	INSOLUBLE MATERIAL	MAXIMUM SYSTEM PRESSURE, P.S.I.G.	FINAL PRESSURE AT ROOM TEMP., P.S.I.G.
MLO 7277	GLASS	74.8	41.9	-44	0.02	0.02	0.01	-	-	-	0.0	NONE	-	-
MLO 7277	P.C.	74.8	40.4	-46	-	-	-	0.06	0.04	0.06	0.0	NONE	75	17

(1) TESTS CONDUCTED IN GLASS TEST TUBES INDICATED AS "GLASS". TESTS CONDUCTED IN STAINLESS STEEL PRESSURE CYLINDER INDICATED AS "P.C.".

Table 27

OXIDATION AND CORROSION CHARACTERISTICS OF MLO 7277 HYDRAULIC FLUID AT 347°F.

Test procedures and techniques in accordance with Spec. MIL-L-7808.
Test conditions include: Test temperature = 347 ± 3°F ; Test time = 72 hours; Air rate = 5 ± 0.5 liters per hour; Test fluid charged = 100 mls.; and catalysts = a 1-inch square each of copper, steel, aluminum, and magnesium.

Test Fluid	Spec. MIL-L-7808	MLO 7277
Overall liquid loss, wt.%	2	2
% change in centistoke viscosity at 100°F.	+2	+7
Neut. no. (mg. KOH/gm. oil)		
Original	0.1	0.0
Final	1.3	0.2
Wt. % oil insoluble material	0.3	0.3
Final catalyst condition		
Appearance		
Copper	Dull	Dull
Steel	Dull	Dull
Aluminum	Dull	Dull
Magnesium	Dull	Dull
Wt. loss (mg./sq. cm.)		
Copper	+0.03	+0.02
Steel	0.02	+0.02
Aluminum	0.01	+0.05
Magnesium	0.02	0.05

Table 28

TYPICAL PROPERTIES OF TWO EXPERIMENTAL MINERAL OIL LUBRICANTS

FORMULATIONS INCLUDE AN ANTIOXIDANT, AN ANTIWEAR ADDITIVE, AND AN ANTIFOAM AGENT.

TEST FLUID	MLO 7485	MLO 7460
BASE STOCK	DEWAXED SUPER-REFINED PARAFFINIC MINERAL OIL	SUPER-REFINED PARAFFINIC MINERAL OIL
CENTISTOKE VISCOSITY AT		
700°F.	0.5	0.5
500°F.	-	0.8
400°F.	1.3	-
210°F.	4.6	4.0
100°F.	27	21
-40°F.	15,400	-
ASTM SLOPE (210° TO 100°F.)	0.77	0.76
ASTM SLOPE (210° TO -40°F.)	0.75	-
VISCOSITY INDEX	92 110*	94 -
13,000 CS. ATTAINED AT TEMP., °F.	-37	-
C.O.C. FLASH POINT, °F.	400	425
C.O.C. FIRE POINT, °F.	450	465
POUR POINT, °F.	-70	+25
DENSITY, D_4^{20}	0.86	0.86

* DETERMINED BY USING THE VISCOSITY-TEMPERATURE CHARACTERISTICS OVER THE RANGE OF 210° TO -40°F.

Table 29

PROPERTIES OF SAMPLES TAKEN DURING HIGH TEMPERATURE PUMP TEST

Data taken from Quarterly Progress Report No. 2, AF Contract No. 33(616)-6398 issued by Vickers Incorporated.

Sample No.	Pump Test Time, Hrs.		C'stoke Viscosity at		Neut. Number mg. KOH/gm. oil
	at 500°F.	Total	100°F.	210°F.	
Mineral Oil MLO 7460 - Test No. 1					
1673*	0.0	0.0	22.08	4.22	0.05
1680*	9.5	14.1	21.84	4.17	0.102
1684*	14.0	19.6	21.64	4.10	0.150
1685*	21.0	27.6	21.11	4.08	0.190
1700*	29.0	37.2	21.45	4.17	0.230
1711*	32.2	41.2	22.31	4.24	0.180
Mineral Oil MLO 7460 - Test No. 2					
1714	0.0	0.0	22.1	4.2	0.02
1717	8.0	11.5	21.4	4.1	0.03
1723**	14.0	18.6	22.0	4.2	-
1735	21.0	26.5	22.1	4.2	0.03
1741	28.0	34.5	22.2	4.2	-
1745	32.0	39.5	22.2	4.2	0.04
1751	39.0	47.5	21.9	4.2	-
1765	48.5	59.3	22.3	4.2	-
1767	50.0	61.8	22.1	4.2	0.03

* A flocculent precipitate was noticed in the daily fluid samples. The amount of precipitate increased in proportion to the time the fluid was at high temperature.

**This sample showed separation of a material which formed liquid droplets.

involving water in the mechanism. Similar low temperature reactions affecting stability can occur due to the chemical action of additives with other additives, water, metals, packaging materials, or base stocks to form insolubles or accelerate overall property changes at storage temperature levels.

1. Storage Stability. The determination of useful fluid life under storage as well as operational conditions is being studied under the current contract. One approach to the determination of fluid life under mild conditions is the critical examination of samples of fluids, lubricants, base stocks, and additives that have been stored for long periods of time under known conditions.

A number of fluid samples have been stored by this Laboratory in an unheated storage building for periods of 2 to 17 years. Temperatures prevailing inside the building range from about 0° to 100°F. Storage samples from 55-gallon drums, 5-gallon cans, one-gallon cans, and glass bottles are included in the study. In essentially all cases of storage, some breathing through the threaded caps is presumed. None of the samples were stored in pressure sealed containers.

About 60 samples have been chosen from storage for a preliminary evaluation. These samples represent esters, mineral oils, hydrocarbons, and silicones as well as blended formulations using these materials as base stocks. One of the obvious limitations of a study of this type is the amount of information available on the sample before the storage period. Preliminary evaluation of these storage samples will include viscosity measurement, neutralization numbers, lubricity level, low temperature fluidity, homogeneity, and oxidative stability.

Several mineral oils and hydrocarbons are shown in Table 30. Two fluids, PRL 1871 and PRL 2843, are mineral oil-base stocks for Spec. MIL-H-5606 and Spec. MIL-F-17111 type fluids. These base stocks have been stored for 12 and 17 years, respectively. Viscosity, neutralization number, and low temperature properties indicate no change in fluid properties due to storage. Oxidation tests will be conducted with these fluids to determine the extent of change in inhibitor susceptibility.

A series of synthetic hydrocarbons are also shown after 7 to 15 years storage. Three samples, PRL 3440, PRL 3473, and PRL 3439 are polyolefins containing one olefinic linkage per molecule. These materials, in general, show some increase in neutralization number and viscosity values. These changes are typical of oxidation and polymerization reactions which are commonly encountered with olefinic hydrocarbons. Studies by this Laboratory indicate that the polyolefins are not adequately inhibited by conventional oxidation inhibitors.

It should be noted that there were no insolubles in these polyolefins after extended storage. The two hydrogenated olefins (PRL 3474 and PRL 2310) show excellent storage stability based on viscosity properties and neutralization number. The hydrogenated olefins (branched chain paraffins) show excellent additive response. The stability of the hydrogenated olefins is equivalent to that of the well-refined mineral oils shown in Table 30.

A series of complete formulations based on highly-refined naphthenic mineral oil base stocks are shown after 4 to 16 years of storage on Table 31. The base stocks used for these fluid formulations are similar in type and quality to PRL 1871 and PRL 2843 shown on Table 30. All of the finished fluid formulations are homogeneous and free of sediment. There is no evidence of change in viscosity or low temperature fluidity with storage. Sixteen of the 17 hydraulic fluid samples show little or no increase in neutralization number.

Sample PRL 2913 exhibits a relatively high neutralization number. However, no original neutralization number is available for this blend. This formulation PRL 2913 is prepared from a special Acryloid which was processed for this application by a high temperature vacuum stripping operation. The stripped polymer is suspected to be the source of the high neutralization number. The lack of initial properties fails to show the role of storage in the high neutralization number.

Spec. MIL-H-5606, Spec. MIL-F-17111, and Spec. O.S. 1113E fluids contain tricresyl phosphate antiwear additive. In most cases, original antiwear values were not determined for these fluids. However, characteristic antiwear values for these three fluids are essentially identical as measured by the Shell four-ball wear tester. Preliminary wear studies on three storage samples show no change in lubricity values with storage. These mineral oil-base fluids show excellent storage stability for extended periods. The effectiveness of the oxidation and corrosion inhibitors and the stability of the storage samples to oxidation have not yet been determined.

Storage data are also available for 19 esters which have been in storage from 10 to 16 years (Table 32). In general, these esters represent early samples of dibasic acid esters. That is, these materials were not prepared to current property levels for lubricants. Instead they were prepared primarily as plasticizer quality materials. Again, in most cases, the original properties available for the fluid are not extensive. Much of the early data indicate that, in the case of neutralization number, values of the order of 0.2 to 2.0 were not uncommon in the samples available.

Ester viscosity values show no excessive changes during storage. Most of the -40°F. viscosity determinations were conducted with cloudy samples. Under these circumstances agreement before and after storage is excellent. Over half of the storage samples exhibit a final neutralization number of 0.2 or less. Only three of these esters exhibit neutralization numbers in excess of 1.0. These data suggest that storage stability of the esters without an additive package is good. Recent data suggest that storage stability of the ester formulations may be a function of the ester quality as well as the additive package. These data suggest that a wide variety of dibasic acid esters show adequate storage stability for extended periods (>10 years) providing initial ester quality is high.

A series of 12 ester-base formulations representing 8 to 11 years of storage are shown on Table 33. All except three of these formulations contain a phosphorous-type lubricity additive. About half of the blends were formulated by this Laboratory while the other half are commercial samples.

Traces of insoluble material have been observed in some of these formulations. Work is proceeding on the quantitative measurement of the fluid insolubles and on the source of the insolubles. None of the diester base stocks evaluated after storage show evidence of insolubles. These data suggest that the choice of the additive package triggers the formation of insolubles.

Viscosity data on the storage samples indicate that no appreciable changes have occurred for fluids formulated with dibasic acid esters. Sample PRL 2979, which is a polyester prepared from a dibasic acid and a glycol containing a secondary alcohol group, shows a slight change in viscosity. Several higher molecular weight polyesters of this same general type have shown similar tendencies to vary in viscosity with storage time. The increased neutralization number in the PRL 2979 fluid with storage is further evidence of a change in structure. It should be noted that this composition is the only formulation showing a substantial increase in neutralization number that does not contain a phosphate lubricity additive.

The difference in storage stability between PRL 3039 and a commercial sample of PRL 3161 illustrates the effect of tricresyl phosphate concentration. Both fluids are prepared from equally stable dibasic acid esters and have the same ingredients in the additive package. The major difference is the concentration of tricresyl phosphate.

None of the long time storage samples of PRL 3039, which is a Spec. MIL-L-6387 ester-base hydraulic fluid, show a neutralization number increase. Test fluid PRL 3161 does show an increase in neutralization number and the formation of fluid insolubles with storage. Test fluid PRL 3161 is the prototype of the Spec. MIL-L-7808 jet engine lube which has also shown a tendency toward poor storage stability.

Storage stability of a typical Spec. MIL-L-7808, until recently, has been of the order of six months. By contrast, these data suggest a storage stability of the order of eight years for the Spec. MIL-L-6387 fluid.

The substantial effect of tricresyl phosphate concentration on storage stability has been discussed in WADC TR 55-30 part 2. In that report, the effect of tricresyl phosphate on storage stability, oxidation stability, hydrolysis stability, and stability under a combination of oxidative and hydrolytic effects are discussed. The role of hydrolysis in storage stability and/or oxidation at test temperatures below 200°F are emphasized. An accelerated storage stability test involving oxidation and hydrolysis at 200°F shows a stable life of 80 hours for a PRL 3161-type fluid containing 5.0 weight per cent tricresyl phosphate but a stable life of greater than 336 hours for a PRL 3161-type fluid containing only 1.0 weight per cent of tricresyl phosphate. These differences in accelerated tests are in good agreement with the differences noted in the actual storage data.

All of the test fluids containing a dialkyl acid phosphate, high concentrations of tricresyl phosphate, or both, also show poor storage stability based on neutralization number increase. Test fluids PRL 2988, PRL 3040, PRL 3059, PRL 3069, and PRL 3084 are fluids containing an extreme-pressure (E.P) lubrication additive package designed to meet Spec. MIL-L-7499 extreme-pressure, synthetic-base lubricating oil. The two formulations PRL 2988 and PRL 3040 which contain no phosphorous-type lubricity additive show high initial neutralization numbers but relatively small changes in neutralization number.

The Spec. MIL-L-7499 type formulations, as a whole, show relatively good storage stability. That is, these materials show storage stability as good as or better than typical Spec. MIL-L-7808 fluids which do not contain E.P. lubricity additives.

The effect of storage on lubricity is shown for several of the ester-base formulations. The Spec. MIL-L-6387 fluid, PRL 3039, shows the same lubricity properties before and after storage. The antiwear properties for PRL 3039 extend through the 10-kilogram load range of the four-ball wear tester but not to the 40-kilogram load. The increase of tricresyl phosphate concentration from 1 to 5 per cent causes an increase in antiwear effectiveness through the 40-kilogram load range as well as some benefits in antiseize properties on the four-ball E.P. tester. The use of an acid phosphate as an E.P. additive is demonstrated in the results from formulations PRL 3312 and PRL 3313. The presence of the acid phosphate is noted in the antiseize and antiweld properties.

In the case of PRL 3161, there is no evidence of change in wear and E.P. properties. The lack of change in E.P. properties would tend to show that the increase in acid number is not due to a substantial formation of acid phosphate but does represent, primarily, a splitting of the ester. The lubricity data for PRL 3312 and PRL 3313 indicate no appreciable change in E.P. properties and good antiwear properties after storage. These data again indicate that there is no substantial loss in acid phosphate concentration upon storage. The acid number in these cases may result from either the formation of a more acidic phosphate than the monoacid dialkyl phosphate or from a splitting of the organic ester into an acidic constituent. The Spec. MIL-L-7496 fluid evaluated for lubricity properties before and after storage shows evidence of good final lubricity values.

The effects of storage on several improved lubricity silicones are shown on Table 34. These samples have been stored for periods of 3 to 6 years. The specific fluid compositions are not known to this Laboratory. Two of the five samples show a viscosity increase on storage and one of these shows an increase in neutralization number. Additional testing of these improved lubricity silicones along with a storage evaluation program on conventional methyl and methylphenyl silicones is continuing.

F. THERMAL STABILITY. A number of thermal stability tests have been employed by various laboratories in evaluating hydraulic fluids, lubricants, and working fluids. These tests involve different test environments and are rated on the basis of various property change values. As a result, a single fluid has been found to be (1) completely unstable at 700°F ; (2) of satisfactory stability for 10 to 20 hours use at 700°F ; and (3) stable for a week or more at 700°F. These data suggest the need for standardization of

Table 30

EFFECT OF STORAGE TIME ON THE PROPERTIES OF SOME MINERAL OILS AND HYDROCARBONS

Samples Stored for Indicated Time in an Unheated Building

PRL DESIG.	DESCRIPTION	SOURCE	DATE RECEIVED	CENTISTOKE VISCOSITY AT 100°F. ORIG.	AT 100°F. 1959	AT 0°F. ORIG.	AT 0°F. 1959	AT -40°F. ORIG.	AT -40°F. 1959	NEUT. NO. (MG. KOH /GM. OIL) ORIG.	NEUT. NO. 1959
PRL 1871	GAS OIL FRACTION (NAPHTHENIC)	SOCONY VACUUM	1943	3.67	3.67			124	126	0.0	0.0
PRL 2843	GAS OIL FRACTION (NAPHTHENIC)	SOCONY VACUUM	1948	3.59	3.59	24.8		115	116		0.0
PRL 3440	INDOPOL L-50 (POLYOLEFIN)	INDOIL CHEM. CO.	1953	111	113	14,360					0.2
PRL 3473	POLYOLEFIN (LF-0741)	SO INDIANA	1953	15.4	21.1	804	1960				2.1
PRL 3474	HYDROGENATED POLYOLEFIN (LF-0742)	SO INDIANA	1953	15.8	15.9	814	834				0.1
PRL 3439	INDOPOL L-10 (POLYOLEFIN)	INDOIL CHEM. CO.	1953	23.9	26.1	1170	1720				1.4
PRL 2310	TETRAISOBUTANE	SONJ	1945	3.64	3.64						0.1

Table 31

EFFECT OF STORAGE TIME ON THE PROPERTIES OF SOME MINERAL OIL FORMULATIONS

Samples Stored for Indicated Time in an Unheated Building

PRL DESIG.	TYPE	SOURCE	DATE REC'D OR PREPARED	CENTISTOKE VISCOSITY AT 100°F.		AT −40°F.		NEUT. NO. (MG. KOH/ GM. OIL)		CLOUD POINT, °F 1959	POUR POINT, °F. 1959	WEAR TESTER SCAR DIAM., MM. 1 KG.		10 KG.	
				ORIG.	1959	ORIG.	1959	ORIG.	1959			ORIG.	1959	ORIG.	1959
PRL 2119	SPEC. AN-VV-0-366B	SOC-VAC	1944	14.1	14.1	435	438	0.0	0.1	<-75	<-75		0.22		0.25
PRL 2125	SPEC. AN-VV-0-366B	SOCAL	1944	14.6	14.6	413	415	0.0	0.1	<-75	<-75				
PRL 2759	SPEC. AN-VV-0-366B	SINCLAIR	1947	14.3	14.3	467	471		0.2	<-75	<-75				
PRL 3115	SPEC. AN-0-366	SONJ	1950	14.2	14.2		488	0.0	0.0	<-75	<-75	0.16	0.16	0.23	0.24
MLO 7020	SPEC. MIL-0-5606	SONJ	1955		14.3		478			<-75	<-75				
PRL 2508	SPEC. AN-VV-0-366B TYPE	PRL	1945	15.2	15.0	504	495		0.0	<-75	<-75				
PRL 2828	SPEC. 51-F-21	SONJ	1948	28.1	28.1	1050	1050	0.3	0.3	<-75	<-75	-	0.17	-	0.22
PRL 3133	SPEC. 51-F-21 WITH ACRYLOID HF-25 IN 2-EHS	PRL	1951	32.7	32.7	833*			0.4						
PRL 2061	SPEC. OS 1113	SONJ	1942	42.1	42.1	23,000	21,800		0.1						
PRL 2721	SPEC. OS 1113E	SONJ	1947	41.2	41.3			0.2	0.3						
PRL 2510	SHEAR STABILITY REFERENCE FLUID	PRL	1946	14.2	14.2		461		0.0						
MLO 7098	SHEAR STABILITY REFERENCE FLUID	PRL	1956	14.2	14.4				0.0						
MLO 7099	SHEAR STABILITY REFERENCE FLUID	PRL	1956	14.1	14.3				0.0						
PRL 2419	RUBBER SWELLING REFERENCE FLUID	PRL	1945	14.0	14.1	341	342		0.0	<-75	<-75				
PRL 2913	SHEAR VISCOSITY PROJECT OIL WITH ACRYLOID HF-25	PRL	1949	32.9	32.8	655**	654**		1.4	-75	<-80				
PRL 2914	SHEAR VISCOSITY PROJECT OIL WITH ACRYLOID HF-160	PRL	1949	33.3	33.4				0.1	-80	<-80				

* VISCOSITY MEASURED AT −25°F.
** VISCOSITY MEASURED AT 0°F.

Table 32

EFFECT OF STORAGE TIME ON THE PROPERTIES OF SOME DIBASIC ACID ESTERS

Samples Stored for Indicated Time in an Unheated Building

PRL DESIG.	ESTER	SOURCE	DATE RECEIVED	CENTISTOKE VISCOSITY AT 100°F. ORIG.	CENTISTOKE VISCOSITY AT 100°F. 1959	CENTISTOKE VISCOSITY AT -40°F. ORIG.	CENTISTOKE VISCOSITY AT -40°F. 1959	NEUT. NO. (MG. KOH/ GM. OIL) ORIG.	NEUT. NO. (MG. KOH/ GM. OIL) 1959
PRL 1899	DICAPRYL SUCCINATE	RH*	1944	7.55	7.49	966	997		0.1
PRL 2996	DI-3-METHYLBUTYL ADIPATE	RH	1949	4.87	4.89			0.2	0.6
PRL 2194	DI-1-ETHYLPROPYL ADIPATE	RH	1945	4.43	4.48				3.0
PRL 2845	DIHEXYL ADIPATE	HARDESTY	1948	5.53	5.58				3.1
PRL 1897	DI-2-ETHYLHEXYL ADIPATE	RH	1944	8.24	8.14				0.2
PRL 1933	SEC-BUTYL ADIPATE	RH	1944	3.64	3.61	SOLID			0.1
PRL 1932	SEC-AMYL ADIPATE	RH	1944	4.48	4.44	245	247		0.2
PRL 2195	DI-1-ETHYLPROPYL AZELATE	RH	1945	6.33	6.29				0.3
PRL 2813	DI-2-ETHYLHEXYL AZELATE	EMERY	1948	10.8	10.7	1110	1110	0.3	0.7
PRL 1934	SEC-BUTYL AZELATE	RH	1944	5.39	5.31	251	252		0.2
PRL 1935	SEC-AMYL AZELATE	RH	1944	6.48	6.41	417	419		0.3
PRL 1901	DI-1-METHYLBUTYL SEBACATE	RH	1944	7.24	7.16	474	486		0.1
PRL 1902	DI-2-METHYLBUTYL SEBACATE	RH	1944	8.00	7.88	SOLID			0.5
PRL 2196	DI-1-ETHYLPROPYL SEBACATE	RH	1945	7.26	7.35	475			7.1
PRL 2863	DIHEXYL SEBACATE	HARDESTY	1948	9.08	9.06	1430	1510		0.6
PRL 1937	1,3-DIMETHYLBUTYL SEBACATE	RH	1944	9.29	9.17	1210	1310		0.0
PRL 1936	1-METHYLHEXYL SEBACATE	RH	1944	10.8	10.7	1130	1130		0.1
PRL 3103	DI-2-ETHYLHEXYL SEBACATE	RH	1950	12.8	12.7			0.1	0.1
PRL 1900	SEC-BUTYL SEBACATE	RH	1944	6.21	6.17	309	316		0.1

* ROHM AND HAAS

Table 33

EFFECT OF STORAGE TIME ON THE PROPERTIES OF SOME ESTER-BASE FORMULATIONS

Samples Stored for Indicated Time in an Unheated Building

PRL DESIG.	COMPOSITION	SOURCE	DATE RECEIVED OR PREPARED AT PRL	CENTISTOKE VISCOSITY AT 100°F.		NEUT. NO. (MG. KOH/GM. OIL)		POUR POINT, °F.	
				ORIG.	1959	ORIG.	1959	ORIG.	1959
PRL 3161	DIBASIC ACID ESTER + THICKENER + TRICRESYL PHOSPHATE + PEHNOTHIAZINE (SPEC. -7808 TYPE)	COMMERCIAL	1951	22.3	22.2	0.1	5.0	<-75	<-75
PRL 3312	DIBASIC ACID ESTER + TRICRESYL PHOSPHATE + DIALKYL ACID PHOSPHATE + PHENOTHIAZINE	COMMERCIAL	1952	13.1	13.3	2.5	9.1	<-75	<-75
PRL 3313	DIBASIC ACID ESTER + THICKENER + TELCRESYL PHOSPHATE + DIALKYL ACID PHOSPHATE + PHENOTHIAZINE	COMMERCIAL	1952	42.0	42.5	3.5	12.2		
PRL 2988	DIBASIC ACID ESTER + THICKENER + SULFURIZED TERPENE + PHENOLTYPE ANTIOXIDANT (SPEC. -7499 TYPE)	PRL	1949	22.7	22.9	1.6	3.1	<-75	
PRL 3040	SAME AS PRL 2988	PRL	1949	22.0	22.0	2.1	1.1		<-75
PRL 3059	DIBASIC ACID ESTER + THICKENER + TRICRESYL PHOSPHATE + CHLORONAPHTHA XANTHATE + PHENOTHIAZINE (SPEC. -7499 TYPE)	PRL	1950	22.8	23.0	0.1	2.4		
PRL 3069	SAME AS PRL 3059	COMMERCIAL	1950	22.4	22.7	0.0	12.4		
PRL 3084	SAME AS PRL 3059	COMMERCIAL	1950	23.4	23.3	0.1	0.1		
PRL 3039	DIBASIC ACID ESTER + THICKENER + TRICRESYL PHOSPHATE + PHENOTHIAZINE (SPEC. -6387 TYPE)	PRL	1950	15.4	15.3	0.1	0.0		
PRL 3319	SAME AS PRL 3039	COMMERCIAL	1952		15.5	0.2	0.4		<-75
PRL 2979	POLYESTER + PHENOTHIAZINE	PRL	1949	58.8	60.5	0.3	7.3		
PRL 3182	POLYESTER + TRICRESYL PHOSPHATE + PHENOTHIAZINE	PRL	1951		53.5				

(TABLE CONCLUDED ON NEXT PAGE)

Table 33 (Concluded)

EFFECT OF STORAGE TIME ON THE PROPERTIES OF SOME ESTER-BASE FORMULATIONS

Samples Stored for Indicated Time in an Unheated Building

FOR COMPOSITIONS OF BLENDS, SEE FIRST PAGE OF THIS TABLE

PRL DESIG.	SOURCE	DATE RECEIVED OR PREPARED AT PRL	WEAR TESTER (SCAR DIAM, M.M.)						E.P. TESTER (LOAD IN KILOGRAMS)			
			ORIGINAL			1959			ORIGINAL		1959	
			1 KG.	10 KG.	40 KG.	1 KG.	10 KG.	40 KG.	INCIPIENT SEIZURE	WELD POINT	INCIPIENT SEIZURE	WELD POINT
3161	COMMERCIAL	1951	0.17	0.22	0.37				90	120	90	120
3312	COMMERCIAL	1952	0.18	0.36	0.39	0.22	0.32	0.34	110	120	110	120
3313	COMMERCIAL	1952	0.20	0.32	0.43	0.27	0.35	0.37	110	160	110	140
3069	COMMERCIAL	1950	0.39	0.43	0.49				150	180		
3084	COMMERCIAL	1950	0.22	0.33	0.44	0.29	0.42	0.44	120	240	120	180
3039	PRL	1950	0.16	0.28	0.78	0.18	0.36	0.84				

Table 34

EFFECT OF STORAGE TIME ON THE PROPERTIES OF SOME IMPROVED LUBRICITY SILICONE FLUIDS

Samples Stored for Indicated Time in an Unheated Building

PRL DESIG.	DESCRIPTION	SOURCE	DATE RECEIVED	CS. VISC. AT 100°F.		NEUT. NO. (MG. KOH/GM. OIL)		FOUR-BALL WEAR TESTER (SCAR DIAM., MM.)			
								ORIG.		1959	
				ORIG.	1959	ORIG.	1959	1 KG.	10 KG.	1 KG.	10 KG.
PRL 3491	SILICONE FLUID 81451	G.E.	1954	154	158	0.1	0.6	–	–	0.26	0.46
MLO 7265	SILICONE FLUID 81406 + TINSIL (WADC DESIG. MLO 57-534)	WADC	1957	71.6	74.3	0.4	0.4	0.36	0.43	0.36	0.44
MLO 7105	SILICONE FLUID (WADC DESIG. MLO 56-320)	WADC	1956	25.8	25.9		0.0				
MLO 7114	SILICONE FLUID (WADC DESIG. MLO 56-491)	WADC	1956	44.3	44.3		0.0				
MLO 7115	SILICONE FLUID (WADC DESIG. MLO 56-492)	WADC	1956	40.2	40.2		0.0				

thermal stability tests and the use of pertinent property changes for test evaluation. A series of thermal stability tests are being conducted by this Laboratory to determine the basic trends in thermal behavior of fluids in a semi-quantitative manner.

The two basic thermal stability tests used in previous studies by this Laboratory are being employed in this investigation. In the PRL pressure cylinder test, the fluid to be evaluated is placed in a stainless steel pressure cylinder under a nitrogen atmosphere. This test may be conducted with or without metal catalysts for the desired time at test temperatures up to 900°F. The gaseous decomposition products in this test are confined in the pressure cylinder in intimate contact with the nitrogen and the liquid charged.

The PRL thermal stability test in glass apparatus is carried out in a modified glass test tube with an air condenser. A nitrogen atmosphere is sealed in the unit by a U-tube containing test fluid. This technique allows nitrogen and decomposition products to escape through the liquid seal when the internal pressure exceeds the surrounding atmospheric pressure by about four inches of test fluid. This thermal stability test in glass may be conducted with or without metal catalysts for the desired time at temperatures up to 800°F. In this test, volatile decomposition products are removed from the high temperature area and may be collected for analysis as gases or in cold traps.

1. Improved Liquid Seal for the Glass Thermal Stability Apparatus. One of the problems encountered with the glass thermal stability apparatus under severe conditions and high rates of deterioration is a fluctuating pressure in the test unit causing pressure changes in the tube which exceed the four inches of test fluid in the U-tube. In many cases this pressure fluctuation causes air flow back into the thermal stability unit from the atmosphere. The presence of air and the resultant oxidation interferes with the thermal stability test. A desirable apparatus in this regard is a unit which will allow passage of gaseous products to the atmosphere if the pressure differential exceeds about four inches of fluid but a seal capable of preventing leakage of air back into the test unit at pressure differentials of half an atmosphere. A satisfactory seal of this type is shown on Figure 1 along with the conventional U-tube seal. By using a capillary tube inserted to a 0.3-inch depth in a large reservoir of mercury as indicated, a pressure drop of four inches of fluid (0.3 inch of Hg) will cause gas leakage from the test unit. However, 24 inches of mercury pressure drop (26.7 feet of test fluid) are required for air leakage into the test unit. The use of this liquid seal has satisfactorily stopped air leakage even under severe bumping caused by a high rate of thermal deterioration to form a volatile liquid product.

a. Property Measurements. A number of property measurements have been made to indicate thermal deterioration. These measurements include volume of gases formed, boiling range of the thermally treated product, viscosity of the product, analysis of the volatile products by gas chromatography, and chemical and physical property changes of the liquid tailored to meet the specific requirements of the fluids.

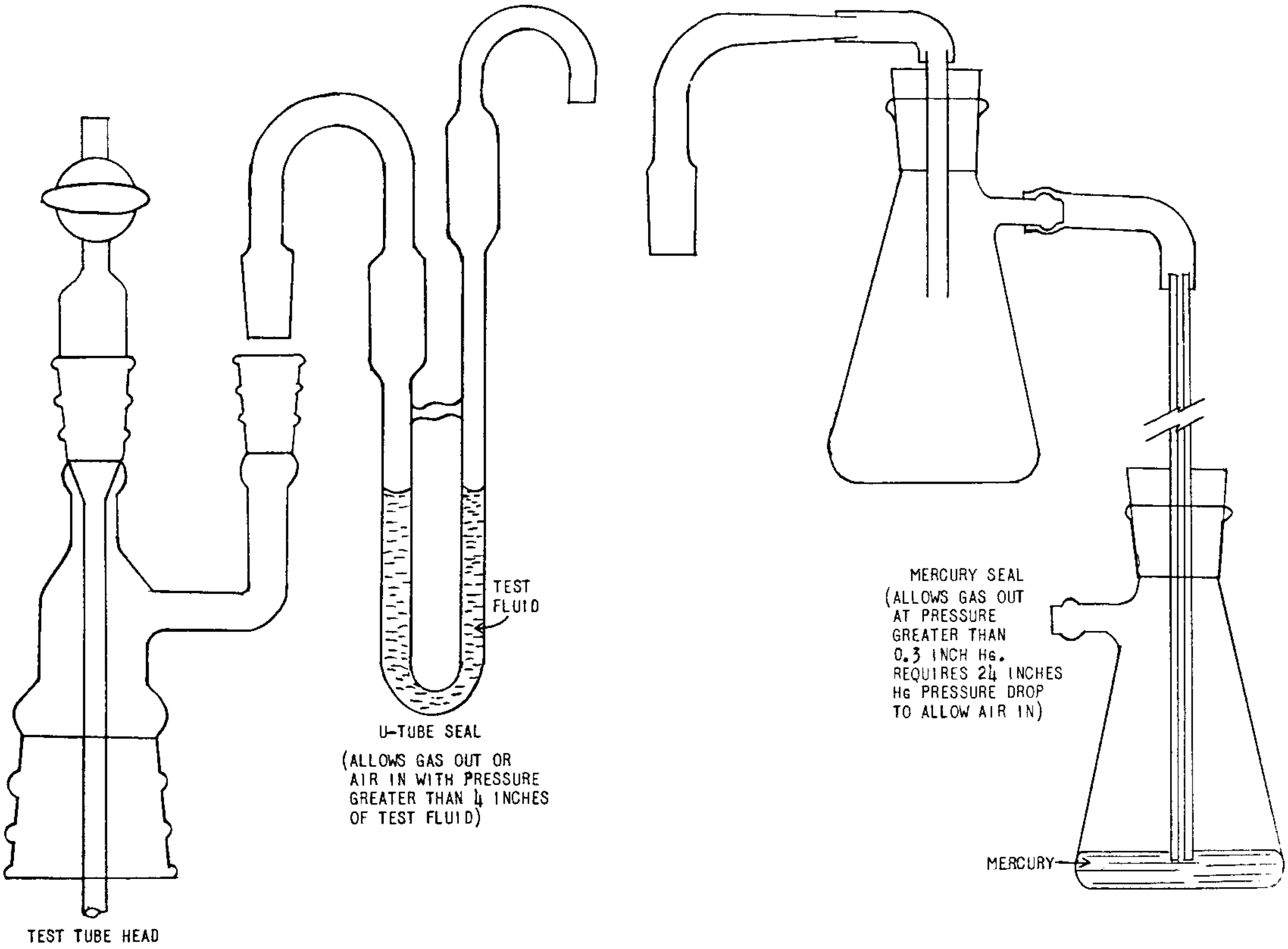


Figure 1. LIQUID SEALS FOR GLASS THERMAL STABILITY APPARATUS

2. Gas Phase Versus Liquid Phase Reactions. The preliminary thermal stability tests conducted in the PRL pressure cylinder and glass test apparatus show some differences in gas formation versus changes in the liquid properties due to the geometry of the test equipment. That is, these differences are independent of test time and test temperature but dependent on the relative volumes occupied by the heated gas and liquid phases.

A series of tests have been conducted in various thermal stability test equipment using mineral oils and esters to emphasize and evaluate the problems noted in the preliminary studies. It is obvious that problems of intra- as well as inter-laboratory reproducibility are dependent upon a better understanding of the thermal degradation reactions occurring. A series of tests conducted at 700°F in the PRL pressure cylinder are shown on Table 35 for a hydrogenated paraffinic mineral oil test fluid. In these tests, the fluid charge was varied from 20 milliliters to 1 milliliter and all tests were of 20 hours duration. The effect on liquid properties and on the metal catalysts is essentially unchanged by variations in the liquid charge.

The rate of gas formation for any specific test from Table 35 is linear with test time. These data are illustrated on Figure 2. That is, the rate of gas formation for any given test is constant for the entire test period. However, the rate of gas formation is not a simple function of the overall test conditions but rather a function of the amount of gas space available in the test unit. Decreasing the fluid charge in the pressure cylinder, resulting in increased volume of gas space, results in an increasing rate of gas formation based on moles of gas per mole of oil per hour. The total moles of gas formation per hour appears to be essentially the same over the range of 20 to 5 milliliters fluid charge. Below five milliliters of fluid charged, there is some decrease in the total rate of gas formation in moles per hour. These data clearly suggest the independence of rate of gas formation on the fluid charged and on the remaining unreacted fluid at any test time.

The rate of gas formation in this thermal stability test appears to be essentially a zero order reaction. It is interesting to note, however, that the liquid property changes vary only slightly with fluid charge indicating substantially different mechanisms for the gas formation reaction and the liquid property changes.

The behavior of the gas pressure build-up in the pressure cylinder reaction has been checked with naphthenic, paraffinic, and aromatic mineral oil fractions. The similarity of the behavior of the gas phase reaction in the pressure cylinder for these fluids is illustrated on Tables 35, 36, and 37 and Figures 2, 3, and 4. In all cases these data confirm those discussed previously. All of these data have been conducted in the PRL pressure cylinder of fixed geometry.

Large volume tests with paraffinic mineral oil MLO 7301 have been conducted in a rocking autoclave. In this series of tests, a temperature of 750°F was employed to enable the tests to be conducted in a short test period and continue the tests to the point where approximately 1 mole of gas per mole of fluid is produced. An Aminco Rocking Autoclave of 2700 milliliters capacity was used for these tests. The results of these 750°F tests are shown on Table 38. Fluid charges of 300 and 1000 milliliters were used to vary the heated free space. Two runs at 1000 milliliters fluid charge were made with the rocker turned on and one run was made with the autoclave in a stationary position. The rate of gas formation for the stationary and rocking tests is essentially the same. In all of these tests the rate of gas formation was constant throughout the test as shown on Figure 5. Again the rate of reaction in the gas phase appears to be directly proportional to the free space. These data are in excellent agreement with the data from the pressure cylinder. It should be emphasized that in the large scale bomb tests, the decomposition to form gas and produce low viscosity products was carried much farther than the conventional 20-hour tests at 700°F.

A number of tests have been conducted at 750°F. in the pressure cylinder. These data are shown on Table 39. The reaction rate as indicated by gas formation is directly proportional to the free space. These observations are in good agreement with the data at 700°F in the pressure cylinder and at 750°F in the large rocking autoclave.

A number of tests in the pressure cylinder were conducted to determine the effect, if any, of increased surface area on the decomposition. The results of these tests are shown on Table 40. These tests show only relatively minor variations in test results attributable to the amounts and types of surface area. In general, the reaction rate in the gas appears to be primarily a function of the available free space. The rate of gas formation in the presence of the increased surface area is constant over the test time. There does appear to be a general trend toward less severe changes in the liquid product with the high catalyst area tests.

To explore further the effect of free space on the gas phase reaction, a series of tests were conducted with essentially no heated free space. Two pressure cylinders were used to conduct these tests. One cylinder was filled with liquid and immersed in the 700°F bath. The second cylinder was connected with the first through a 1/8-inch tube and maintained at room temperature above the bath. This second cylinder provides a lower temperature gas space for expansion and decomposition products from the heated cylinder. Results of tests with no heated gas space show a reduction in rate of gas formation over the values obtained in the tests with large volumes of heated free space.

All of the data on the rate of gas formation at 700°F with MLO 7301 (paraffinic neutral) have been used to plot a curve of heated gas space versus gas reaction rate in moles of gas per mole of fluid per hour. These data are shown on Figure 6.

These differences in rate of thermal decomposition to form gas occur in tests where the changes in liquid product are essentially the same in all cases. These data suggest that the reaction behavior of the hydrocarbon residues in the gas phase differs from the reaction patterns in the liquid phase at high temperatures. The approximation of a zero order reaction in the gas phase indicates that the concentration of molecules which can undergo further pyrolytic scission is not substantially reduced by the gas phase reactions encountered in these tests.

a. Analysis of the Gas From High Temperature Thermal Stability Tests. The gas phase of many of the thermal stability tests has been evaluated quantitatively using gas chromatography. This analysis has been applied only to the materials still in the gas phase at room temperature. The analyses were made using a Perkin-Elmer Single-Stage Vapor Fractometer, Model 154C. Quantitative analysis is affected by the thermal response values which are applied to the measured areas under the curves logged by the individual gas components.

Three adsorption columns were used in this study. Column V is 20 feet long and packed with type 5A molecular sieves. It is used for the analysis of hydrogen, oxygen, nitrogen, methane, and carbon monoxide. Column W is a 7.5-foot column packed with 13X type molecular sieves. It is used to analyze for ethane and ethylene. Column Y which is a 27-foot column packed with hexamethyl phosphoramide on an inert carrier is suitable for the analysis of the individual hydrocarbon components from methane through the five-carbon atom molecules and carbon dioxide.

Columns V and W are used at 100°C. while column Y is used at 30°C. When a combination of columns V and W are used to analyze the same gas, the areas under the curves are corrected for thermal response and the resultant values added together to obtain 100 per cent of the gas for quantitative purposes. When columns V and Y are used together, in addition to the thermal response factor, allowance must be made for the differences in temperature of the columns. The five gases analyzed in column V appear as a single peak in column Y. This peak can then be used as a common factor to determine quantitatively the individual gases analyzed for by both columns. This method for using columns V and Y has been successfully checked with a gas mixture of known composition.

The gases analyzed were sampled at room temperature. This gas analysis does not include appreciable quantities of hydrocarbons in the range of C_5 to C_{18} which are gaseous products at 700°F. The distribution of the C_5 to C_{18} hydrocarbons is indicated by distillation data of the residual liquid products from the thermal stability tests. An approximation of the relative amounts of gaseous materials at room temperature and volatile liquids boiling below 700°F can be obtained from a comparison of the pressure in the thermal stability apparatus at 700° and at 70°F (room temperature). Using the perfect gas laws as an approximation, an absolute pressure of one p.s.i. at room temperature is equivalent to 2.2 p.s.i. at 700°F. The difference between the corrected pressure at 700°F. from the gases noted at room temperature and the pressure at 700°F noted in the test is due to volatile liquid products, predominantly C_5 to C_{18} hydrocarbons.

Analysis of the gaseous samples from the thermal stability tests of a hydrogenated paraffinic bright stock, a paraffinic neutral, a naphthenic neutral, an aromatic hydrocarbon, and two polyolefins are shown on Tables 41, 42, 43, 44, 45, and 46. In general, the hydrogenated paraffinic bright stock (MLO 7289), hydrogenated paraffinic neutral (MLO 7301), and super-refined naphthenic neutral (MLO 7357) show similar thermal stability behavior. In all cases, these three fluids show about the same ratio of gas pressure at 70°F to gas pressure at 700°F. These data indicate that about half of the pressure noted at 700°F is accounted for in the detailed analysis of the gas sample. The other half of the pressure is due to the formation of C_5 to C_{18} hydrocarbons by thermal cracking.

There are indications that, for these fluids, the volatile products are formed in the same ratios over a wide range of test temperatures and degrees of severity. Tests ranging in severity from the formation of 0.02 moles to 1.00 moles of gas formed at 700°F. for each mole of fluid charged show essentially the same range of gaseous product distribution. Similarly, tests conducted at 650°, 700°, and 750°F which show a wide variation in rate of gas formation show essentially no variation in the ratio of gaseous products formed.

In all of the tests with naphthenic and paraffinic mineral oils, methane is the predominant product with substantial quantities of hydrogen, ethane-ethylene, and propane with trace quantities of propylene and C_4 and C_5 hydrocarbons.

The hydrogenated paraffinic bright stock, MLO 7289, consistently shows evidence of small volumes of carbon monoxide. The source of the carbon monoxide is attributed to oxygen-containing impurities present in the fluid charged. The combined amount of carbon dioxide and carbon monoxide for the super-refined neutrals MLO 7301 and MLO 7357 is very low and may be attributed to traces of dissolved air and oxygen-containing impurities.

Two thermal stability tests on Table 39 have been conducted with an atmosphere of air instead of nitrogen. The oxygen available in the air combines with carbon to form predominantly carbon monoxide. The oxygen from the air in both of these tests is all accounted for as carbon monoxide and carbon dioxide.

The volatile thermal decomposition products of the aromatic hydrocarbon differ substantially from those of the naphthenic or paraffinic mineral oil. Data presented on Table 44 at 700°F were obtained with columns V and W, while the data at 650° and 750°F were obtained with gas chromatography columns V and Y. The expected difference in gas phase reaction rate is noted over the temperature range of 650° to 750°F. The quantitative gas analysis data for 650° and 750°F show the relative quantities of the gaseous products to be the same. In the case of the 700°F tests, the difference in relative amounts of the gases in these analyses compared with those at 650° and 750°F are attributed directly to inherent differences in the use of different chromatographic columns.

The gaseous products hydrogen, methane, ethane-ethylene, and propane comprise essentially all of the volatile products below C_{18} produced in the thermal stability test units with MLO 7218. It should be emphasized that, for the naphthenic and paraffinic mineral oils, these same gaseous components represented only half or less of the volatile products below C_{18} in size.

The series of five 20-hour tests shown on Table 44 were all conducted as consecutive tests on the same fluid charge. The gas was vented at room temperature after each 20-hour test at 700°F and the pressure cylinder purged with nitrogen. It should be noted that each 20-hour increment produced the same gaseous products in the same proportions. The data shown on Figure 7 indicate that the rate of gas formation is essentially constant over the entire 100-hour test period. The total 100-hour test period at 700°F produced a total of 0.37 moles of gas per mole of fluid charged.

The data for the two polyolefin types indicate still different thermal behavior from that of the mineral oils and aromatic hydrocarbon. A number of thermal stability tests were run with polybutene oil MLO 7123. Thermal stability tests show no appreciable differences between the olefinic and the completely saturated polybutene oil. From a comparison of gas pressures at 70° and 700°F , there is indication that only about one-third of the total gas pressure generated is due to materials which are gases at 70°F. The analysis of the gaseous products shows that C_4 hydrocarbons predominate. There is little hydrogen but substantial quantities of methane and C_3 hydrocarbons. These products suggest depolymerization as a rapid reaction with carbon to carbon pyrolysis of the resultant monomer. It should be emphasized that the polybutene oil gave the same final gas pressure at 700°F in 12 minutes that is obtained in 20 hours with typical high quality paraffinic and naphthenic mineral oils.

A second polyolefin (MLO 7346) has also been evaluated in the thermal stability test. This polyolefin was obtained from the Atlantic Refining Company. The specific monomer used to prepare this material is not known to this Laboratory. Tests at 650°, 700°, and 750°F indicate that this material is much more thermally stable than MLO 7123 polybutene. The thermal stability of MLO 7346 approaches that of conventional mineral oils of the paraffinic and naphthenic types. The ratio of gas pressure at 70° and at 700°F also approaches that noted for the paraffinic and naphthenic mineral oils. It is interesting to note that hydrogen, methane, and C_2 hydrocarbons are present in about equal concentration in the gas and comprise most of the total gas volume.

Both of the polyolefins show an appreciable quantity of carbon monoxide in the decomposition gases. As in the case of the bright stock discussed previously, this carbon monoxide is attributed to oxygen-containing impurities present in the oil. In the case of the polyolefins, oxygen assimilation is relatively rapid and is not effectively prevented by conventional oxidation inhibitors.

The polyolefins exhibit some difference in rate of thermal degradation with time when compared with the mineral oils and esters. It has been indicated that based on gas formation, thermal decomposition rate is essentially constant with continued test time (essentially a zero order reaction) for the mineral oils and aromatic hydrocarbons. In the case of the polyolefins, the initial rate of gas formation drops off with continued test time as shown on Figure 8.

b. The Effect of Temperature on the Formation of Gaseous Products. The quantitative analysis of the gaseous products indicates that the composition of the gas recovered at room temperature is essentially independent of the temperature of the thermal test over the range of 650° to 750°F. This trend in gas composition has already been demonstrated for paraffinic and naphthenic mineral oils, aromatic hydrocarbons, and polyolefins. The rate of gas generation has also been shown to be a function of the heated gas space involved in the thermal stability tests. If the test fluid and the test system geometry are held constant and the temperature varied, relative reaction rates of the gas can be determined as a function of temperature. The effects of temperatures of 650°, 700°, and 750°F on the various fluids are summarized on Table 47, and the rates for each fluid plotted at the three temperatures on Figures 9, 10, 11, 12, 13, 14, and 15. For these tests, a 20-milliliter charge was employed. The time necessary to produce a 300 p.s.i. pressure in the test apparatus or 20 hours test time, whichever occurred first, was used as the test time.

c. Rate of Thermal Decomposition. The pressure readings at the test temperature were used as a measure of reaction rate. The thermal decomposition rate shown on the tables in this section is calculated from the average slope of the pressure versus time curve. The rate of formation of gas is expressed as moles of gas per hour or moles of gas per hour per mole of fluid. In all cases the perfect gas laws are used to determine the moles of gas present. The values for moles of actual gas are close approximations for the materials that are gaseous at 70°F but deviate somewhat more for the volatile C_5 to C_{18} hydrocarbons. These values do provide useful comparative data for the determination of overall changes due to thermal breakdown.

In the terminology used, a breakdown to form one mole of gas per mole of original fluid is shown as 1.0 on the tables. This value of 1.0 is equivalent to 100 per cent degradation based on the formation of one volatile fragment per molecule of original fluid. However, a single mole of paraffinic or naphthenic mineral oil, containing on the order of 20 to 30 carbon atoms per molecule, can produce more than one mole of hydrogen, methane, ethylene, or ethane under thermal degradation.

The reaction rates based on gas pressure build-up have been used to determine the temperature interval for rate doubling. The rate doubling temperature is a relative expression based on temperature coefficient of reaction rates. The rate doubling temperatures over two consecutive 50°F temperature intervals are summarized on Table 48.

All of the data are given for the same test conditions for each fluid at the indicated temperatures. There is a general trend toward less temperature effect on reaction rate with increasing temperature. This trend is typical of that noted for the thermal cracking of gas oils to gasoline at higher cracking temperatures. Over the 100°F temperature interval studied, the aromatic hydrocarbon shows the lowest rate of increase in thermal cracking of the materials studied. The paraffinic neutral MLO 7301, on the other hand, shows the highest rate of thermal cracking over the same temperature interval. It is interesting to note that at 650°F the paraffinic neutral MLO 7301 (Table 42) and the aromatic hydrocarbon MLO 7218-16 (Table 44) have about the same rate of gas formation. At 750°F, however, the rate of gas formation for the paraffinic neutral is more than five times that of the aromatic hydrocarbon.

A comparison of three paraffinic mineral oils including neutral, bright stock, and resin shows an interesting trend in decomposition (Table 47). For any given temperature, the rate of decomposition increases with increasing molecular weight. That is, at any given temperature, gas formation per mole of fluid charged is highest for the resin and lowest for the neutral.

3. Quantitative Evaluation of the Liquid Product From Thermal Stability Tests. The foregoing discussion relates to the thermal reaction to form gas. In any hydraulic application, thermal conditions will of necessity have to be limited to temperatures at which the gaseous products represent a small portion of the total products. That is, to be useful in a hydraulic cycle, the fluid will have to remain predominantly a liquid under operating conditions. The property changes of the liquid portion of the product from the thermal stability tests, therefore, require a critical evaluation.

Viscosity change, neutralization number, and degree of unsaturation (bromine number) have been used to characterize the liquid product from the thermal stability tests. In most cases these properties do not, in themselves, provide an adequate quantitative picture of the liquid products of thermal deterioration. A vacuum fractionation has been used to round out the quantitative understanding. For this purpose, a small scale vacuum distillation apparatus is used.

a. Apparatus and Procedure for Small Scale Vacuum Distillations. A diagram of the apparatus used in these small scale distillations is shown on Figure 16. The 50 milliliter flask and condenser are made as one piece of glass. The product receiver is a 10 milliliter buret graduated in 0.1 milliliter units. The pressure is measured by a mercury manometer and a McLeod gage attached in parallel. The gages and vacuum pump are protected from volatile products by a dry ice-acetone trap maintained at -110°F. The holdup in the distillation flask and condenser is about 0.5 milliliter. Approximately 10 milliliters of ceramic beads are used in the still pot to prevent bumping under vacuum. The distillation flask is heated with a "Glas-Col" heating mantle and the top and neck of the flask are insulated with aluminum foil to a point above the mercury reservoir of the ASTM distillation thermometer.

Table 35

EFFECT OF VARYING GAS SPACE ON THE THERMAL DECOMPOSITION OF A PARAFFINIC NEUTRAL

ALL TESTS CONDUCTED IN THE PRL STAINLESS STEEL PRESSURE CYLINDER
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 700°F ± 10°F ; TEST TIME = 20 HOURS; TOTAL VOLUME OF CYLINDER = 46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 28 POUNDS AT 700°F.

TEST FLUID	A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)					
TEST CONDITIONS:						
TEST FLUID CHARGED, ML.	20	15	10	5	3	1
FREE SPACE, ML..						
AT TEST TEMPERATURE	17	23	30	36	39	42
AT ROOM TEMPERATURE	23	28	33	38	40	42
DECOMPOSITION DATA:						
GAS FORMATION						
MOLES OF GAS/HR. (X10^3)	0.212	0.305	0.312	0.242	0.145	0.066
MOLES OF GAS/MOLE OF OIL/HR.	0.0063	0.0132	0.0181	0.0281	0.0296	0.0345
TOTAL MOLES GAS/MOLE OF OIL	0.12	0.27	0.36	0.63	0.52	0.62
SYSTEM PRESSURE, P.S.I.G.						
MAXIMUM OF TEST TEMP.	220	224	180	133	77	41
RESIDUAL AT ROOM TEMP.	32	29	24	20	8	5
SLOPE, P.S.I.G./HR.	9.6	10.0	8.1	5.2	2.9	1.2
FLUID PROPERTIES						
% CHANGE IN CS. VISC. AT 100°F.	-61	-61	-62	-52	-	-
NEUT. NO. (MG. KOH/GM. OIL)						
ORIGINAL	0.0	0.0	0.0	0.0	0.0	0.0
FINAL	0.0	0.1	0.1	0.1	0.0	0.0
CATALYST WT. LOSS(MG./SQ. CM.)						
M-10 TOOL STEEL	0.04	0.02	0.04	+0.04	+0.02	0.04
52-100 STEEL	0.00	0.00	0.06	+0.06	0.04	+0.02
NAVAL BRONZE	0.00	0.00	+0.02	+0.06	0.06	0.04

ALL TESTS CONDUCTED IN THE PRL PRESSURE CYLINDER.

TEST CONDITIONS: TEST TEMPERATURE = 700° ± 10°F ; TEST TIME = 20 HOURS; VOLUME OF CYLINDER=46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 28 LBS. AT 700°F.

TEST FLUID: A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)

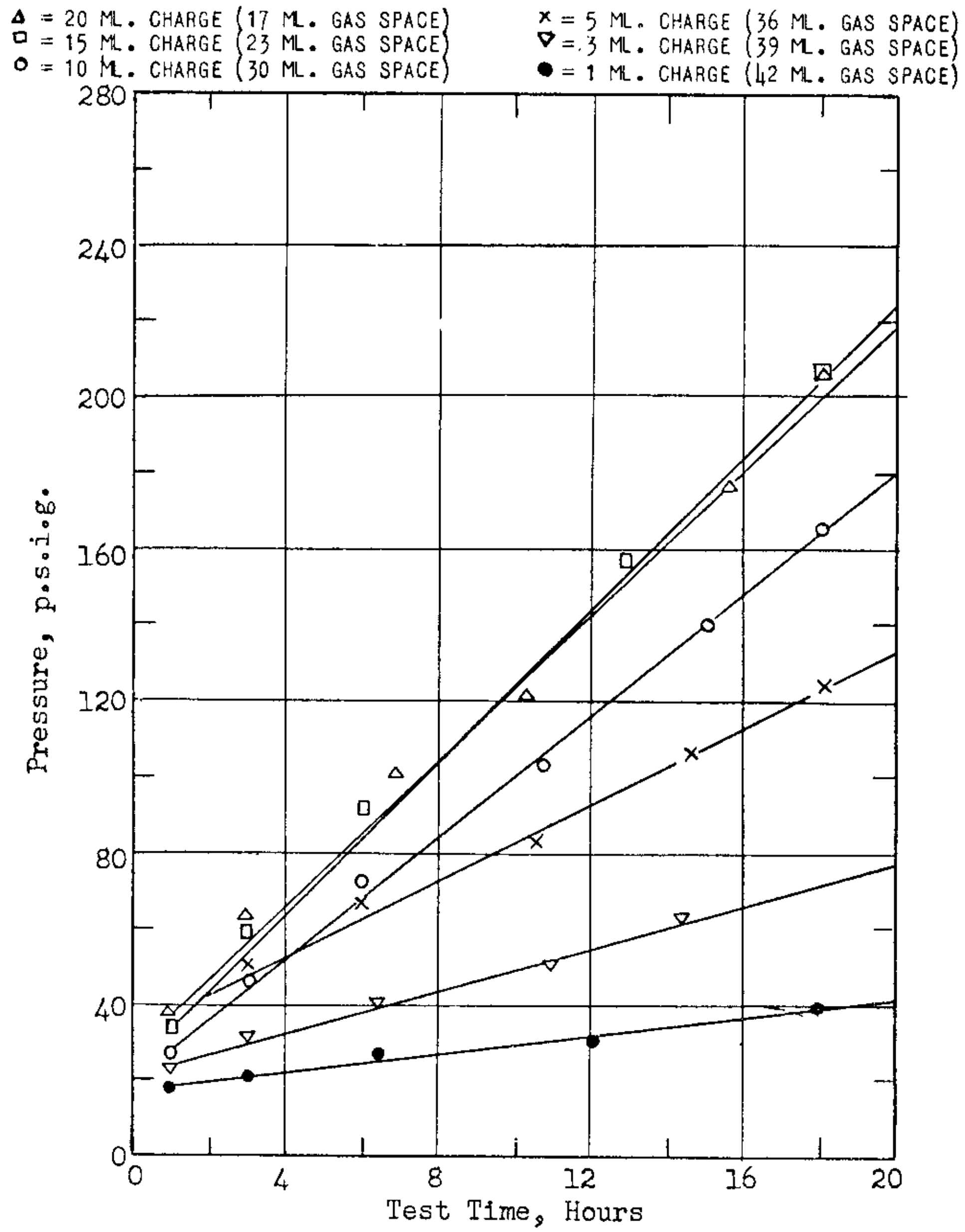


Figure 2. EFFECT OF VARYING GAS SPACE ON RATE OF GAS FORMATION

Table 36

EFFECT OF VARYING GAS SPACE ON THE THERMAL DECOMPOSITION OF A NAPHTHENIC NEUTRAL

ALL TESTS CONDUCTED IN THE PRL STAINLESS STEEL PRESSURE CYLINDER
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 700 ± 10°F ; TEST TIME = 20 HOURS; TOTAL VOLUME OF CYLINDER = 46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 28 POUNDS AT 700°F.

TEST FLUID	A SUPER-REFINED NAPHTHENIC NEUTRAL (MLO 7357)				
TEST CONDITIONS:					
TEST FLUID CHARGED, ML.	20	10	5	3	1
FREE SPACE, ML					
AT TEST TEMPERATURE	17	30	36.5	39	42
AT ROOM TEMPERATURE	23	33	38	40	42
DECOMPOSITION DATA:					
GAS FORMATION					
MOLES OF GAS/HR. ($X10^3$)	0.241	0.383	0.258	0.156	0.068
MOLES OF GAS/MOLE OF OIL/HR.	0.0055	0.0195	0.0248	0.0269	0.0294
TOTAL MOLES OF GAS/MOLE OF OIL	0.12	0.40	0.51	0.58	0.85
SYSTEM PRESSURE, P.S.I.G.					
MAXIMUM AT TEST TEMP.	267	222	129	85	48
RESIDUAL AT ROOM TEMP.	50	33	16	12	7.5
SLOPE, P.S.I.G./HR.	11.0	9.9	5.6	3.1	1.3
FLUID PROPERTIES					
% CHANGE IN CS. VISC. AT 100°F.	-57	-80	-69	-	-
NEUT. NO. (MG. KOH/GM. OIL)					
ORIGINAL	0.0	0.0	0.0	0.0	0.0
FINAL	0.0	0.0	0.1	0.0	0.0
CATALYST WT. LOSS (MG./SQ. CM.)					
M-10 TOOL STEEL	+0.04	+0.18	+0.04	+0.02	0.00
52-100 STEEL	+0.02	+0.04	+0.02	0.00	0.00
NAVAL BRONZE	0.00	+0.02	+0.16	+0.04	0.04

ALL TEST CONDUCTED IN THE PRL PRESSURE CYLINDER

TEST CONDITIONS: TEST TEMPERATURE = 700° ± 10°F ; TEST TIME = 20 HOURS; VOLUME OF CYLINDER=46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 28 LBS. AT 700°F.

TEST FLUID: A SUPER-REFINED NAPHTHENIC NEUTRAL (MLO 7357)

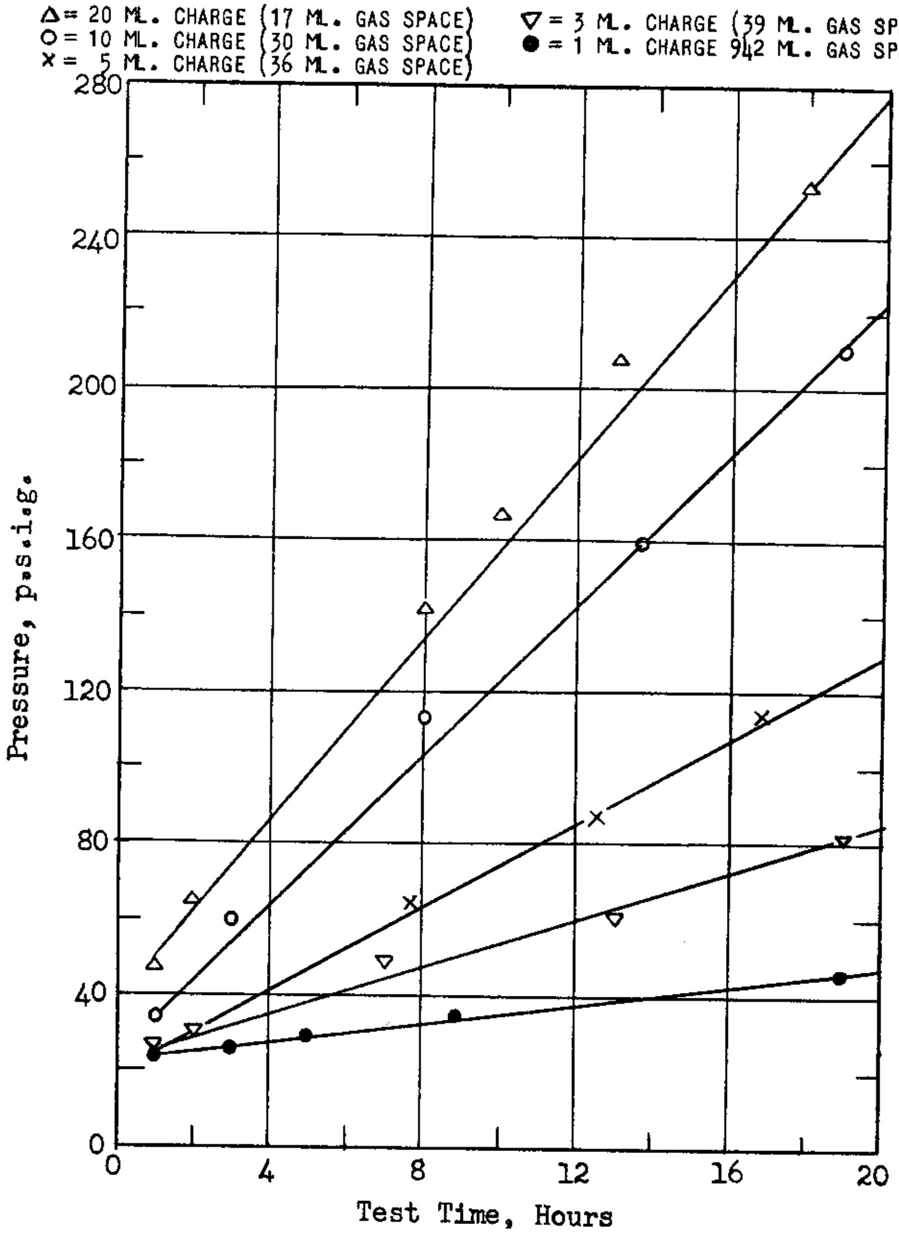


Figure 3. EFFECT OF VARYING GAS SPACE ON RATE OF GAS FORMATION

Table 37

EFFECT OF VARYING GAS SPACE ON THE THERMAL DECOMPOSITION OF A PARTIALLY HYDROGENATED AROMATIC HYDROCARBON

ALL TESTS CONDUCTED IN THE PRL STAINLESS STEEL PRESSURE CYLINDER
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 700 ± 10°F ; TEST TIME = 20 HOURS; TOTAL VOLUME OF CYLINDER = 46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 28 POUNDS AT 700°F.

TEST FLUID	A PARTIALLY HYDROGENATED AROMATIC HYDROCARBON (MLO 7218)				
TEST CONDITIONS:					
TEST FLUID CHARGED, ML.	20	15	10	5	1
FREE SPACE, ML.					
AT TEST TEMPERATURE	17	23.5	30	36.5	42
AT ROOM TEMPERATURE	23	28	33	38	42
DECOMPOSITION DATA:					
GAS FORMATION					
MOLES OF GAS/HR. ($X10^3$)	0.228	0.342	0.214	0.111	0.129
MOLES OF GAS/MOLE OF OIL/HR.	0.0032	0.0048	0.0061	0.0052	0.0615
TOTAL MOLES OF GAS/MOLE OF OIL	0.07	0.13	0.12	0.16	0.84
SYSTEM PRESSURE, P.S.I.G.					
MAXIMUM AT TEST TEMP.	248	263	138	82	76
RESIDUAL AT ROOM TEMP.	102	103	46	22	24
SLOPE, P.S.I.G./HOUR	10.4	11.3	6.8	2.4	2.4
FLUID PROPERTIES					
% CHANGE IN CS. VISC. AT 100°F.	-	-16	-14	-15	-
NEUT. NO. (MG. KOH/GM. OIL)					
ORIGINAL	-	0.0	0.0	0.0	-
FINAL	-	0.1	0.3	0.1	-
CATALYST WT. LOSS (MG./SQ. CM.)					
M-10 TOOL STEEL	-	+0.08	+0.04	+0.08	0.00
52-100 STEEL	-	+0.08	+0.02	+0.04	0.02
NAVAL BRONZE	-	+0.06	0.00	+0.10	0.00

ALL TESTS CONDUCTED IN THE PRL PRESSURE CYLINDER

TEST CONDITIONS: TEST TEMPERATURE = 700° ± 10°F ; TEST TIME = 20 HOURS; VOLUME OF CYLINDER=46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 28 LBS AT 700°F.

TEST FLUID: A PARTIALLY HYDROGENATED AROMATIC HYDROCARBON (MLO 7218-16)

△ = 20 ML. CHARGE (17 ML. GAS SPACE)
□ = 15 ML. CHARGE (23 ML. GAS SPACE)
○ = 10 ML. CHARGE (30 ML. GAS SPACE)
× = 5 ML. CHARGE (36 ML. GAS SPACE)
● = 1 ML. CHARGE (42 ML. GAS SPACE)

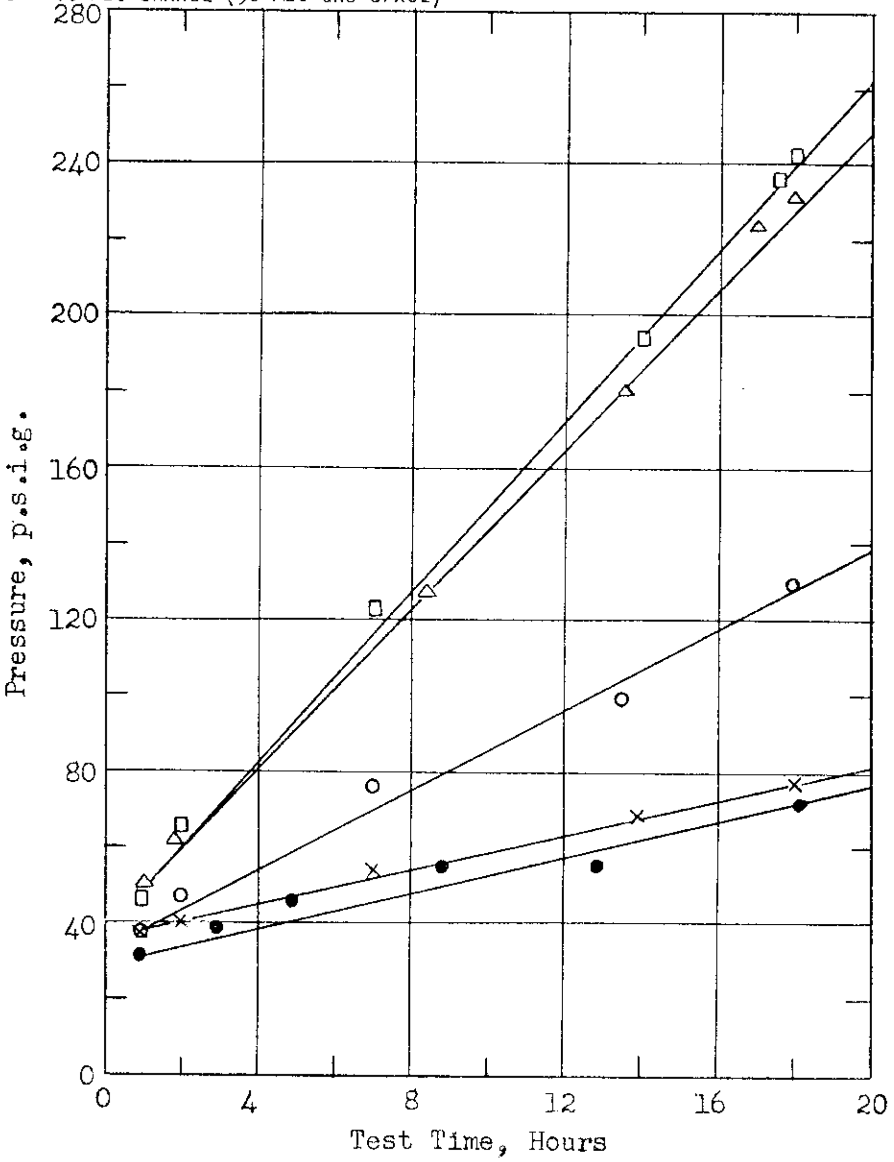


Figure 4. EFFECT OF VARYING GAS SPACE ON RATE OF GAS FORMATION

Table 38

LARGE VOLUME THERMAL STABILITY TESTS

ALL TESTS CONDUCTED IN AN AMINCO ROCKING AUTOCLAVE
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 750 ± 10°F ; TOTAL VOLUME OF AUTOCLAVE = 2650 MLS. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE AUTOCLAVE IS ABOUT 30 POUNDS AT 750°F.

TEST FLUID	A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)			
TEST CONDITIONS:				
TEST TIME, HOURS	3.8	10.8	11.3	6 (1)
TEST FLUID CHARGED, ML.	300	1000	1000	1000
FREE SPACE, ML.				
AT TEST TEMPERATURE	2260	1350	1350	1350
AT ROOM TEMPERATURE	2350	1650	1650	1650
DECOMPOSITION DATA:				
GAS FORMATION				
MOLES OF GAS/HR. ($X10^3$)	116	138	135	112
MOLES OF GAS/MOLE OF OIL/HR.	0.236	0.084	0.083	0.068
TOTAL MOLES GAS/MOLE OF OIL	1.0	1.0	1.0	0.5
SYSTEM PRESSURE, P.S.I.G.				
MAXIMUM AT TEST TEMP.	195	1030	1025	520
RESIDUAL AT ROOM TEMP.	29	220	195	120
SLOPE, P.S.I.G./HR.	42	83	81	68
FLUID PROPERTIES				
% CHANGE IN CS. VISC. AT 100°F.	-85	-96	-96	-88
NEUT. NO. (MG. KOH/GM. OIL)				
ORIGINAL	0.0	0.0	0.0	0.0
FINAL	0.1	0.1	0.1	0.0

(1) THIS TEST CONDUCTED WITH AUTOCLAVE IN STATIONARY POSITION.

ALL TESTS CONDUCTED IN AN AMINCO ROCKING AUTOCLAVE.

<u>TEST CONDITIONS</u>: TEST TEMPERATURE = 750 + 10°F ; TOTAL VOLUME OF CYLINDER = 2650 ML. PRIOR TO START OF TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE AUTOCLAVE IS ABOUT 30 POUNDS AT 750°F.

<u>TEST FLUID</u> = A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301).

● AND ○ = 1000 ML. CHARGE (1350 ML. GAS SPACE)
△ = 300 ML. CHARGE (2260 ML. GAS SPACE)
□ * = 1000 ML. CHARGE (1350 ML. GAS SPACE)*

* FOR THIS TEST, THE AUTOCLAVE WAS HELD STATIONARY

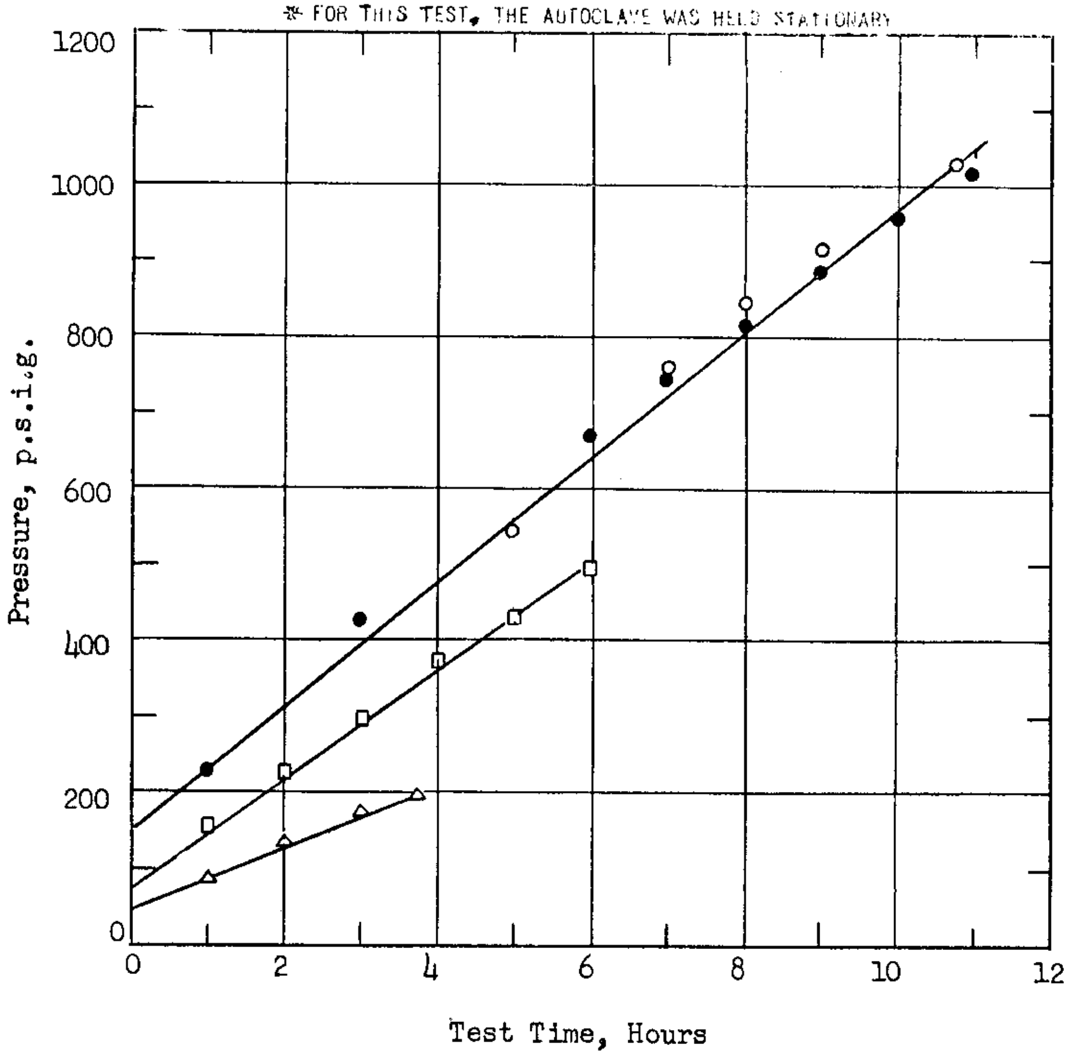


Figure 5. EFFECT OF VARYING GAS SPACE ON RATE OF GAS FORMATION IN A LARGE VOLUME TEST

Table 39

THERMAL DECOMPOSITION BEHAVIOR OF A PARAFFINIC NEUTRAL AT 750°F.

ALL TESTS CONDUCTED IN THE PRL STAINLESS STEEL PRESSURE CYLINDER.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 750 ± 10°F; TOTAL VOLUME OF CYLINDER = 46 ML.; AND CATALYSTS = 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 30 POUNDS AT 750°F.

TEST FLUID	A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)					
TEST CONDITIONS:						
TEST TIME, HOURS	2.8	2.5	2.3(1)	2.8	2.5(1)	4
TEST FLUID CHARGED, ML.	20	20	20	20	20	5
FREE SPACE, ML.						
AT TEST TEMPERATURE	17	17	17	20	20	39.5
AT ROOM TEMPERATURE	23	23	23	26	26	41.0
DECOMPOSITION DATA:						
GAS FORMATION						
MOLES OF GAS/HR. ($X10^3$)	1.98	2.20	2.63	2.44	2.70	2.30
MOLES OF GAS/MOLE OF OIL/HR.	0.059	0.065	0.077	0.073	0.081	0.267
TOTAL MOLES GAS/MOLE OF OIL	0.16	0.16	0.17	0.19	0.19	1.02
SYSTEM PRESSURE, P.S.I.G.						
MAXIMUM AT TEST TEMP.	286	286	298	289	292	200
RESIDUAL AT ROOM TEMP.	39	40	38	36	39	24
SLOPE, P.S.I.G./HR.	94.8	105	125	98.8	109.5	47.3
FLUID PROPERTIES						
% CHANGE IN CS. VISC. AT 100°F.	-63	-71	-67	-64	-69	-84
NEUT. NO. (MG. KOH/GM. OIL)						
ORIGINAL	0.0	0.0	0.0	0.0	0.0	0.0
FINAL	0.1	0.0	0.0	0.0	0.0	0.0
CATALYST WT. LOSS (MG./SQ. CM)						
M-10 TOOL STEEL	0.00	0.08	0.08	-	-	-
52-100 STEEL	0.02	0.06	0.06	-	-	-
NAVAL BRONZE	0.02	0.04	+0.06	-	-	-

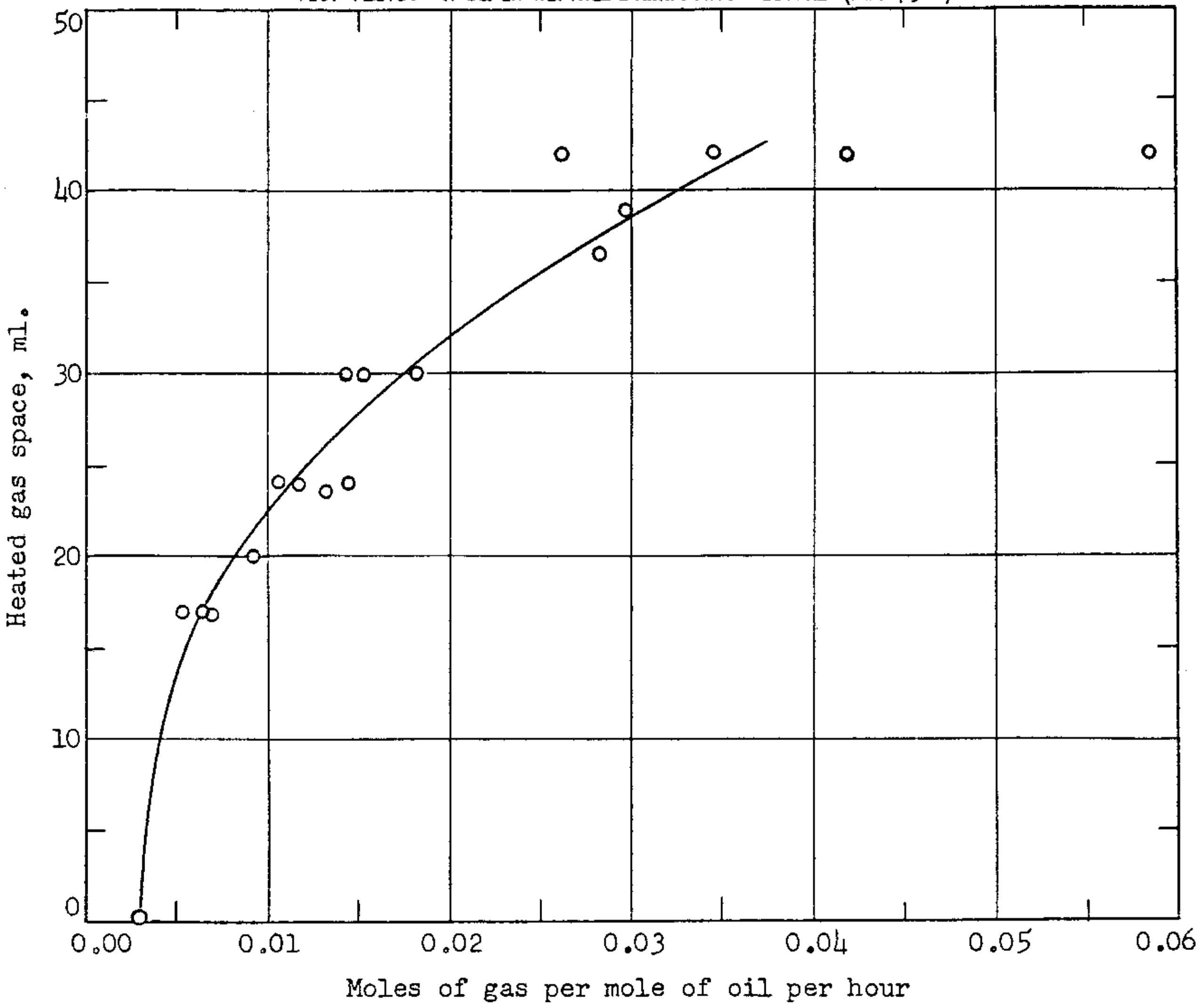
(1) TEST CONDUCTED WITHOUT PURGING WITH NITROGEN. THAT IS, AIR WAS PRESENT IN THE CYLINDER AT THE START OF THE TEST.

Table 40

EFFECT OF CATALYST AREA ON THE THERMAL DECOMPOSITION OF A PARAFFINIC NEUTRAL

ALL TESTS CONDUCTED IN THE PRL STAINLESS STEEL PRESSURE CYLINDER
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 700 ± 10°F ; TEST TIME = 20 HOURS; TOTAL VOLUME OF CYLINDER = 46 ML. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 28 POUNDS AT 700°F.

TEST FLUID	A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)				
TEST CONDITIONS:					
CATALYST	NONE	STEEL CHAIN	STEEL SHOT	ALUMINA	STAINLESS STEEL PLUG
AREA, SQ. CM.	–	415	2050	6230	–
TEST FLUID CHARGED, ML.	20	10	10	10	5
FREE SPACE, ML.					
AT TEST TEMPERATURE	20	24	24	24	17
AT ROOM TEMPERATURE	26	27	27	27	18.5
DECOMPOSITION DATA:					
GAS FORMATION					
MOLES OF GAS/HR. ($X10^3$)	0.305	0.250	0.198	0.282	0.133
MOLES OF GAS/MOLE OF OIL/HR.	0.0091	0.0145	0.0116	0.0164	0.0155
TOTAL MOLES OF GAS/MOLE OF OIL	0.18	0.30	0.24	0.36	0.31
SYSTEM PRESSURE, P.S.I.G.					
MAXIMUM AT TEST TEMP.	260	185	154	209	141
RESIDUAL AT ROOM TEMP.	40	27	25	32	24
SLOPE, P.S.I.G./HR.	11.9	8.15	6.42	9.1	6.1
FLUID PROPERTIES					
% CHANGE IN CS. VISC. AT 100°F.	-76	-64	-55	–	-56
NEUT. NO. (MG. KOH/GM. OIL)					
ORIGINAL	0.0	0.0	0.0	0.0	0.0
FINAL	0.0	0.3	0.1	0.1	0.0



ALL TESTS CONDUCTED IN THE PRL PRESSURE CYLINDER.
FOR TEST CONDITIONS, SEE FIGURE 2.
TEST FLUID: A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)

Figure 6. EFFECT OF VARYING GAS SPACE ON REACTION RATE IN THE GAS PHASE

Table 41

EFFECT OF TEMPERATURE ON THE THERMAL DECOMPOSITION OF A PARAFFINIC BRIGHT STOCK

ALL TESTS CONDUCTED IN THE PRL STAINLESS STEEL PRESSURE CYLINDER
TEST CONDITIONS INCLUDE: TEST TIME AND TEMPERATURE AS INDICATED; TEST FLUID CHARGED = 20 ML.; TOTAL VOLUME OF THE CYLINDER = 46 ML.; GAS SPACE = 17 ML. AT TEST TEMPERATURE AND 23 ML. AT ROOM TEMPERATURE; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 26 P.S.I.G. AT 650°F, 28 P.S.I.G. AT 700°F, AND 30 P.S.I.G. AT 750°F.

TEST FLUID	SUPER-REFINED PARAFFINIC BRIGHT STOCK (MLO 7289)			
TEST TEMPERATURE, °F.	650	700 (1)		750
TEST TIME, HOURS	20	20	10	3.3
DECOMPOSITION DATA:				
GAS FORMATION				
MOLES OF GAS/HR. (X10^{3})	0.0314	0.240	0.240	1.58
MOLES OF GAS/MOLE OF OIL/HR.	0.0013	0.0099	0.0099	0.0654
TOTAL MOLES GAS/MOLE OF OIL	0.02	0.21	0.22	0.22
SYSTEM PRESSURE, P.S.I.G.				
MAXIMUM AT TEST TEMP.	53	255	270	284
RESIDUAL AT ROOM TEMP.	7	45	39	41
SLOPE, P.S.I.G./HR.	1.37	10.9	10.9	75
ANALYSIS OF RESIDUAL GASEOUS PRODUCT, %				
HYDROGEN		11.8	9.9	16.6
METHANE		39.2	37.2	45.8
CARBON MONOXIDE		2.8	0.8	2.3
CARBON DIOXIDE		0.3	0.2	-
ETHANE-ETHYLENE		27.3	29.2	21.1
PROPANE		13.6	17.7	10.1
PROPYLENE		1.3	1.5	1.7
ISOBUTANE		0.9	1.5	0.4
N-BUTANE		2.0	2.9	1.2
ISO- AND N-1-BUTENE		0.3	0.3	0.3
TRANS-2-BUTENE		0.1	TRACE	TRACE
CIS-2-BUTENE		TRACE	TRACE	TRACE
ISOPENTANE		0.1	0.2	TRACE
N-PENTANE		0.1	0.2	TRACE
FLUID PROPERTIES				
% CHANGE IN CS. VISC. AT 100°F.	-30	-	-90	-82
NEUT. NO. (MG. KOH/GM. OIL)				
ORIGINAL	0.0	-	0.0	0.0
FINAL	0.0	-	0.3	0.1
CATALYST WT. LOSS (MG./SQ. CM.)				
M-10 TOOL STEEL	+0.02	-	+0.02	+0.06
52-100 STEEL	0.02	-	+0.02	+0.06
NAVAL BRONZE	+0.14	-	+0.22	+0.04

(1) TEST WAS INTERRUPTED AFTER 20 HOURS. CYLINDER WAS COOLED TO ROOM TEMPERATURE, VENTED, AND PURGED WITH NITROGEN. TEST WAS THEN CONTINUED FOR AN ADDITIONAL 10 HOURS.

Table 42

EFFECT OF TEMPERATURE ON THE THERMAL DECOMPOSITION OF A PARAFFINIC NEUTRAL

ALL TESTS CONDUCTED IN THE PRL STAINLESS STEEL PRESSURE CYLINDER
TEST CONDITIONS INCLUDE: TEST TIME AND TEMPERATURE AS INDICATED; TEST FLUID CHARGED = 20 ML.; TOTAL VOLUME OF THE CYLINDER = 46 ML.; GAS SPACE = 17 ML. AT TEST TEMPERATURE AND 23 ML. AT ROOM TEMPERATURE; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 26 P.S.I.G. AT 650°F, 28 P.S.I.G. AT 700°F, AND 30 P.S.I.G. AT 750°F.

TEST FLUID	A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)			
TEST TEMPERATURE, °F	650	700 (1)		750
TEST TIME, HOURS	96	20	10	2.8
DECOMPOSITION DATA:				
GAS FORMATION				
MOLES OF GAS/HR. ($X10^3$)	0.015	0.230	-	1.98
MOLES OF GAS/MOLE OF OIL/HR.	0.0004	0.0068	-	0.059
TOTAL MOLES GMS/MOLE OF OIL	0.04	0.28	-	0.16
SYSTEM PRESSURE, P.S.I.G.				
MAXIMUM AT TEST TEMP.	82	228	-	286
RESIDUAL AT ROOM TEMP.	8	34	-	39
SLOPE, P.S.I.G./HR.	0.66	10.4	-	94.8
ANALYSIS OF RESIDUAL GASEOUS PRODUCT, %				
HYDROGEN	35.3	-	24.0	20.0
METHANE	64.6	-	51.0	46.0
CARBON MONOXIDE	-		-	-
CARBON DIOXIDE	-		-	-
ETHANE-ETHYLENE	-		13.0	20.0
PROPANE	-		8.9	9.2
PROPYLENE	-		0.8	1.8
ISOBUTANE	-		0.3	0.5
N-BUTANE	-		1.2	1.1
ISO- AND N-1-BUTENE	-		0.3	0.3
TRANS-2-BUTENE	-		TRACE	0.2
CIS-2-BUTENE	-		TRACE	-
ISOPENTANE	-		0.1	0.2
N-PENTANE	-		0.1	TRACE
FLUID PROPERTIES				
% CHANGE IN CS. VISC. AT 100°F	-34	-	-80	-63
NEUT. NO. (MG. KOH/GM. OIL)				
ORIGINAL	0.0	-	0.0	0.0
FINAL	0.0	-	0.0	0.1
CATALYST WT. LOSS (MG./SQ. CM.)				
M-10 TOOL STEEL	+0.06	-	+0.02	0.00
52-100 STEEL	0.04	-	+0.06	0.02
NAVAL BRONZE	+0.06	-	0.00	0.02

(1) TEST WAS INTERRUPTED AFTER 20 HOURS. CYLINDER WAS COOLED TO ROOM TEMPERATURE, VENTED, AND PURGED WITH NITROGEN. TEST WAS THEN CONTINUED FOR AN ADDITIONAL 10 HOURS.

Table 43

EFFECT OF TEMPERATURE ON THE THERMAL DECOMPOSITION OF A NAPHTHENIC NEUTRAL

ALL TESTS CONDUCTED IN THE PRL STAINLESS STEEL PRESSURE CYLINDER
TEST CONDITIONS INCLUDE: TEST TIME AND TEMPERATURE AS INDICATED; TEST FLUID CHARGED = 20 ML.; TOTAL VOLUME OF THE CYLINDER = 46 ML.; GAS SPACE = 17 ML. AT TEST TEMPERATURE AND 23 ML. AT ROOM TEMPERATURE; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 26 P.S.I.G. AT 650°F , 28 P.S.I.G. AT 700°F , AND 30 P.S.I.G. AT 750°F.

TEST FLUID	A SUPER-REFINED NAPHTHENIC NEUTRAL (MLO 7357)			
TEST TEMPERATURE, °F	650	700 (1)		750
TEST TIME, HOURS	103.5	18	12	2.8
DECOMPOSITION DATA:				
GAS FORMATION				
MOLES OF GAS/HR. (X10^3)	0.026	0.298	0.269	1.90
MOLES OF GAS/MOLE OF OIL/HR.	0.0006	0.0074	0.0067	0.0470
TOTAL MOLES GAS/MOLE OF OIL	0.06	0.14	0.15	0.13
SYSTEM PRESSURE, P.S.I.G.				
MAXIMUM AT TEST TEMP.	126	286	299	286
RESIDUAL AT ROOM TEMP.	15	52	48	42
SLOPE, P.S.I.G./HR.	1.1	13.6	12.3	90.5
ANALYSIS OF RESIDUAL GASEOUS PRODUCT, %				
HYDROGEN	18.6	16.7	16.1	17.8
METHANE	55.1	49.2	47.4	56.9
CARBON MONOXIDE	-	-	-	-
CARBON DIOXIDE	-	-	-	-
ETHANE-ETHYLENE	16.8	18.9	17.0	15.7
PROPANE	6.9	11.0	14.3	6.6
PROPYLENE	0.6	1.4	1.4	1.1
ISOBUTANE	0.2	0.4	0.7	0.3
N-BUTANE	0.6	1.4	2.0	0.9
ISO- AND N-1-BUTENE	0.2	0.4	0.6	0.3
TRANS-2-BUTENE	-	0.1	TRACE	TRACE
CIS-2-BUTENE	-	TRACE	TRACE	TRACE
ISOPENTANE	0.2	0.1	0.1	TRACE
N-PENTANE	0.2	0.1	0.1	TRACE
FLUID PROPERTIES				
% CHANGE IN CS. VISC. AT 100°F.	-52	-	-74	-62
NEUT. NO. (MG. KOH/GM. OIL)				
ORIGINAL	0.0	-	0.0	0.0
FINAL	0.1	-	0.0	0.1
CATALYST WT. LOSS (MG./SQ. CM.)				
M-10 TOOL STEEL	+0.08	-	+0.04	+0.04
52-100 STEEL	+0.04	-	0.01	0.00
NAVAL BRONZE	+0.04	-	+0.08	0.04

(1) TEST WAS INTERRUPTED AFTER 18 HOURS. CYLINDER WAS COOLED TO ROOM TEMPERATURE, VENTED, AND PURGED WITH NITROGEN. TEST WAS THEN CONTINUED FOR AN ADDITIONAL 12 HR.

Table 44

EFFECT OF TEMPERATURE ON THE THERMAL DECOMPOSITION OF A PARTIALLY HYDROGENATED AROMATIC HYDROCARBON

ALL TESTS CONDUCTED IN THE PRL STAINLESS STEEL PRESSURE CYLINDER
TEST CONDITIONS INCLUDE: TEST TIME AND TEMPERATURE AS INDICATED; TEST FLUID CHARGED = 20 ML.; TOTAL VOLUME OF THE CYLINDER = 46 ML.; GAS SPACE = 17 ML. AT TEST TEMPERATURE AND 23 ML. AT ROOM TEMPERATURE; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 26 P.S.I.G. AT 650°F, 28 P.S.I.G. AT 700°F, AND 30 P.S.I.G. AT 750°F.

TEST FLUID	A PARTIALLY HYDROGENATED AROMATIC HYDROCARBON (MLO 7218)						
TEST TEMPERATURE, °F.	650	<- - - - - - - - - - 700 (1)				- - - - - - - ->	750
TEST TIME, HOURS	26	20	20	20	20	20	4.5
DECOMPOSITION DATA:							
GAS FORMATION							
MOLES OF GAS/HR. ($X10^3$)	0.032	0.228	0.197	0.220	0.206	0.202	0.692
MOLES OF GAS/MOLE OF OIL/HR.	0.0004	0.0032	0.0028	0.0031	0.0029	0.0028	0.0102
TOTAL MOLES GAS/MOLE OF OIL	0.02	0.07	0.06	0.07	0.07	0.06	0.08
SYSTEM PRESSURE, P.S.I.G.							
MAXIMUM AT TEST TEMP.	73	248	237	271	260	255	288
RESIDUAL AT ROOM TEMP.	22	102	91	107	94	92	109
SLOPE, P.S.I.G./HR.	2.2	10.4	9.0	10.0	9.4	9.2	51
ANALYSIS OF RESIDUAL GASEOUS PRODUCT, %							
HYDROGEN	32.9	36.3	34.7	32.6	36.2	31.1	32.5
METHANE	50.1	60.9	62.4	63.9	59.6	64.1	54.4
CARBON MONOXIDE	-	-	-	-	-	-	-
CARBON DIOXIDE	-	-	-	-	-	-	-
ETHANE-ETHYLENE	9.0	2.8	2.8	3.5	4.2	4.8	7.2
PROPANE	5.0	-	-	-	-	-	3.7
PROPYLENE	0.4	-	-	-	-	-	0.4
ISOBUTANE	0.5	-	-	-	-	-	0.2
N-BUTANE	1.4	-	-	-	-	-	0.9
ISO- AND N-1-BUTENE	0.2	-	-	-	-	-	0.2
TRANS-2-BUTENE	TRACE	-	-	-	-	-	TRACE
CIS-2-BUTENE	TRACE	-	-	-	-	-	TRACE
ISOPENTANE	0.2	-	-	-	-	-	0.1
N-PENTANE	0.2	-	-	-	-	-	0.1
FLUID PROPERTIES							
% CHANGE IN CS. VISC. AT 100°F.	-6	-	-	-	-	-	-19
NEUT. NO. (MG. KOH/GM. OIL)							
ORIGINAL	0.0	-	-	-	-	-	0.0
FINAL	0.1	-	-	-	-	-	0.0
CATALYST WT. LOSS (MG./SQ. CM.)							
M-10 TOOL STEEL	+0.04	-	-	-	-	-	+0.10
52-100 STEEL	0.04	-	-	-	-	-	+0.08
NAVAL BRONZE	+0.04	-	-	-	-	-	+0.10

(1) THIS TEST WAS RUN FOR A TOTAL OF 100 CONSECUTIVE HOURS IN 20-HOUR INCREMENTS. AFTER EACH 20-HOUR TEST THE CYLINDER WAS COOLED TO ROOM TEMPERATURE, VENTED, AND PURGED WITH NITROGEN.

ALL TESTS CONDUCTED IN THE PRL PRESSURE CYLINDER.

TEST CONDITIONS: TEST TEMPERATURE = 700° ± 10°F ; TEST TIME = 20 HRS.; TEST FLUID CHARGED = 20 ML.; TOTAL VOLUME OF CYLINDER = 46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52 - 100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE CYLINDER IS ABOUT 28 P.S.I.G. AT 700°F.

TEST WAS RUN FOR A TOTAL OF 100 CONSECUTIVE HOURS IN 20-HOUR INCREMENTS. AFTER EACH 20 HOURS, THE CYLINDER WAS COOLED TO ROOM TEMPERATURE, VENTED, AND PURGED WITH NITROGEN.

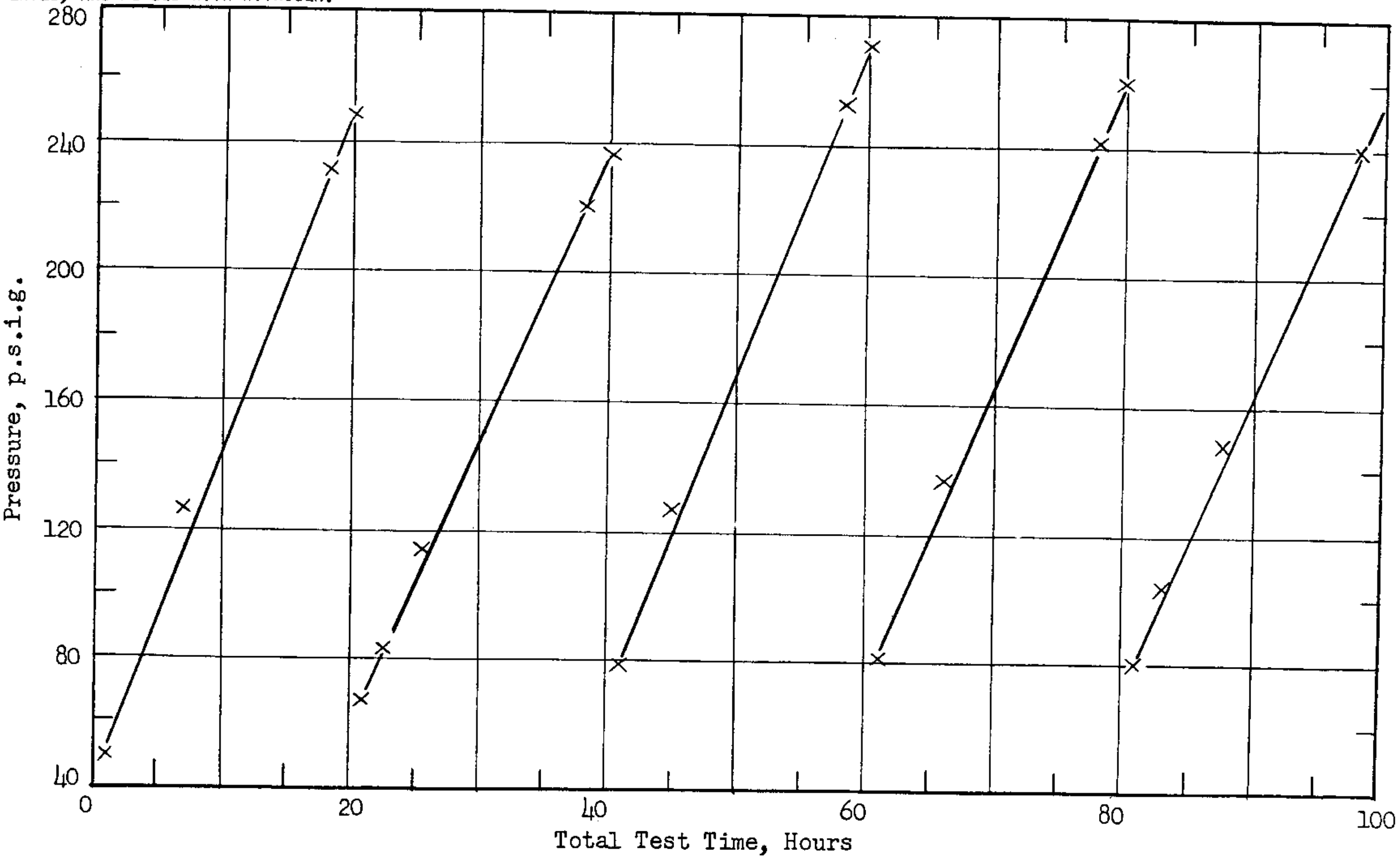


Figure 7. RATE OF GAS FORMATION IN INCREMENTAL TESTS WITH A PARTIALLY HYDROGENATED AROMATIC HYDROCARBON

Table 45

EFFECT OF TEMPERATURE ON THE THERMAL DECOMPOSITION OF A POLYOLEFIN

ALL TESTS CONDUCTED IN THE PRL STAINLESS STEEL PRESSURE CYLINDER
TEST CONDITIONS INCLUDE: TEST TIME AND TEMPERATURE AS INDICATED; TEST FLUID CHARGED = 20 ML.; TOTAL VOLUME OF THE CYLINDER = 46 ML.; GAS SPACE = 17 ML. AT TEST TEMPERATURE AND 23 ML. AT ROOM TEMPERATURE; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 26 P.S.I.G. AT 650°F, 28 P.S.I.G. AT 700°F, AND 30 P.S.I.G. AT 750°F.

TEST FLUID	A POLYOLEFIN (MLO 7345)		
TEST TEMPERATURE, °F.	650	700	750
TEST TIME, HOURS	20	6	1.5
DECOMPOSITION DATA:			
GAS FORMATION			
MOLES OF GAS/HR. ($X10^3$)	0.068	0.503	3.04
MOLES OF GAS/MOLE OF OIL/HR.	0.0021	0.0151	0.0917
TOTAL MOLES GAS/MOLE OF OIL	0.04	0.12	0.17
SYSTEM PRESSURE, P.S.I.G.			
MAXIMUM AT TEST TEMP.	99	210	300
RESIDUAL AT ROOM TEMP.	10	27	33
SLOPE, P.S.I.G./HR.	3.0	22.8	145
ANALYSIS OF RESIDUAL GASEOUS PRODUCT, %			
HYDROGEN	-	31.7	27.3
METHANE	-	26.4	29.6
CARBON MONOXIDE	-	6.9	3.4
CARBON DIOXIDE	-	-	-
ETHANE-ETHYLENE	-	23.2	28.5
PROPANE	-	7.8	7.2
PROPYLENE	-	2.2	2.3
ISOBUTANE	-	0.1	TRACE
N-BUTANE	-	1.0	0.8
ISO- AND N-1-BUTENE	-	0.4	0.3
TRANS-2-BUTENE	-	0.1	0.2
CIS-2-BUTENE	-	0.1	-
ISOPENTANE	-	TRACE	-
N-PENTANE	-	TRACE	0.2
FLUID PROPERTIES			
% CHANGE IN CS. VISC. AT 100°F.	-23	-45	-54
NEUT. NO. (MG. KOH/GM. OIL)			
ORIGINAL	0.0	0.0	0.0
FINAL	0.9	0.3	0.2
CATALYST WT. LOSS (MG./SQ. CM.)			
M-10 TOOL STEEL	+0.04	+0.02	+0.04
52-100 STEEL	+0.02	0.00	+0.04
NAVAL BRONZE	+0.12	0.14	0.00

Table 46

EFFECT OF TEMPERATURE ON THE THERMAL DECOMPOSITION OF A POLYBUTENE

ALL TESTS CONDUCTED IN THE PRL STAINLESS STEEL PRESSURE CYLINDER

TEST CONDITIONS INCLUDE: TEST TIME AND TEMPERATURE AS INDICATED; TEST FLUID CHARGED = 20 ML.; TOTAL VOLUME OF THE CYLINDER = 46 ML.; GAS SPACE = 17 ML. AT TEST TEMPERATURE AND 23 ML. AT ROOM TEMPERATURE; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 23 P.S.I.G. AT 550°F, 25 P.S.I.G. AT 600°F, AND 26 P.S.I.G. AT 650°F.

TEST FLUID	A POLYBUTENE (MLO 7123)			
TEST TEMPERATURE, °F.	550	600	650	700
TEST TIME, HOURS	28	6	1.3	0.2
DECOMPOSITION DATA:				
GAS FORMATION				
MOLES OF GAS/HR. (X10^3)	0.088	0.699	4.20	-
MOLES OF GAS/MOLE OF OIL/HR.	0.0026	0.0206	0.124	-
TOTAL MOLES GAS/MOLE OF OIL	0.08	0.15	0.16	0.17
SYSTEM PRESSURE, P.S.I.G.				
MAXIMUM AT TEST TEMP.	125	232	274	297
RESIDUAL AT ROOM TEMP.	10	20	18	26
SLOPE, P.S.I.G./HR.	3.5	29.2	183	-
ANALYSIS OF RESIDUAL GASEOUS PRODUCT, %				
HYDROGEN	-	-	-	3.3
METHANE	-	-	-	25.2
CARBON MONOXIDE	-	-	-	3.8
CARBON DIOXIDE	-	-	-	-
ETHANE-ETHYLENE	-	-	-	10.2
PROPANE	-	-	-	12.5
PROPYLENE	-	-	-	8.7
ISOBUTANE	-	-	-	5.6
N-BUTANE	-	-	-	0.2
ISO- AND N-1-BUTENE	-	-	-	29.9
TRANS-2-BUTENE	-	-	-	0.2
CIS-2-BUTENE	-	-	-	0.2
ISOPENTANE	-	-	-	0.2
N-PENTANE	-	-	-	0.2
FLUID PROPERTIES				
% CHANGE IN CS. VISC. AT 100°F.	-32	-51	-48	-66
NEUT. NO. (MG. KOH/GM. OIL)				
ORIGINAL	0.0	0.0	0.0	0.0
FINAL	0.2	0.1	0.2	0.1
CATALYST WT. LOSS (MG./SQ. CM.)				
M-10 TOOL STEEL	+0.02	0.00	+0.06	+0.02
52-100 STEEL	0.02	+0.06	+0.10	+0.08
NAVAL BRONZE	+0.08	0.00	+0.04	+0.06

ALL TESTS CONDUCTED IN THE PRL PRESSURE CYLINDER

TEST CONDITIONS: TEST TEMPERATURE = 700° ± 10°F ; TEST TIME = 20 HOURS; VOLUME OF CYLINDER=46 ML ;AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 28 LBS. AT 700°F.

TEST FLUID: A POLYBUTENE OIL (MLO 7123)

■ = 25 ML. CHARGE (10 ML. GAS SPACE)
△ = 20 ML. CHARGE (17 ML. GAS SPACE)
□ = 15 ML. CHARGE (23 ML. GAS SPACE)
○ = 10 ML. CHARGE (30 ML. GAS SPACE)
× = 5 ML. CHARGE (36 ML. GAS SPACE)
● = 1 ML. CHARGE (42 ML. GAS SPACE)

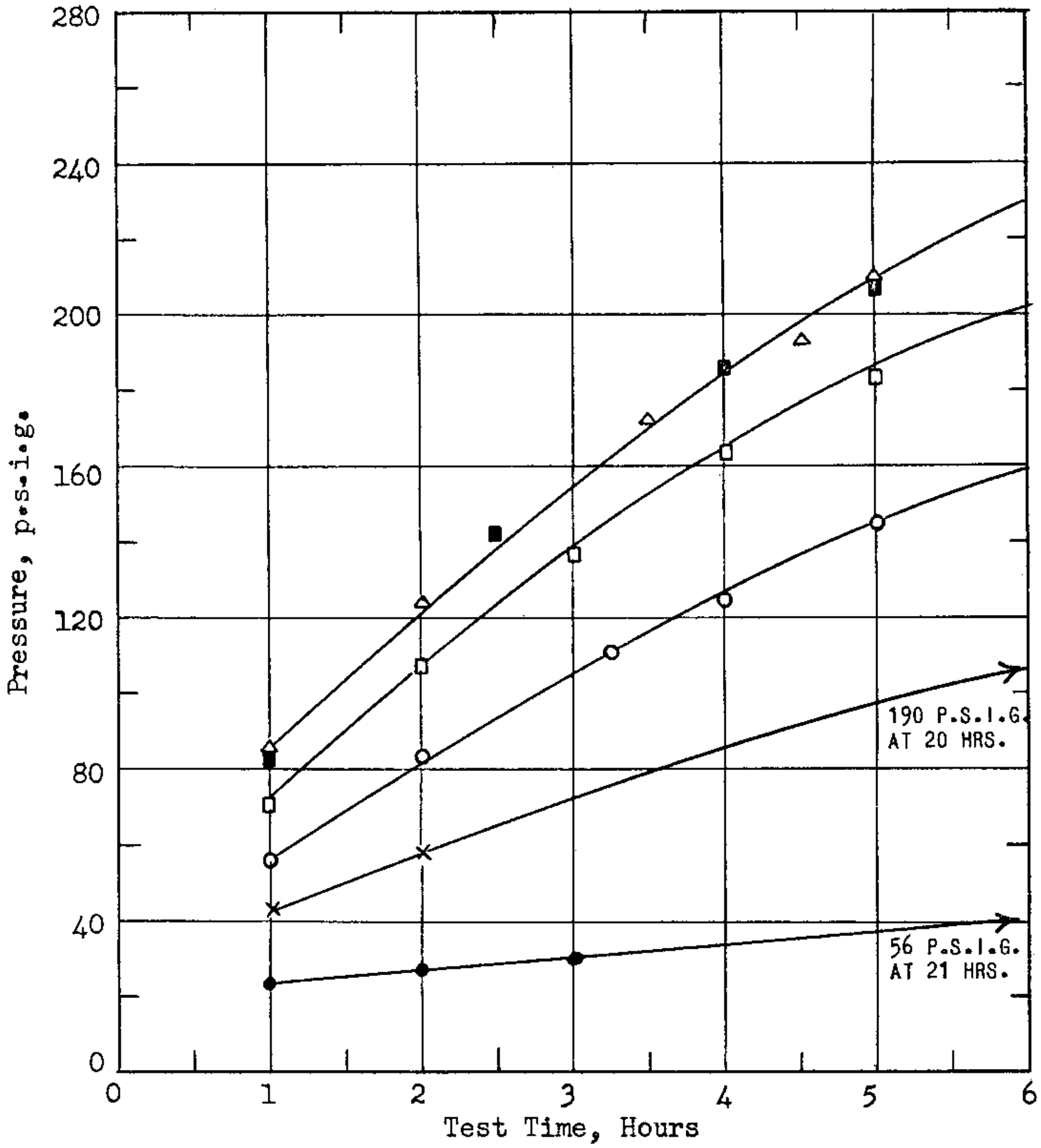


Figure 8, EFFECT OF VARYING GAS SPACE ON RATE OF GAS FORMATION

Table 47

EFFECT OF TEMPERATURE ON THE THERMAL DEGRADATION OF VARIOUS FLUIDS

ALL TESTS CONDUCTED IN THE PRL STAINLESS STEEL PRESSURE CYLINDER
TEST CONDITIONS INCLUDE: TEST FLUID CHARGED = 20 ML.; TOTAL VOLUME OF THE CYLINDER = 46 ML.; GAS SPACE = 17 ML. AT TEST TEMPERATURE AND 23 ML. AT ROOM TEMPERATURE; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED.

	RATE OF GAS FORMATION (MOLES GAS PER MOL OIL PER HOUR) AT				
TEST FLUID	550°F.	600°F.	650°F.	700°F.	750°F.
SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)	-	-	0.0004	0.0068	0.059
HYDROGENATED PARAFFINIC BRIGHT STOCK (MLO 7289)	-	-	0.0013	0.0099	0.065
PARAFFINIC LIGHT RESIN (MLO 7308)	-	-	0.0023	0.0212	0.163
SUPER-REFINED NAPHTHENIC NEUTRAL (MLO 7357)	-	-	0.0006	0.0074	0.047
PARTIALLY HYDROGENATED AROMATIC HYDROCARBON (MLO 7218)	-	-	0.0004	0.0032	0.010
A POLYOLEFIN (MLO 7346)	-	-	0.0021	0.0151	0.092
A POLYBUTENE (MLO 7123)	0.0026	0.0206	0.124	-	-

ALL TESTS CONDUCTED IN THE PRL PRESSURE CYLINDER

TEST CONDITIONS: TEST TEMPERATURE AND TIME AS INDICATED; FLUID CHARGED = 20 ML.; TOTAL VOLUME OF CYLINDER = 46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. NITROGEN PRESSURE IN THE CYLINDER IS ABOUT 26 P.S.I.G. AT 650°F , 28 P.S.I.G. AT 700°F., AND 30 P.S.I.G. AT 750°F.

TEST FLUID: SUPER-REFINED PARAFFINIC BRIGHT STOCK (MLO 7289)

TEST TEMPERATURE: X = 750°F ; O = 700°F ; △ = 650°F.

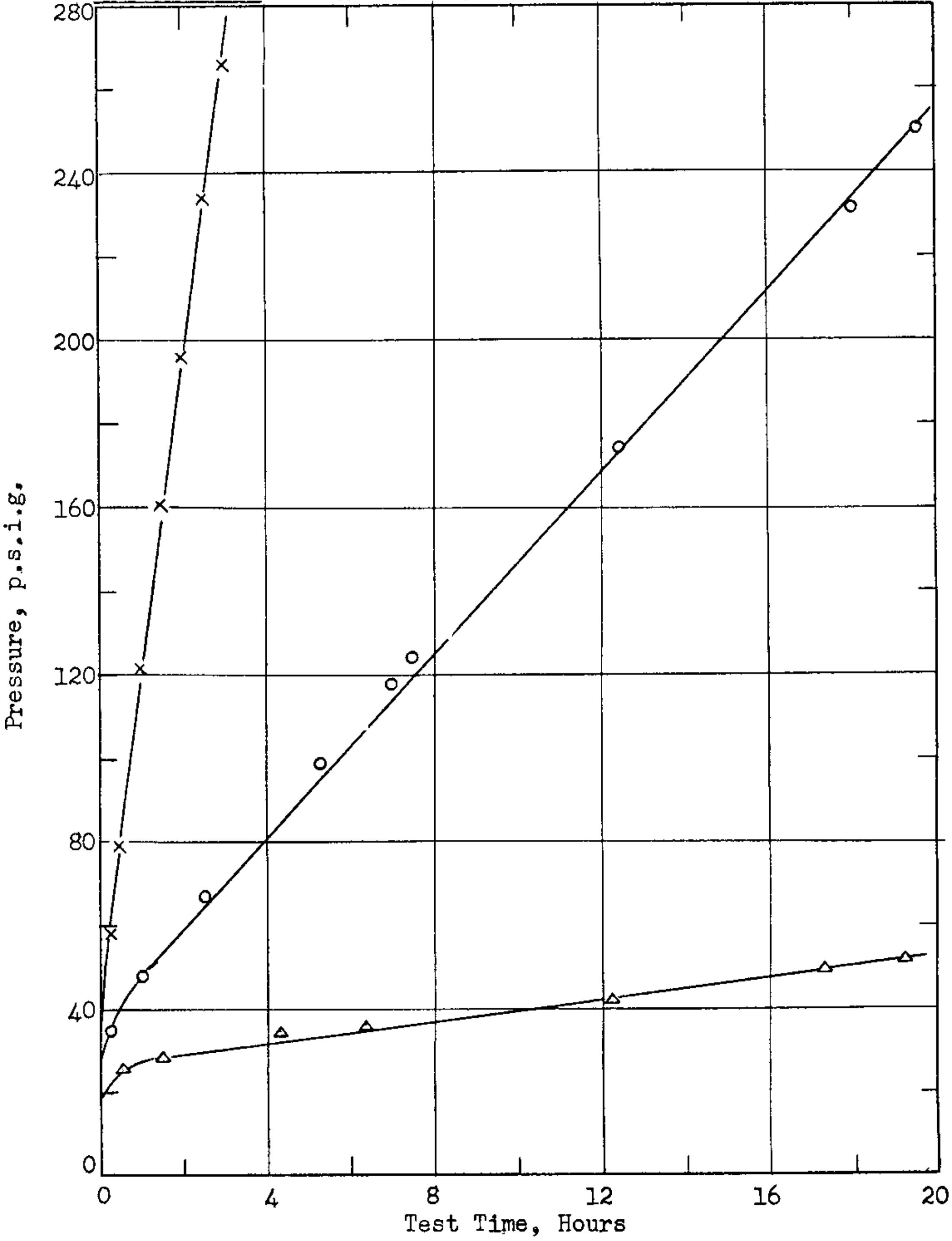


Figure 9. EFFECT OF TEMPERATURE ON RATE OF GAS FORMATION

ALL TESTS CONDUCTED IN THE PRL PRESSURE CYLINDER

TEST CONDITIONS: TEST TEMPERATURE AND TIME AS INDICATED; FLUID CHARGED = 20 ML.; TOTAL VOLUME OF CYLINDER = 46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. NITROGEN PRESSURE IN THE CYLINDER IS ABOUT 26 P.S.I.G. AT 650°F, 28 P.S.I.G. AT 700°F, AND 30 P.S.I.G. AT 750°F.

TEST FLUID: A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)
TEST TEMPERATURE: × = 750°F; ○ = 700°F; △ = 650°F.

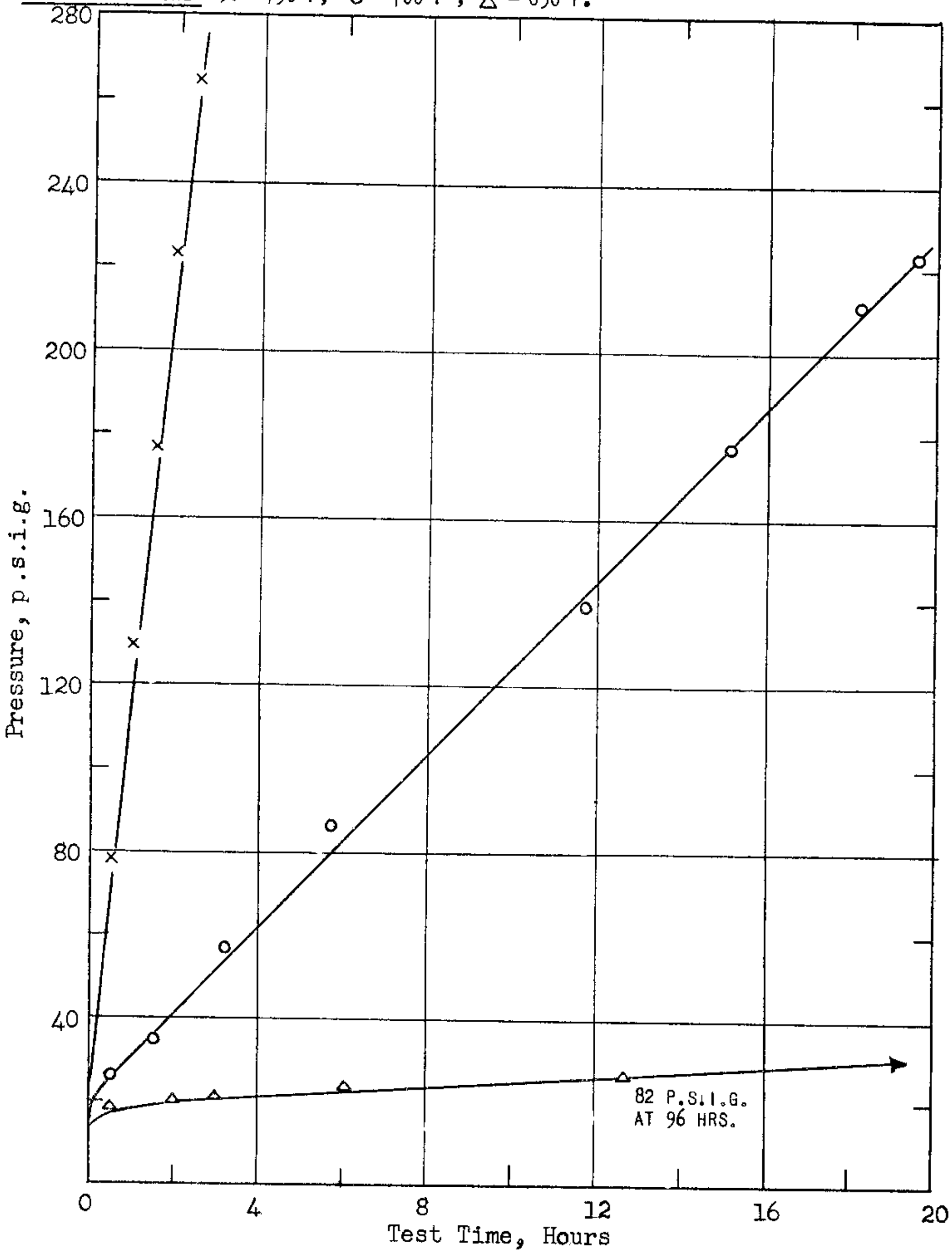


Figure 10. EFFECT OF TEMPERATURE ON RATE OF GAS FORMATION

ALL TESTS CONDUCTED IN THE PRL PRESSURE CYLINDER

TEST CONDITIONS: TEST TEMPERATURE AND TIME AS INDICATED; FLUID CHARGED = 20 ML.; TOTAL VOLUME OF CYLINDER = 46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. NITROGEN PRESSURE IN THE CYLINDER IS ABOUT 26 P.S.I.G. AT 650°F, 28 P.S.I.G. AT 700°F, AND 30 P.S.I.G. AT 750°F.

TEST FLUID: A SUPER-REFINED NAPHTHENIC NEUTRAL (MLO 7357)

TEST TEMPERATURE: × = 750°F; ○ = 700°F.; △ = 650°F.

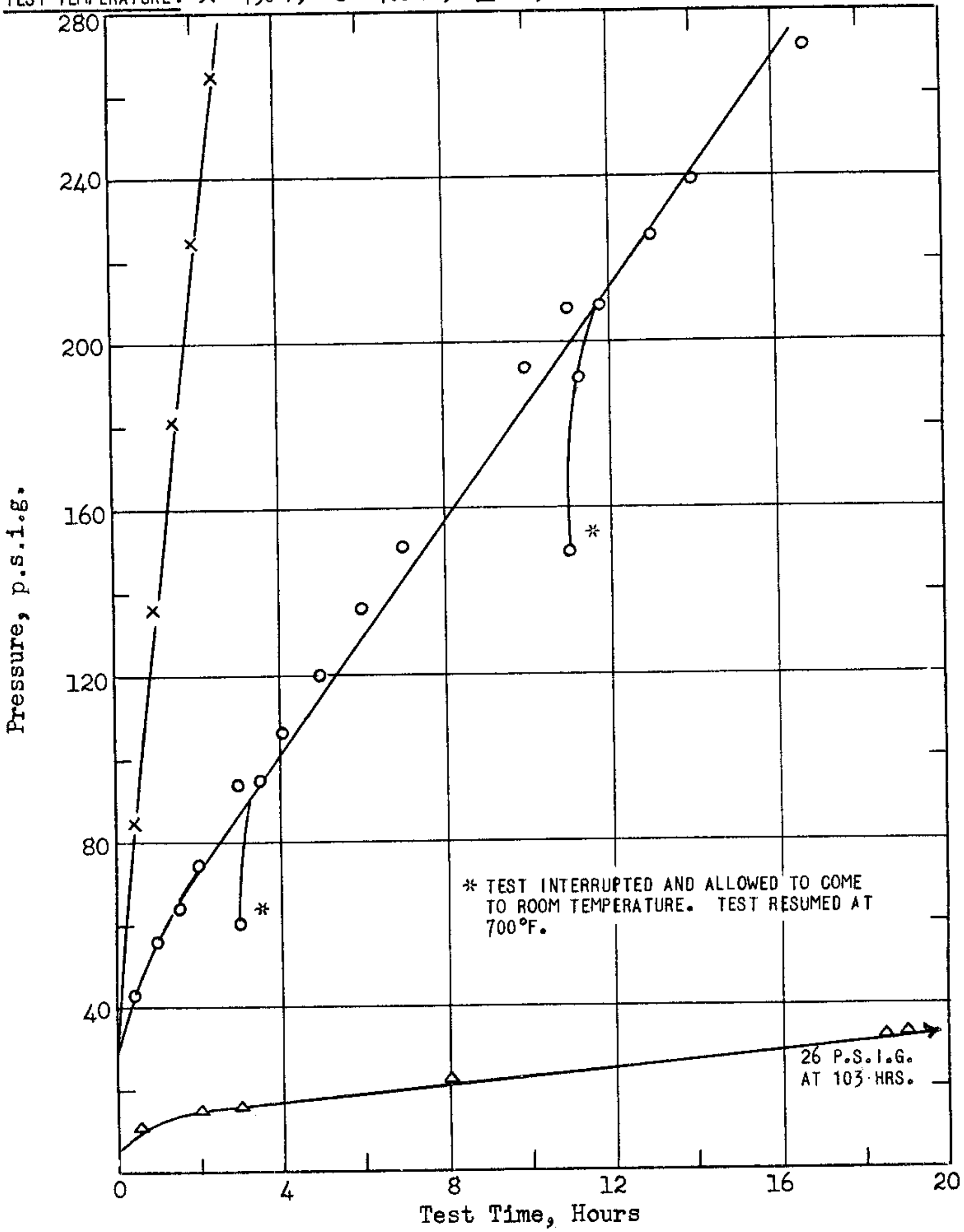


Figure 11. EFFECT OF TEMPERATURE ON RATE OF GAS FORMATION

ALL TESTS CONDUCTED IN THE PRL PRESSURE CYLINDER

TEST CONDITIONS: TEST TEMPERATURE AND TIME AS INDICATED; FLUID CHARGED = 20 ML.; TOTAL VOLUME OF CYLINDER = 46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. NITROGEN PRESSURE IN THE CYLINDER IS ABOUT 26 P.S.I.G. AT 650°F, 28 P.S.I.G. AT 700°F, AND 30 P.S.I.G. AT 750°F.

TEST FLUID: A PARTIALLY HYDROGENATED AROMATIC HYDROCARBON (MLO 7218-16)

TEST TEMPERATURE: × = 750°F ; ○ = 700°F ; △ = 650°F.

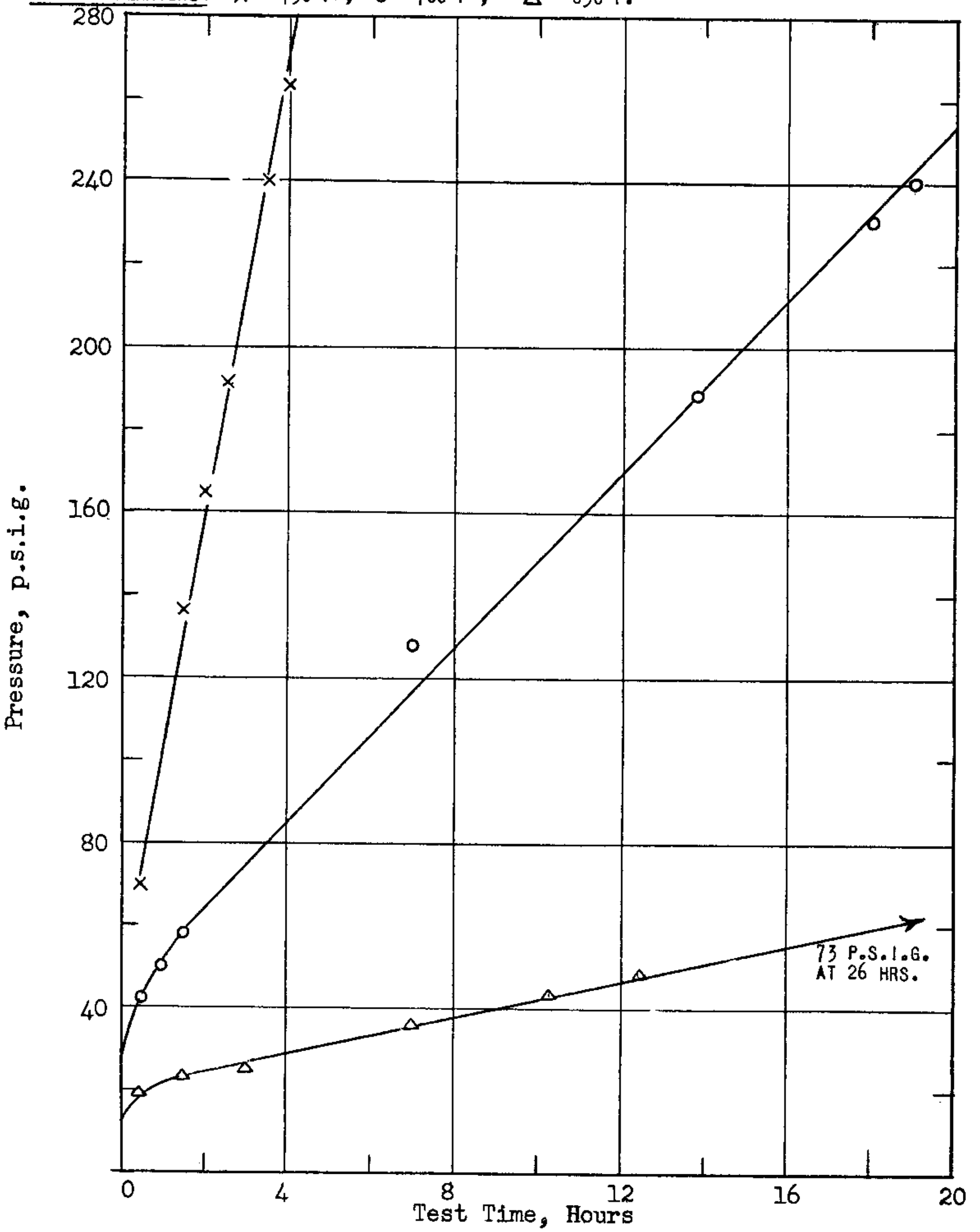


Figure 12. EFFECT OF TEMPERATURE ON RATE OF GAS FORMATION

ALL TESTS CONDUCTED IN THE PRL PRESSURE CYLINDER

TEST CONDITIONS: TEST TEMPERATURE AND TIME AS INDICATED; FLUID CHARGED = 20 ML.; TOTAL VOLUME OF CYLINDER = 46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. NITROGEN PRESSURE IN THE CYLINDER IS ABOUT 23 P.S.I.G. AT 550°F , 25 P.S.I.G. AT 600°F , AND 26 P.S.I.G. AT 650°F.

TEST FLUID: A POLYBUTENE OIL (MLO 7123)

TEST TEMPERATURE: × = 650°F ; ○ = 600°F , △ = 550°F.

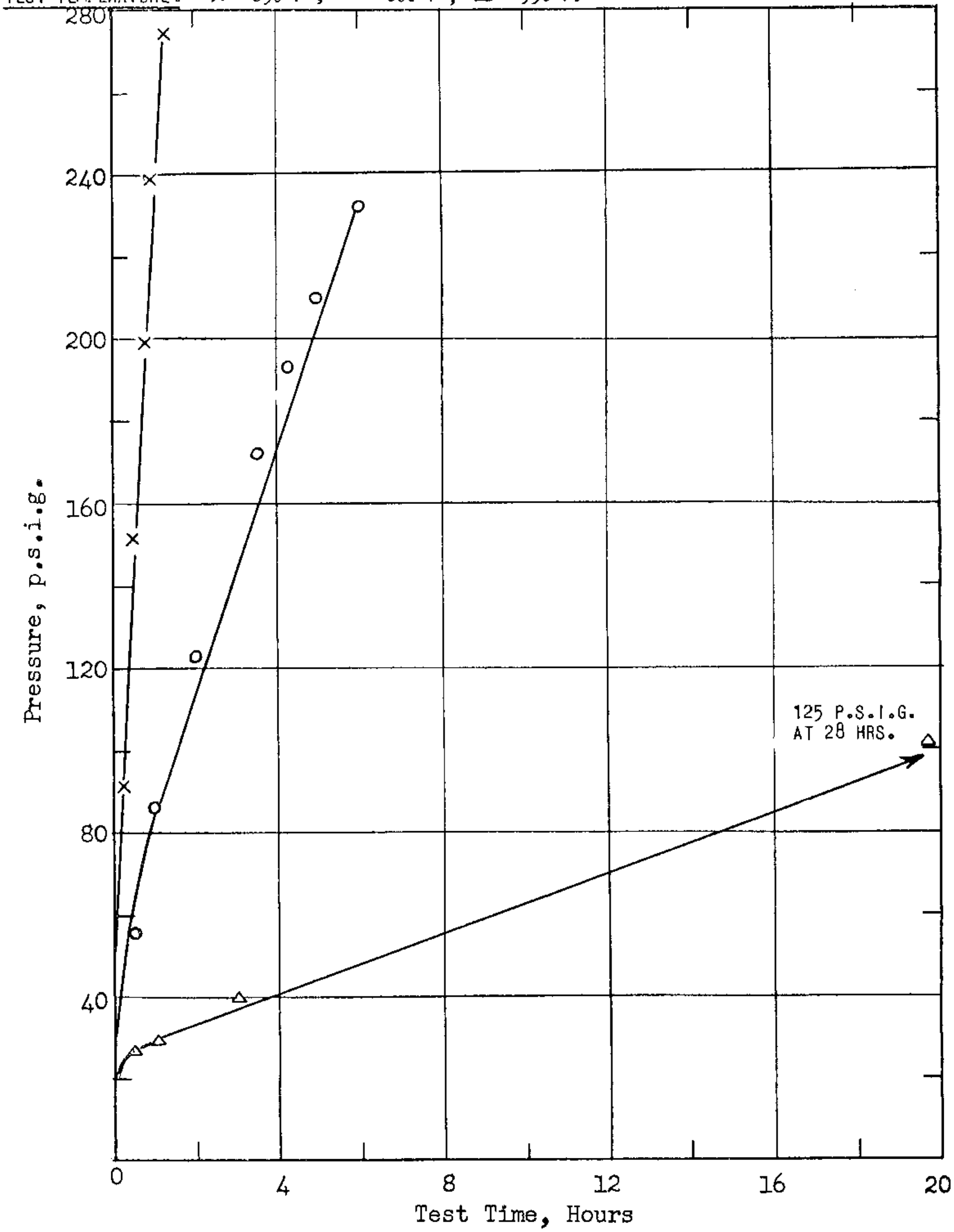


Figure 13. EFFECT OF TEMPERATURE ON RATE OF GAS FORMATION

ALL TESTS CONDUCTED IN THE PRL PRESSURE CYLINDER

TEST CONDITIONS: TEST TEMPERATURE AND TIME AS INDICATED; FLUID CHARGED = 20 ML.; TOTAL VOLUME OF CYLINDER = 46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. NITROGEN PRESSURE IN THE CYLINDER IS ABOUT 26 P.S.I.G. AT 650°F, 28 P.S.I.G. AT 700°F, AND 30 P.S.I.G. AT 750°F.

TEST FLUID: A POLYOLEFIN OIL (MLO 7346)

TEST TEMPERATURE: × = 750°F; ○ = 700°F; △ = 650°F.

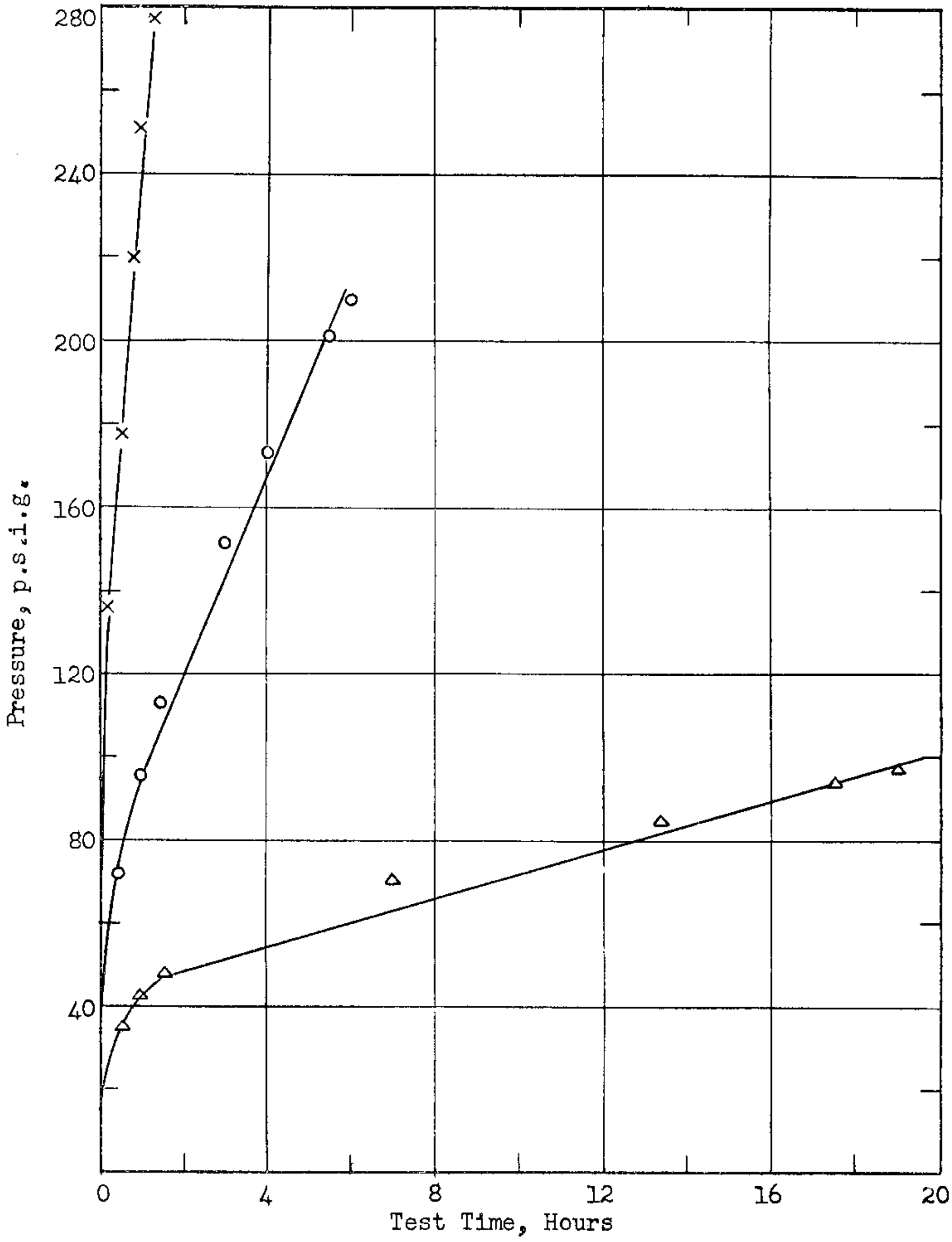


Figure 14. EFFECT OF TEMPERATURE ON RATE OF GAS FORMATION

ALL TESTS CONDUCTED IN THE PRL PRESSURE CYLINDER

TEST CONDITIONS: TEST TEMPERATURE AND TIME AS INDICATED; FLUID CHARGED = 20 ML.; TOTAL VOLUME OF CYLINDER = 46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. NITROGEN PRESSURE IN THE CYLINDER IS ABOUT 26 P.S.I.G. AT 650°F , 28 P.S.I.G. AT 700°F , AND 30 P.S.I.G. AT 750°F.

TEST FLUID: A PARAFFINIC LIGHT RESIN (MLO 7308)

TEST TEMPERATURE: X = 750°F ; O = 700°F ; △ = 650°F.

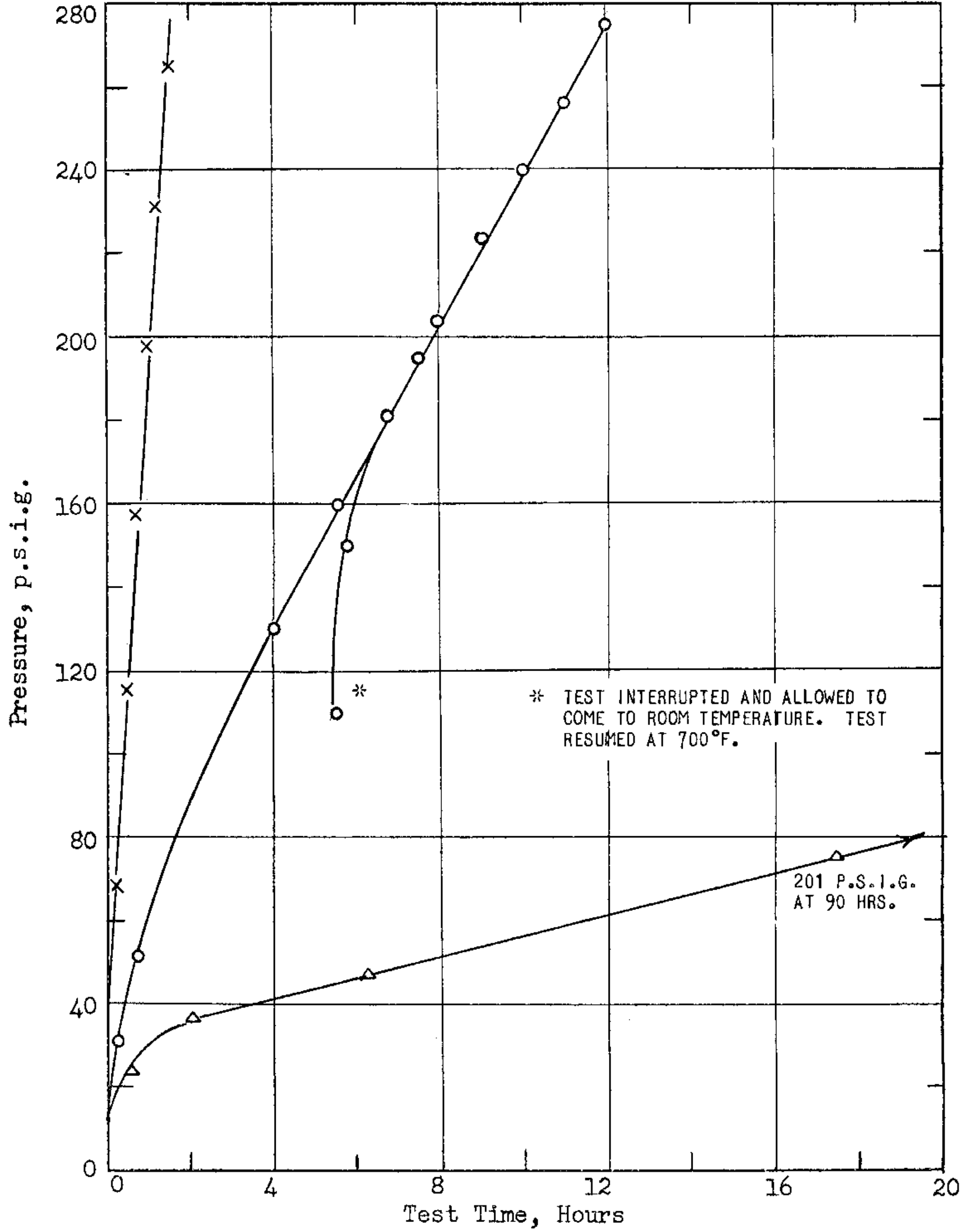


Figure 15. EFFECT OF TEMPERATURE ON RATE OF GAS FORMATION

Table 48

TEMPERATURE INCREASE REQUIRED TO DOUBLE RATE OF GAS FORMATION

ALL TESTS CONDUCTED IN THE PRL STAINLESS STEEL PRESSURE CYLINDER
TEST CONDITIONS INCLUDE: TEST FLUID CHARGED = 20 ML.; TOTAL VOLUME OF THE CYLINDER = 46 ML.; GAS SPACE = 17 ML. AT TEST TEMPERATURE AND 23 ML. AT ROOM TEMPERATURE; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52-100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED.

	TEMPERATURE INCREASE, °F, REQUIRED TO DOUBLE RATE OF GAS FORMATION			
TEMPERATURE RANGE	550°-600°F	600°-650°F	650°-700°F	700°-750°F
SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)	-	-	12.1	16.3
HYDROGENATED PARAFFINIC BRIGHT STOCK (MLO 7289)	-	-	17.1	26.6
PARAFFINIC LIGHT RESIN (MLO 7308)	-	-	15.6	16.9
SUPER-REFINED NAPHTHENIC NEUTRAL (MLO 7357)	-	-	14.2	27.0
PARTIALLY HYDROGENATED AROMATIC HYDROCARBON (MLO 7218)	-	-	17.6	45.1
A POLYOLEFIN (MLO 7346)	-	-	17.3	27.8
A POLYBUTENE (MLO 7123)	16.7	27.8	-	-

Under conventional operating conditions, the product from the thermal stability test is heated at atmospheric pressure to 500° to 550°F. The products boiling below this point are removed at a rate of 0.2 to 1.0 milliliter per minute. This initial heating at atmospheric pressure serves as a degassing operation as well as to remove volatile liquids that may contaminate the oil in the vacuum pump. The degassed sample is then cooled and the vacuum pump attached. The remainder of the sample is distilled at a pressure of less than 0.1 millimeter Hg (0.03 to 0.1). During the distillation, a product rate of 0.2 to 1.0 milliliter per minute is maintained. The distillation is discontinued when 95 per cent of the liquid product charged is taken overhead, or a normal boiling point of 1000°F is exceeded, or cracking causes an increase in pressure exceeding the 0.1 millimeter Hg pressure. During the course of the distillation, the boiling point and pressure are recorded for every 0.2 milliliter increment of product obtained.

Duplicate tests using this procedure give normal boiling point curves as a function of volume per cent distilled that are within 10°F of each other. This small scale fractionation unit has also been checked against the boiling point of pure esters, the boiling point curves of mineral oil fractions obtained from pilot plant distillation equipment (WADC TR 55-30 part VII), and large scale ASTM distillations. The values from the small scale unit are in good agreement with all three of the larger scale procedures.

b. Products From Tests with Paraffinic and Naphthenic Mineral Oils. Distillation curves for a series of paraffinic and naphthenic mineral oils before and after thermal stability tests at 700°F are shown on Figures 17, 18, 19, and 20. The paraffinic and naphthenic neutrals illustrate the trend noted with mineral oils upon thermal degradation. The thermal degradation product comprises a fraction boiling below the charging stock, a fraction boiling in the same range as the original charging stock, and a fraction boiling higher than the original material. These data indicate that thermal degradation acts to make molecules which are smaller and molecules which are larger than those in the original mineral oil fraction. In the case of the bright stock and paraffinic resin, the boiling point of the original material exceeds the 1000° to 1100°F limit of the distillation equipment. The low boiling products of thermal degradation can be demonstrated, but the higher boiling products cannot be illustrated by this distillation technique.

The distillation range of the thermal deterioration products clearly illustrates the problem involved in using viscosity measurement as a measure of thermal degradation. The volatile products formed in the low boiling ranges dominate the viscosity change. For example, the addition of 10 per cent of a one centistoke viscosity fluid to a mineral oil of 100 centistokes will result in a blend of oil having about 44 centistokes. A contamination of 20 per cent of a fluid of one centistoke in a 100 centistoke fluid will give an overall fluid viscosity of about 15 centistokes.

If the 100 centistoke fluid is first contaminated with 10 per cent of a 500 centistoke fluid and then 10 per cent of a one centistoke fluid is added, the overall viscosity of the blend is about 47 centistokes. These data further illustrate the extreme sensitivity of overall viscosity to small quantities of volatile non-viscous products.

The products of thermal decomposition for the paraffinic and naphthenic mineral oils shown on Figures 17 and 18 contain approximately 10 per cent of material which is in the 0.5 to 2.0 centistoke viscosity range based on boiling point. The viscosity of the fluid after thermal degradation in an actual application would be dependent upon the volatility level of the first products that are retained in the system.

It is estimated from the boiling point curves on Figures 17 and 18 that the 90 per cent of the liquid with 10 per cent of the most volatile products removed would have a viscosity value within 20 per cent of the original mineral oil. The viscosity relationships of the various fractions of thermal degradation products of mineral oils will be determined on several fluids to illustrate quantitatively the yield of various liquid products.

In the gas phase reaction at 700°F , differences in reaction rate could be demonstrated for the quantity of fluid charged (volume of heated gas space). Distillation of the liquid products from the series of 700°F thermal stability tests involving 5,10,15, and 20 milliliter charges in the PRL pressure cylinder are shown on Figures 21 and 22 for a paraffinic and naphthenic neutral, respectively. These two series of tests show essentially the same liquid product for the same charging stock despite the volume of fluid charged. This liquid behavior differs considerably from that of the gas phase.

The gas phase reaction shows a constant rate as a function of time. The gas pressure as a function of unreacted fluid appears to follow a zero order reaction mechanism. The behavior of the liquid product for a paraffin and a naphthene mineral oil is shown as a function of test time at 700°F on Figures 23 and 24. These data show that the same reaction products, based on boiling point curves, exist after 6 or 20 hours test time.

Plots of the per cent of fluid degraded (no longer in the initial boiling range) versus test time for the paraffinic and naphthenic mineral oil are shown on Figures 25 and 26. These figures show a curve for the total fluid degraded as well as separate curves for the higher boiling products and the lower boiling products. All of these degradation products appear to approach an asymptote or constant concentration for a given set of test conditions. This behavior can be explained by either of two theories. First, the unstable molecules at the specific test conditions have all been degraded and the remaining materials in the original boiling range are stable under the test conditions. Second, the reaction forming thermal degradation products may be an equilibrium, or approaching a steady state, in which the reaction products are merely replacing the reactants.

To determine the mechanism of the reaction, the material having the original boiling range of the paraffinic mineral oil was taken from the products of the 700° and 750°F thermal stability tests. This corresponds to the fractions between 32 and 85 per cent overhead from the 700°F test and between 70 and 92 per cent overhead from the 750°F test. These two materials were subjected to additional 20-hour thermal stability tests at 700°F. in the PRL pressure cylinder under nitrogen. The results of these tests are shown on Table 49 and Figures 27 and 28. In both cases, the products formed are essentially the same as those formed from the original mineral oil charging stock. These data suggest that there are no extremely stable molecular species in the paraffinic and naphthenic mineral oils evaluated.

The fractions of the thermally treated products which have been revaluated may in fact be reaction products of thermal degradation in which the active thermal decomposition fragments combined to form hydrocarbon molecules of about the same molecular size as the original mineral oil. The behavior of the thermal degradation of these mineral oils suggest the establishment of an equilibrium. The removal of the high and low boiling products destroys the equilibrium and forces a shift in the reaction toward the reestablishment of the equilibrium conditions.

The thermal stability of paraffinic and naphthenic mineral oils has been investigated as a function of temperature over the range of 650° to 750°F. Boiling point curves for the liquid products of four such mineral oils are shown on Figures 29, 30, 31, and 32 as a function of temperature. The length of the tests, in most cases, was determined by the maximum gas pressure build-up allowable in the PRL pressure cylinder.

It has been shown that the changes in the liquid viscosity properties do not follow directly the gas pressure build-up. These curves, therefore, show the types of reaction products formed over the temperature range of 650° to 750°F. In fact, the data show that the same reaction is taking place and the same reaction products are being formed at 650°, 700°, and 750°F. In all cases, lower and higher boiling constituents are formed in addition to the boiling range originally present. The data on thermal deterioration of the liquid product as a function of time, shown on Figures 23 and 24, indicate that the data for six hours at 700°F could be substituted equally well for the 20-hour tests at 700°F shown on Figures 29 and 30. These data illustrate that insufficient facts are available to assay critically the effect of temperature, per se, on the liquid products formed.

c. Products from Tests with a Partially Hydrogenated Aromatic Hydrocarbon. The liquid products of the thermally degraded partially hydrogenated condensed ring aromatic hydrocarbons have also been evaluated. These materials have shown somewhat more overall stability at 700° and 750°F than the conventional paraffinic and naphthenic mineral oils. The product from an 18-hour thermal stability test at 700°F is compared with the original aromatic hydrocarbon fraction (MLO 7218-16) on Figure 33. These data show essentially no production of volatile liquid products and the formation of less than five per cent of material boiling higher than the original fraction.

As shown in Table 37, gas formation for the 700°F tests with MLO 7218-16 follows the conventional pattern for the hydrocarbons tested. That is, gas pressure in the pressure cylinder increased linearly with time. Because of the excellent stability of the liquid products, a series of thermal stability tests were run on the same liquid charge at 700°F. After each 20-hour increment, the test was cooled and the gas vented. The test was then continued for an additional 20 hours. Following this sequence, a total of 100 hours of test time at 700°F was obtained. The overall property changes for this test are shown on Table 44.

The results of the distillation of the liquid product from this 100-hour test are compared with 6- and 18-hour tests on Figure 34. These data show some slight increase in degradation for the 100-hour test over the 6- and 18-hour tests. However, after 100 hours at 700°F, the formation of volatile liquid products is about five per cent and the formation of higher boiling products about 10 per cent (see Figure 35). The MLO 7218-16, on this basis, shows better stability of the liquid product at 700°F than do the paraffinic and naphthenic mineral oils at 650°F (see Figures 29 and 30).

The effect of temperature on thermal stability of the liquid products of MLO 7218-16 is shown in Figure 36 over the range of 650° to 750°F. These data show again the improved stability of the aromatic hydrocarbons compared to the paraffinic and naphthenic mineral oils over this entire temperature range. In general, the aromatic hydrocarbon MLO 7218-16 tends to make more higher boiling constituents than volatile liquid components.

These data confirm the preliminary results which indicate that by altering the degree of condensation and hydrogenation of condensed ring aromatic hydrocarbons, the trends of the liquid properties upon thermal degradation at 700°F are substantially changed. A highly condensed aromatic hydrocarbon with little hydrogenation can be made to increase in viscosity at 700°F with time under thermal conditions. Increased hydrogenation and decreasing condensation of the ring result in viscosity decrease in 700°F thermal stability tests. A proper choice of degree of hydrogenation and condensation will result in a fluid which shows little change in fluid viscosity under severe 700°F thermal stability test conditions. Test fluid MLO 7218-16 approaches this optimum condition for 700°F thermal stability.

d. Products From Tests With A Polyphenyl Ether. The polyphenyl ethers are a class of aromatic compounds showing excellent high temperature thermal stability. A four-gallon sample of polyphenyl ether designated as MLO 59-142 has been obtained from the Wright Air Development Division for study. This material has been evaluated in the PRL pressure cylinder type thermal stability test over the range of 700° to 900°F. The results of these tests are shown on Table 50. The tests at 800°F show little change in pressure or fluid properties. Tests at 850°F begin to show an appreciable rate of gas formation. The viscosity for the 850° and 900°F thermal tests of MLO 59-142 increases over that of the unused fluid.

Distillation curves for the liquid products from the 850° and 900°F tests are shown on Figure 37. These data show 10 per cent volatile liquid product and 25 per cent heavier liquid in the case of the 850°F. thermal stability test and about the same percentage of reaction products for the 900°F test. It should be noted that this total of 35 to 40 per cent of thermal degradation product boiling at temperatures outside the range of the charging stock was produced with very little gas formation. This behavior can be contrasted with the aromatic hydrocarbon MLO 7218 which produced substantial quantities of gas at 700° and 750°F but with much less change in the character of the liquid product. A third type of thermal behavior noted is that of the paraffinic and naphthenic mineral oils which produced substantial quantities of gases as well as substantial charges in the liquid boiling range.

e. Products From Tests With a Polybutene Oil. The liquid product from thermal stability tests with a polybutene polymeric oil, MLO 7123, has been evaluated using the distillation technique. The polybutenes show evidence of breaking down thermally to produce butene monomer. The threshold of thermal deterioration of the polybutenes is about 500°F which is 150°F lower in temperature than the corresponding threshold of a paraffinic or naphthenic mineral oil. The change in boiling range of the liquid product from a thermal test with polybutene is shown on Figure 38. The boiling point curve for the starting material is shown for comparison. It should be noted that the curve is not defined beyond the 75 per cent point or at about 900°F normal boiling point.

At an operating pressure of 0.05 millimeter Hg and a measured overhead temperature of about 450°F, sufficient cracking is taking place in the still pot to adversely affect the minimum pressure that can be maintained in the system. Therefore, the formation of higher boiling fractions cannot be clearly shown in the case of the polybutenes because of experimental difficulties. The formation of volatile liquid products can be demonstrated, however. The formation of monomer as the predominant gaseous product and of low boiling liquid products suggests a depolymerization of the polymer to the monomer.

The effect of increasing temperature on the formation of low boiling products is shown on Figure 39 for temperatures of 550° to 700°F. It can be seen that there is no marked change in the residual liquid products with increasing temperature. The rate of the reaction is accelerated by increased temperature.

G. EFFECT OF OXIDATION INHIBITORS AND INHIBITOR COMBINATIONS ON ESTER FLUIDS.

The use of 5-ethyl-10,10-diphenylphenazasiline (5,10,10) alone and in combination with other inhibitors as an oxidation inhibitor for a Spec. MIL-L-9236 ester-base lubricant has been suggested by recent research and development work by the Wright Air Development Division. The 5-10-10 in combination with phenyl-alpha-naphthylamine (PAN) in a trimethylol propane ester has shown up well in qualitative Spec. MIL-L-7808 and Spec. MIL-L-9236 oxidation and corrosion tests, as well as mock-up high temperature bearing tests and 400°F. engine tests in the J-57 jet engine.

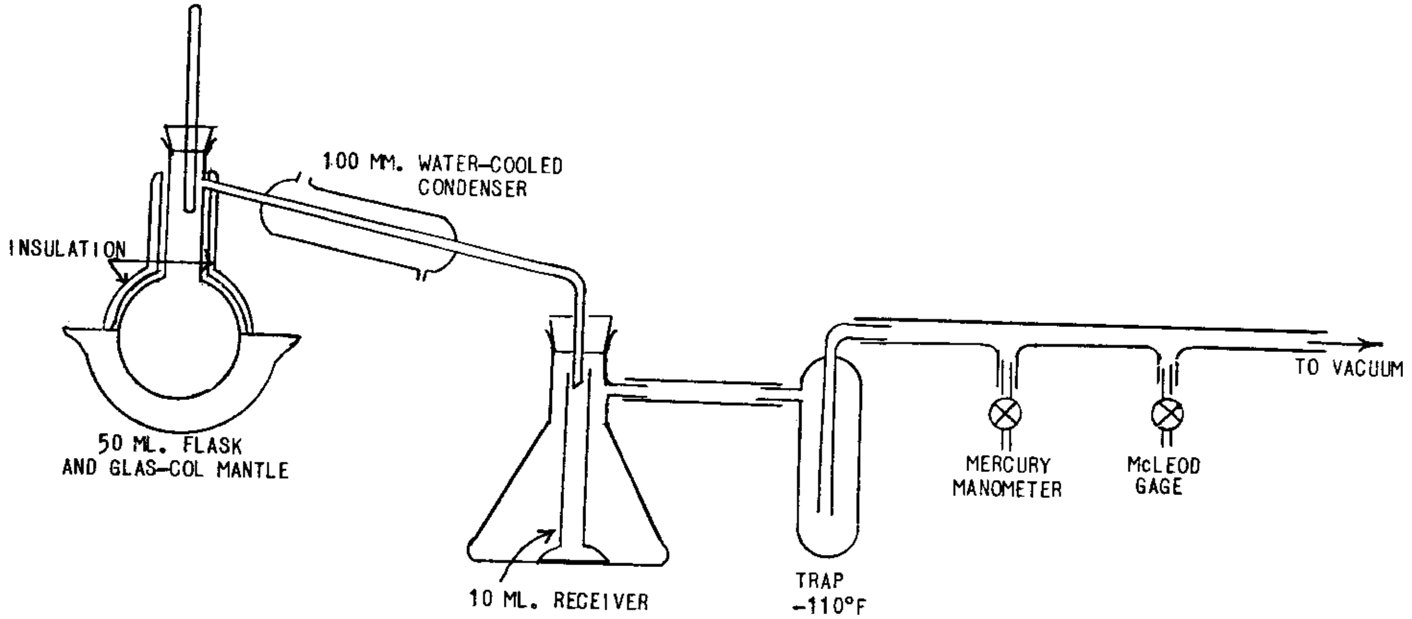


Figure 16. SMALL VOLUME VACUUM DISTILLATION APPARATUS

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER Hg PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE EXCEEDS 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)

× = ORIGINAL TEST FLUID
○ = PRODUCT FROM 20-HOUR THERMAL STABILITY TEST AT 700°F.
(FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 35.)

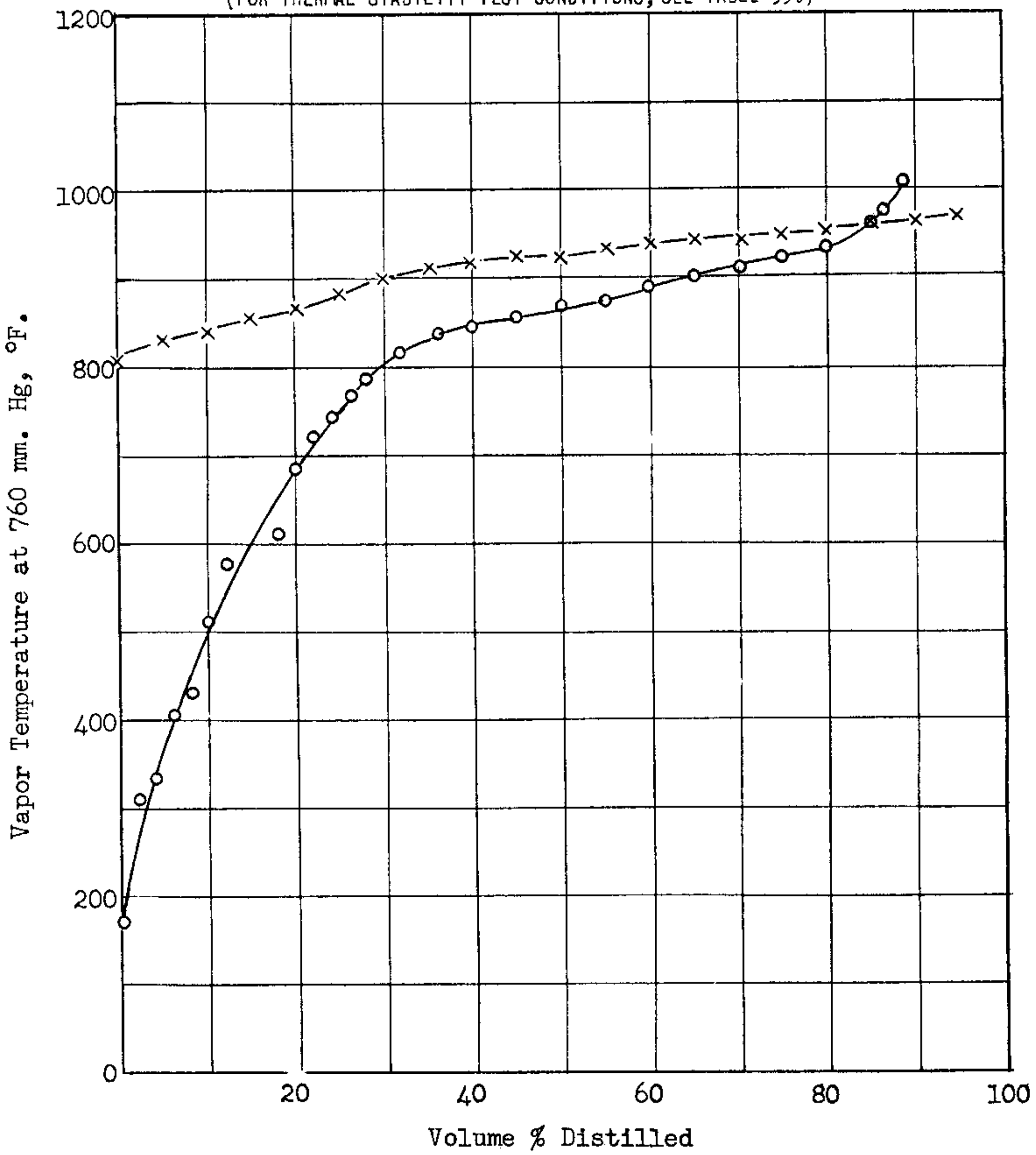


Figure 17. DISTILLATION OF THE PRODUCT FROM A THERMAL STABILITY TEST

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER Hg PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE EXCEEDS 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A SUPER-REFINED NAPHTHENIC NEUTRAL (MLO 7357)

× = ORIGINAL TEST FLUID
○ = PRODUCT FROM 20-HOUR THERMAL STABILITY TEST AT 700°F.
(FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 36.)

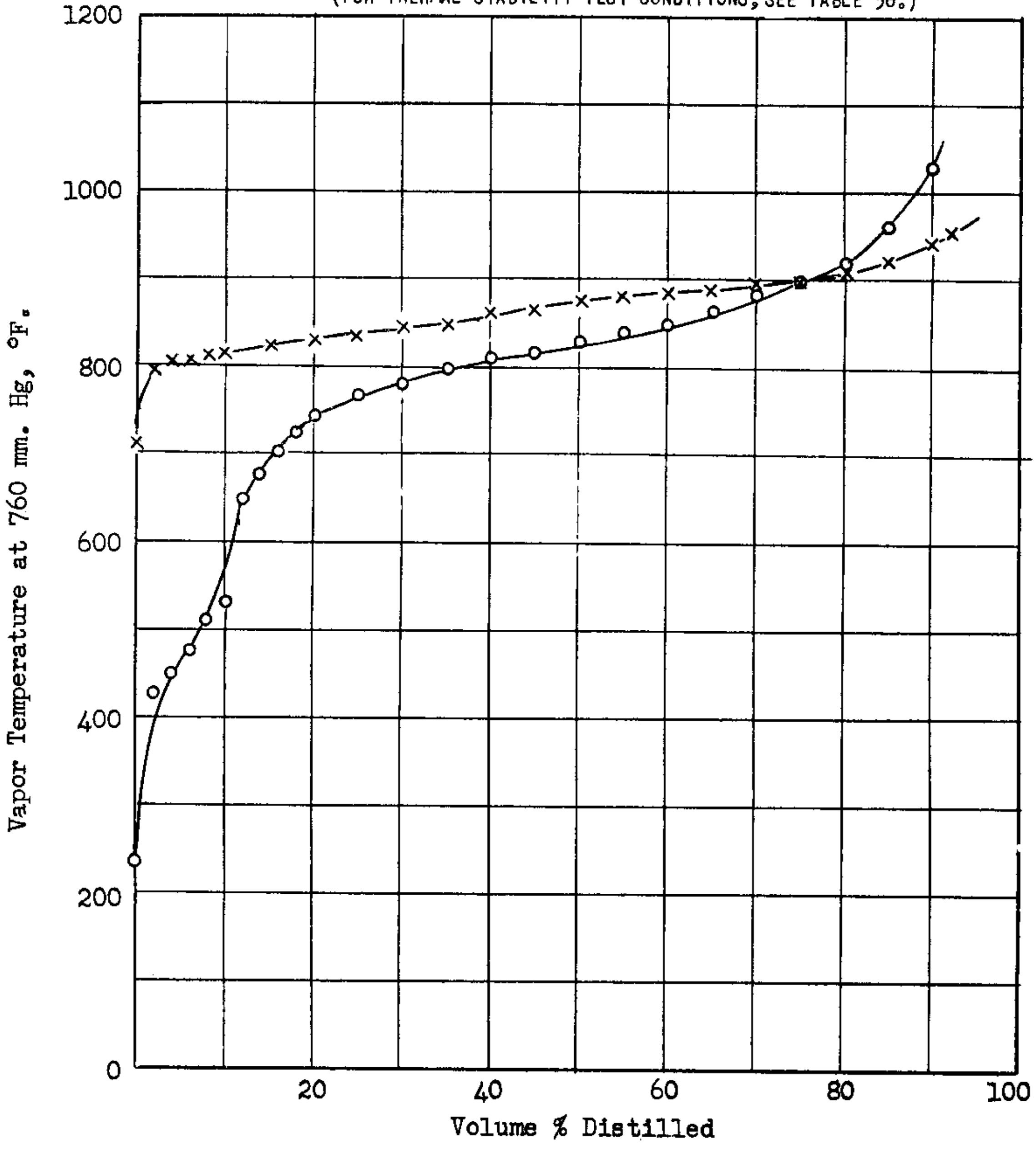


Figure 18. DISTILLATION OF THE PRODUCT FROM A THERMAL STABILITY TEST

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER HG PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE EXCEED 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A SUPER-REFINED PARAFFINIC BRIGHT STOCK (MLO 7289)

× = ORIGINAL TEST FLUID
○ = PRODUCT FROM A 30-HOUR THERMAL STABILITY TEST AT 700°F. (FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 41.)

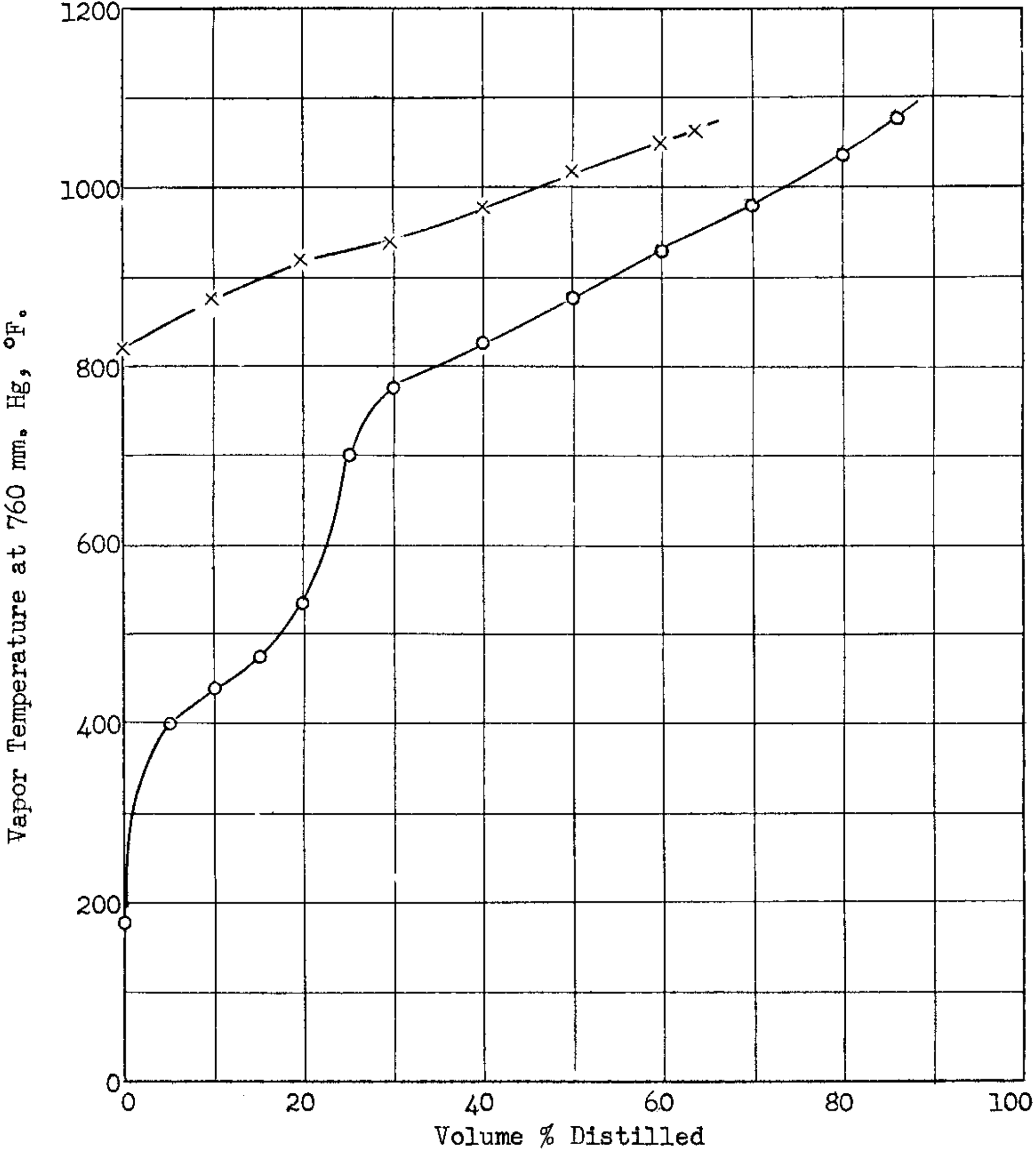


Figure 19. DISTILLATION OF THE PRODUCT FROM A THERMAL STABILITY TEST

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER Hg PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE EXCEEDS 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A PARAFFINIC LIGHT RESIN (MLO 7308)

× = ORIGINAL TEST FLUID
○ = PRODUCT FROM 12-HOUR THERMAL STABILITY TEST AT 700°F.
(FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 35.)

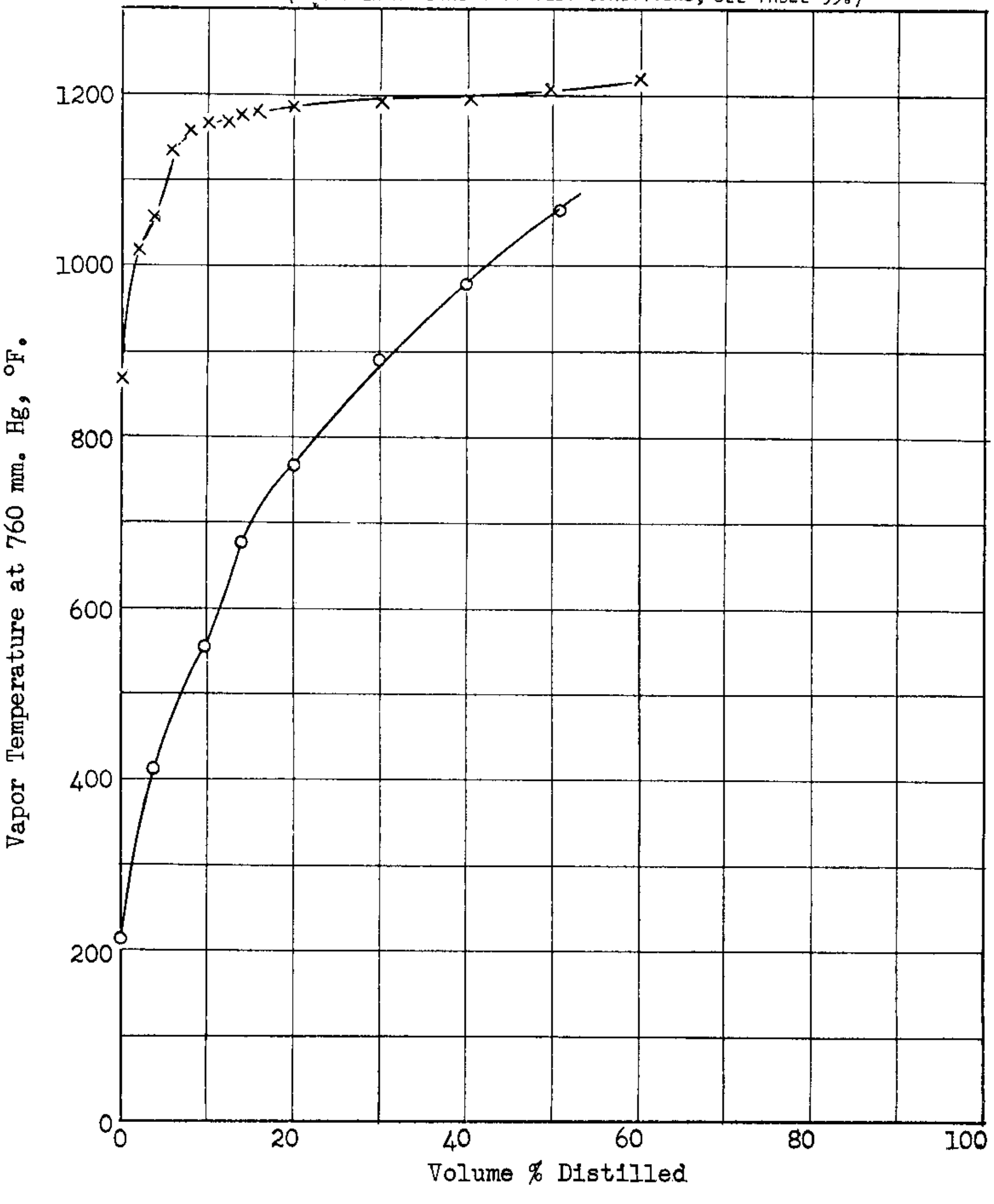


Figure 20. DISTILLATION OF THE PRODUCT FROM A THERMAL STABILITY TEST

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS.

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER Hg PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE EXCEEDS 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A SUPER REFINED PARAFFINIC NEUTRAL (MLO 7301).

PRODUCTS FROM 20-HOUR THERMAL STABILITY TESTS AT 700°F.
(FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 35.)

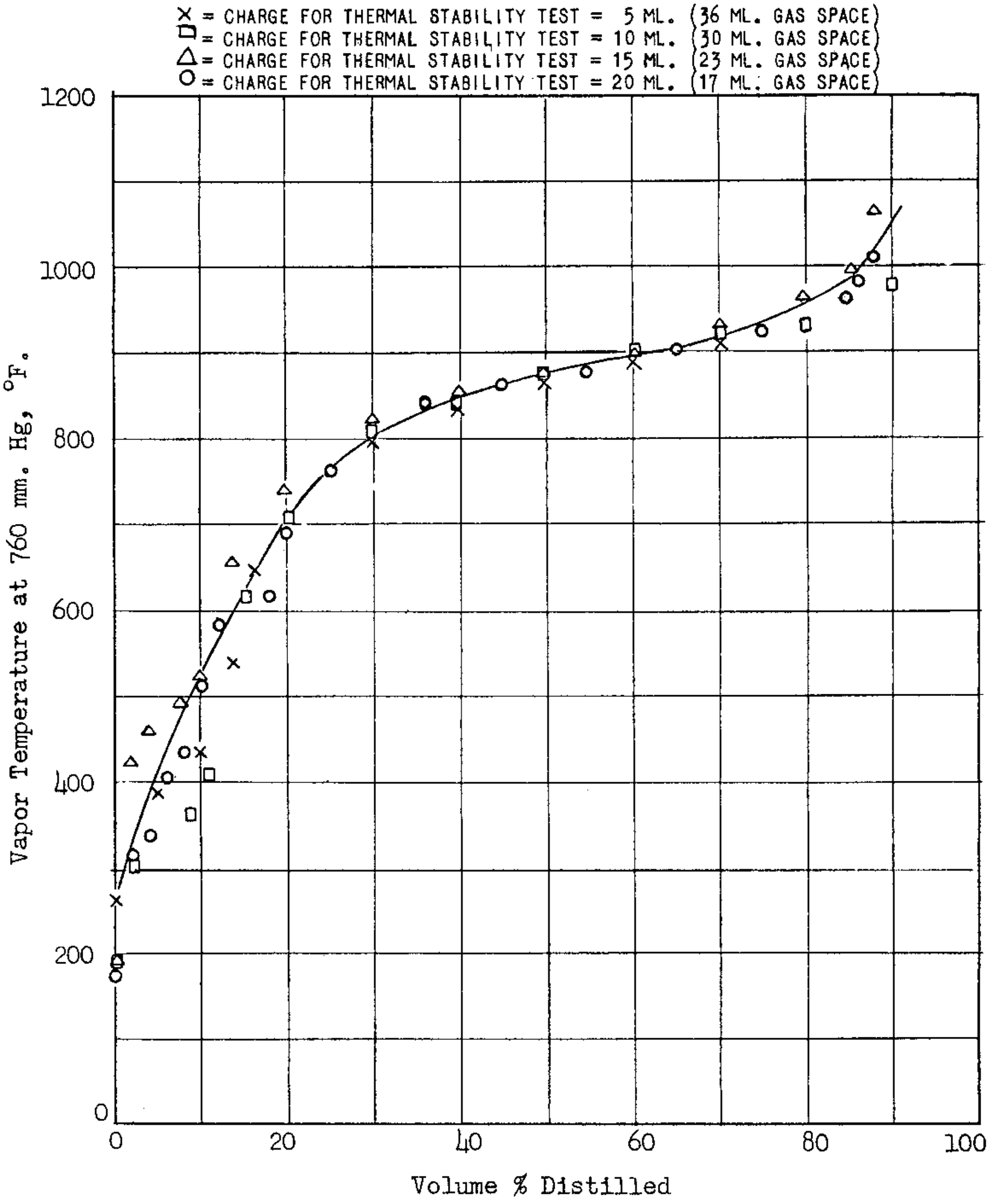


Figure 21. DISTILLATION OF PRODUCTS FROM THERMAL STABILITY TESTS WITH A DIFFERENT GAS SPACE

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS.

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER Hg PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE EXCEEDS 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A SUPER-REFINED NAPHTHENIC NEUTRAL (MLO 7357).

PRODUCTS FROM 20-HOUR THERMAL STABILITY TESTS AT 700°F.
(FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 36.)

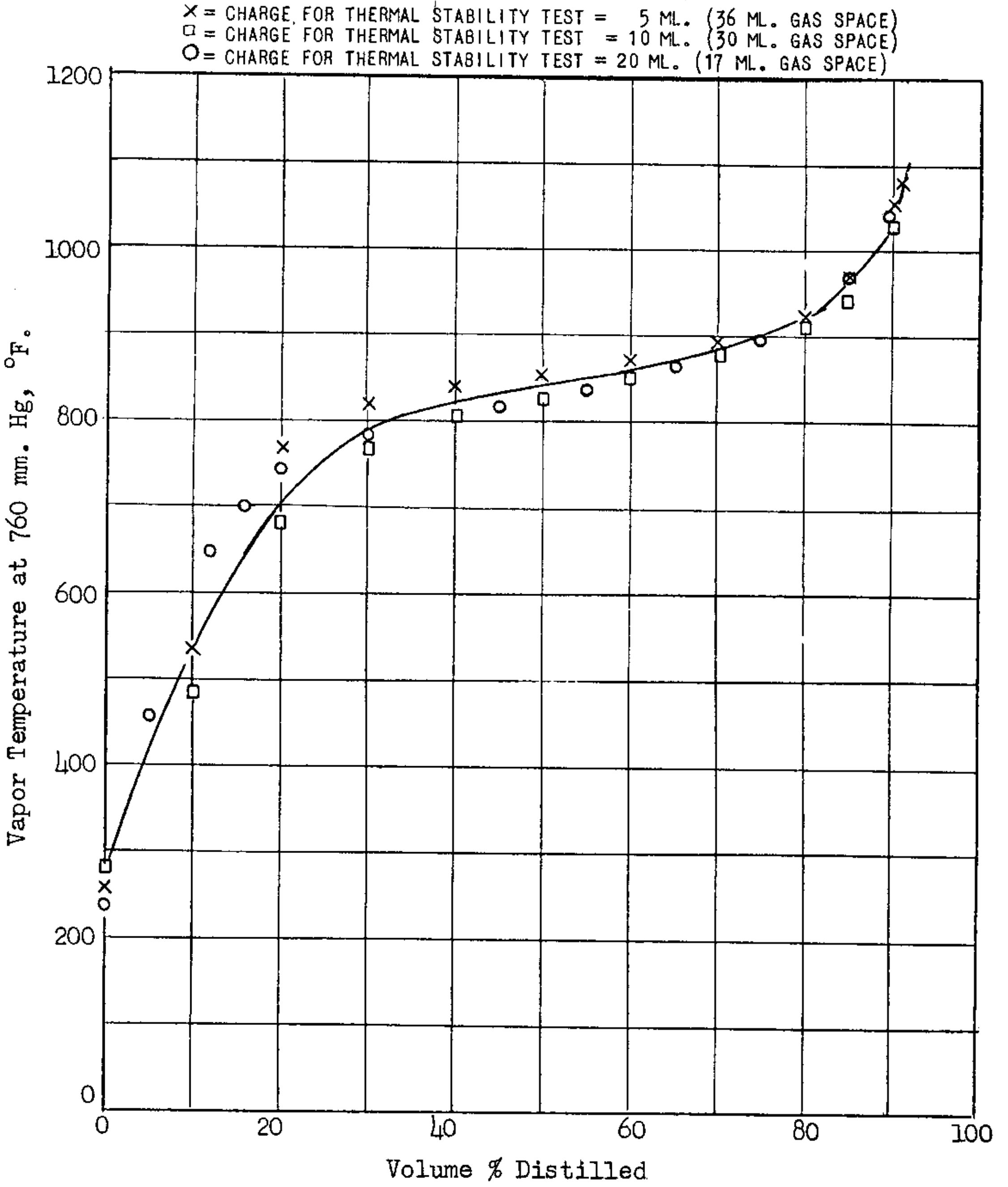


Figure 22. DISTILLATION OF PRODUCTS FROM THERMAL STABILITY TESTS WITH DIFFERENT GAS SPACE

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS.

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER HG PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE EXCEEDS 1000°F (NORMAL B.PT.), OR CRACKING OCCURS.

TEST FLUID: A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301). PRODUCTS FROM THERMAL STABILITY TESTS AT 700°F. FOR TIME NOTED. (FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 42.)

× = 6-HOUR TEST
○ = 12-HOUR TEST
△ = 20-HOUR TEST

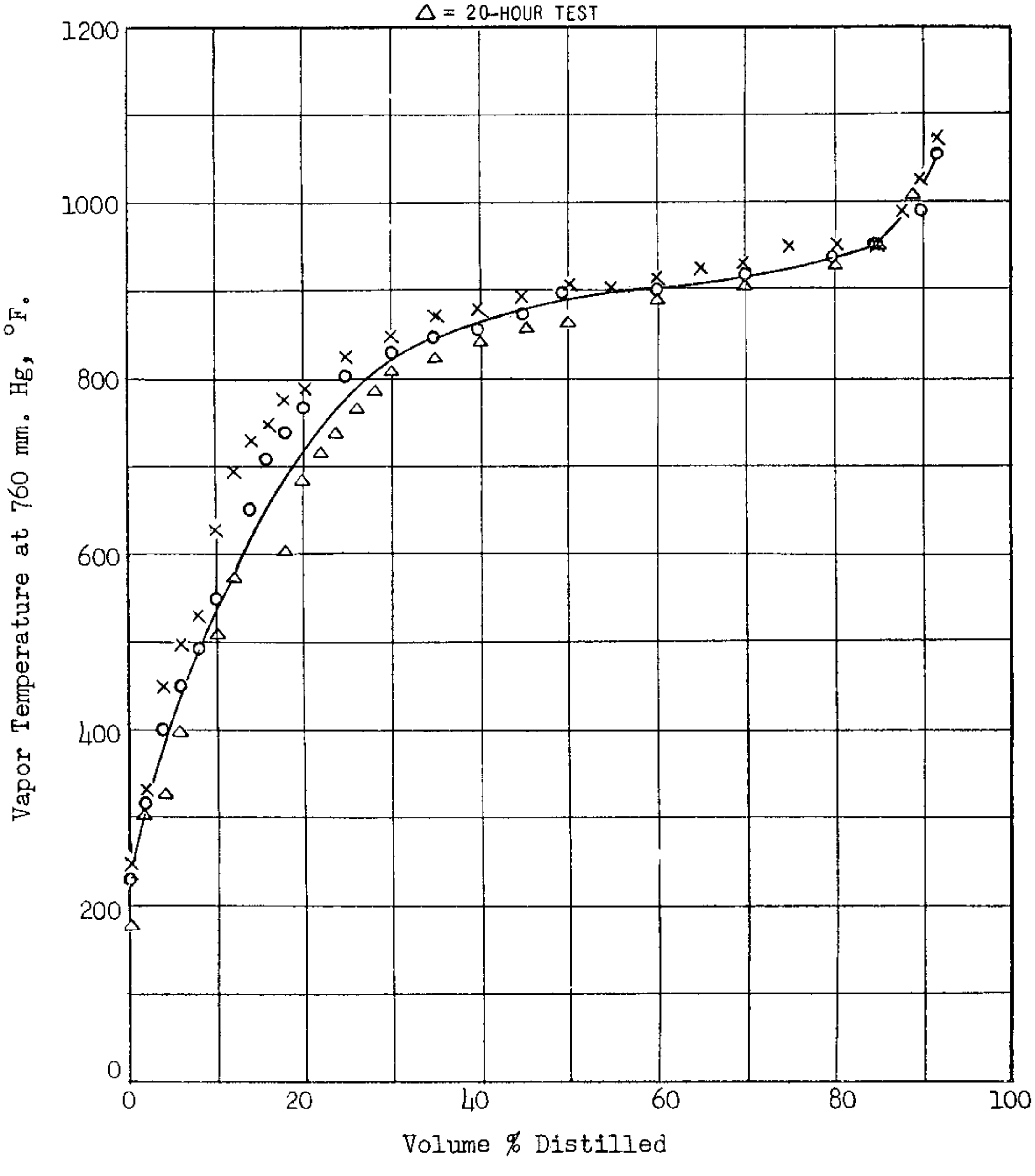


Figure 23. DISTILLATION OF PRODUCTS FROM THERMAL STABILITY TESTS OF DIFFERENT TEST TIME

DISTILLATION CONDUCTED IN A SMALL SCALE VACUUM APPARATUS.

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER Hg PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE EXCEEDS 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A SUPER-REFINED NAPHTHENIC NEUTRAL (MLO 7357).
PRODUCT FROM THERMAL STABILITY TESTS AT 700°F. FOR TIME NOTED. (FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 43.)

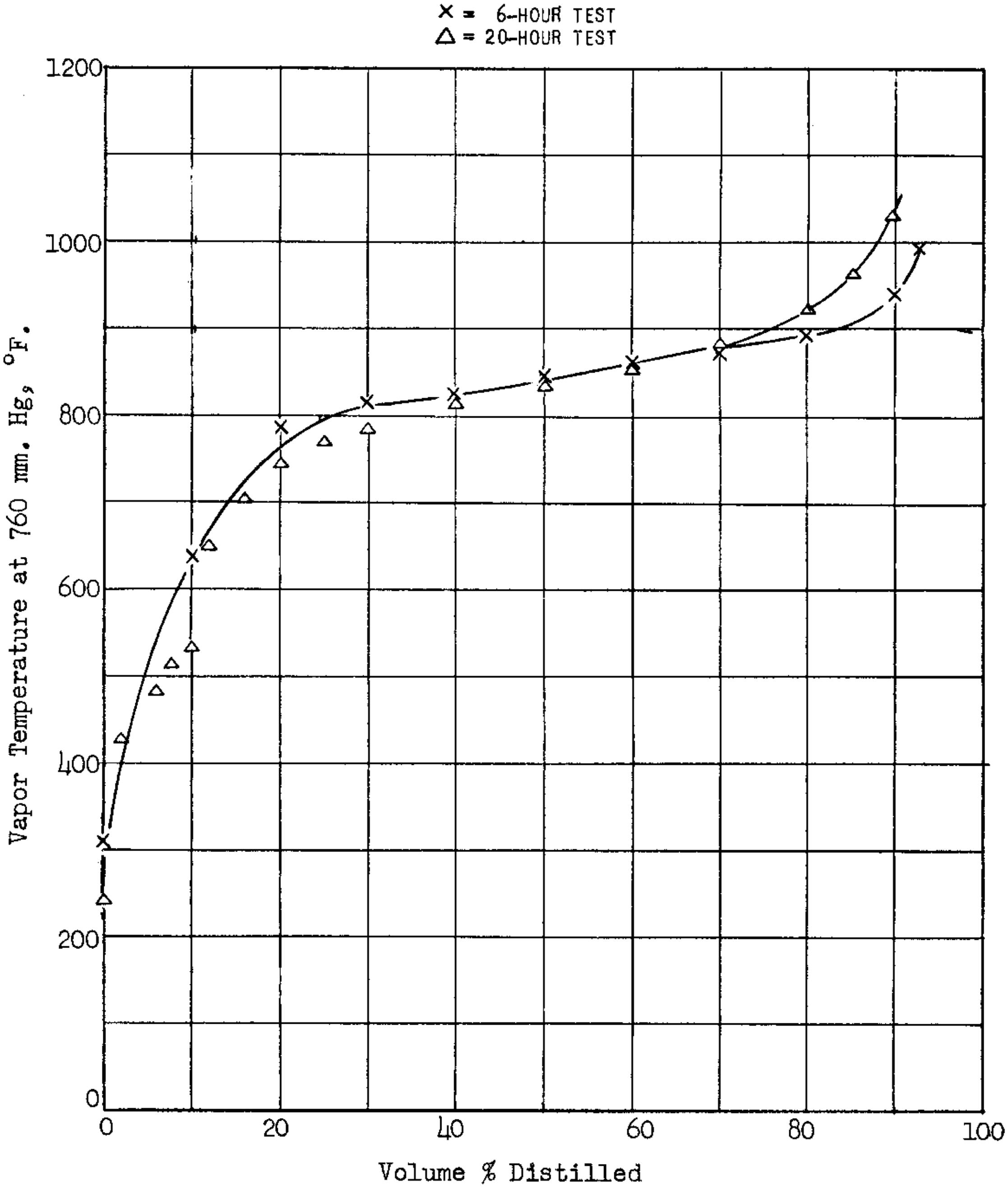
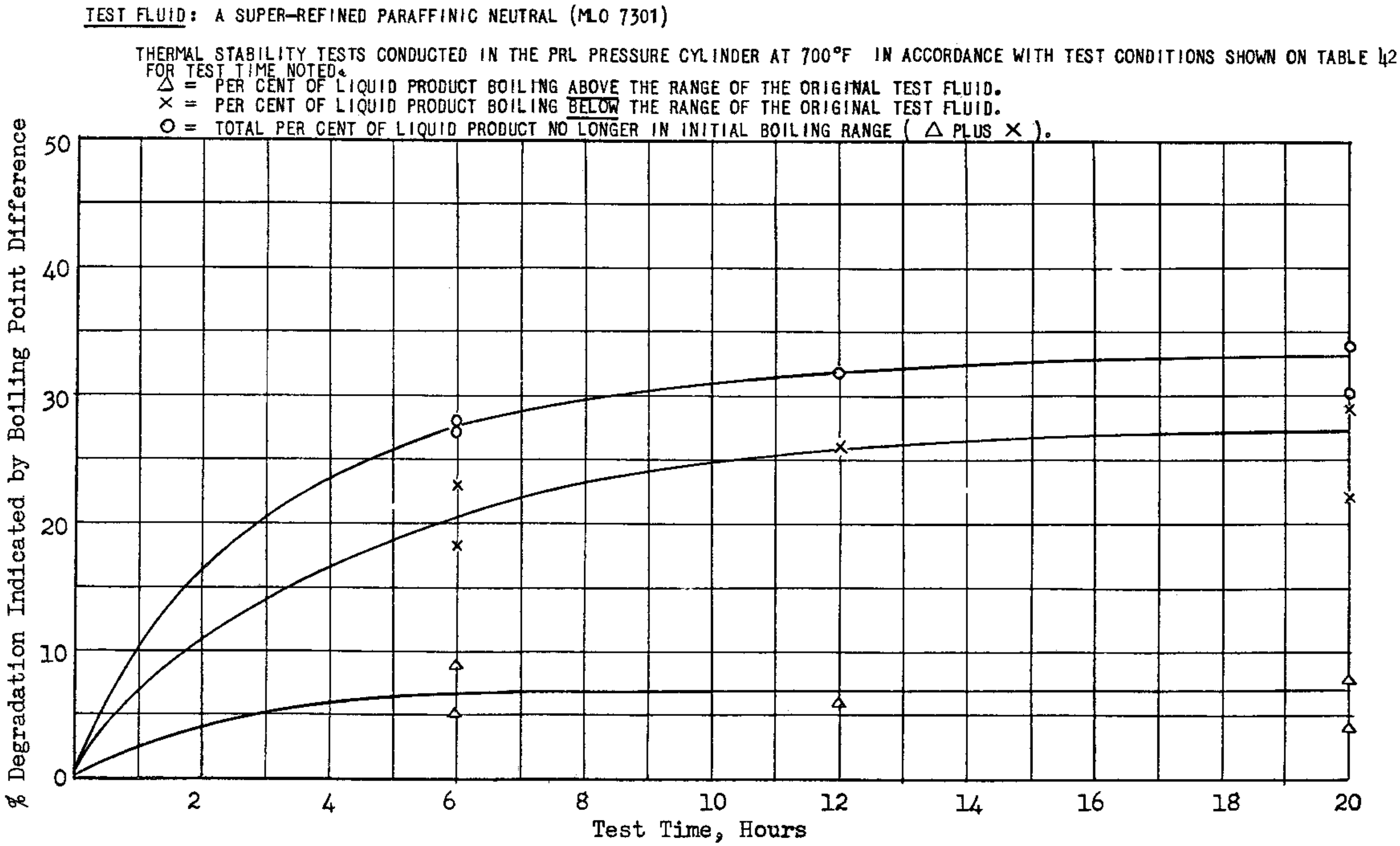


Figure 24. DISTILLATION OF PRODUCTS FROM THERMAL STABILITY TESTS OF DIFFERENT TEST TIME



TEST FLUID: A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)

THERMAL STABILITY TESTS CONDUCTED IN THE PRL PRESSURE CYLINDER AT 700°F IN ACCORDANCE WITH TEST CONDITIONS SHOWN ON TABLE 42 FOR TEST TIME NOTED.

△ = PER CENT OF LIQUID PRODUCT BOILING ABOVE THE RANGE OF THE ORIGINAL TEST FLUID.
× = PER CENT OF LIQUID PRODUCT BOILING BELOW THE RANGE OF THE ORIGINAL TEST FLUID.
○ = TOTAL PER CENT OF LIQUID PRODUCT NO LONGER IN INITIAL BOILING RANGE (△ PLUS ×).

Figure 25. PER CENT DEGRADATION AS INDICATED BY BOILING POINT DIFFERENCES

TEST FLUID: A SUPER-REFINED NAPHTHENIC NEUTRAL (MLO 7357)

THERMAL STABILITY TESTS CONDUCTED IN THE PRL PRESSURE CYLINDER AT 700°F IN ACCORDANCE WITH TEST CONDITIONS SHOWN ON TABLE 43 FOR TEST TIME NOTED.

△ = PER CENT OF LIQUID PRODUCT BOILING ABOVE THE RANGE OF THE ORIGINAL TEST FLUID.
× = PER CENT OF LIQUID PRODUCT BOILING BELOW THE RANGE OF THE ORIGINAL TEST FLUID.
○ = TOTAL PER CENT OF LIQUID PRODUCT NO LONGER IN INITIAL BOILING RANGE (△ PLUS ×).

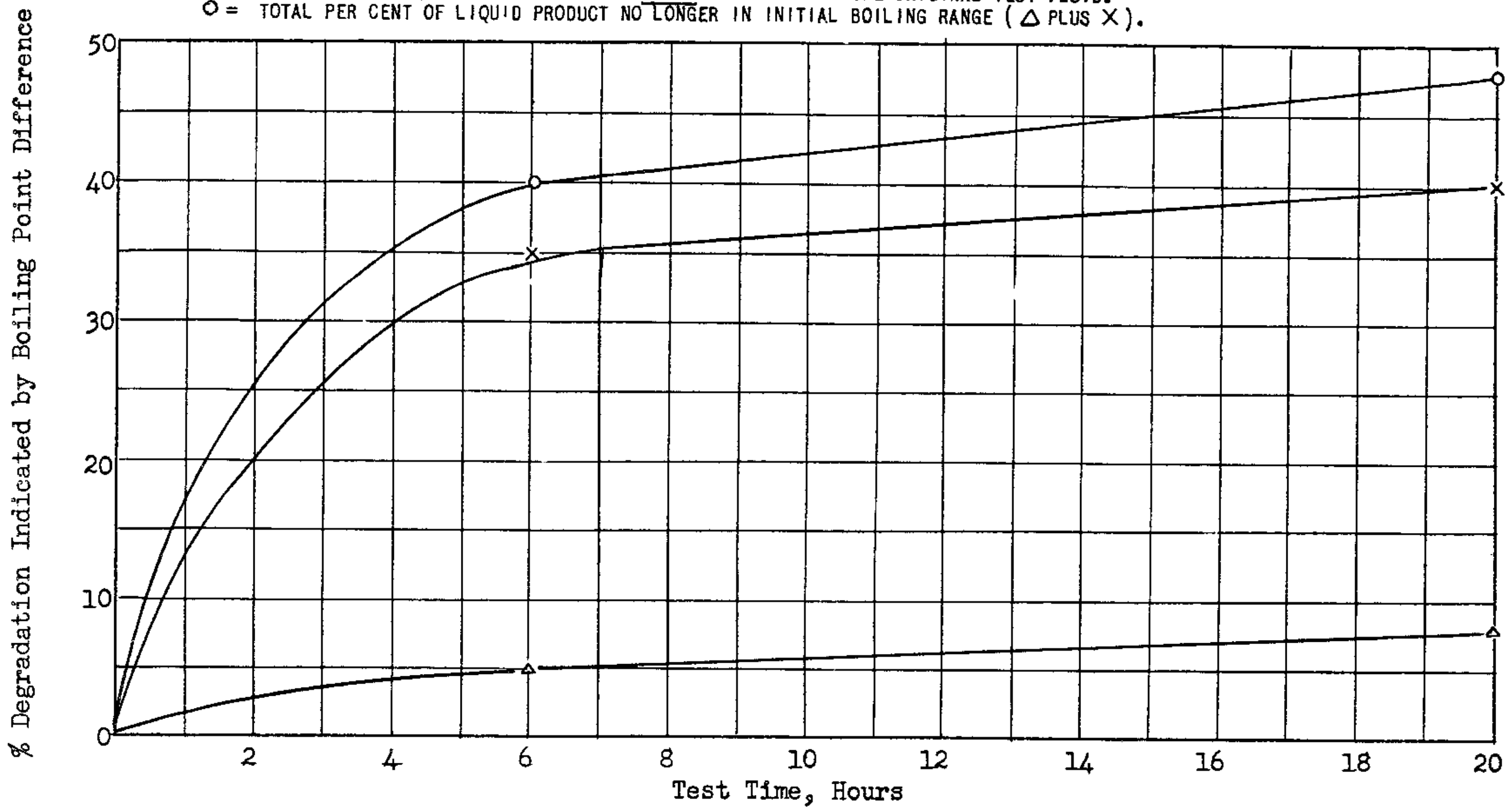


Figure 26. PER CENT DEGRADATION AS INDICATED BY BOILING POINT DIFFERENCES

Table 49

EFFECT OF PRIOR TREATMENT ON THE THERMAL STABILITY OF A PARAFFINIC NEUTRAL

ALL TESTS CONDUCTED IN THE PRL STAINLESS STEEL PRESSURE CYLINDER.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 700 + 10°F ; TEST TIME = 20 HOURS; TEST FLUID CHARGED = 20 ML.; TOTAL VOLUME OF CYLINDER = 46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 STEEL, 52 - 100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 28 POUNDS AT 700°F.

TEST FLUIDS: MLO 7301 = A SUPER-REFINED PARAFFINIC NEUTRAL.
MLO 7483 = 32 TO 85% OVERHEAD FROM DISTILLATION PRODUCT FROM A 20-HR. TEST AT 700°F. WITH MLO 7301.
MLO 7484 = 70 TO 92% OVERHEAD FROM DISTILLATION PRODUCT FROM AN 11.8-HR. TEST AT 750°F. WITH MLO 7301.

TEST FLUID	MLO 7301	MLO 7483	MLO 7484
DECOMPOSITION DATA			
GAS FORMATION			
MOLES OF GAS/HR. (X 10^3)	0.212	0.224	0.212
MOLES OF GAS/MOLE OF OIL/HR.	0.0063	0.0067	0.0063
TOTAL MOLES OF GAS/MOLE OF OIL	0.12	0.17	0.12
SYSTEM PRESSURE, P.S.I.G.			
MAXIMUM AT TEST TEMP.	220	286	220
RESIDUAL AT ROOM TEMP.	32	52	40
SLOPE, P.S.I.G./HR.	9.6	10.2	9.6
FLUID PROPERTIES			
% CHANGE IN CS. VISC. AT 100°F.	-61	-70	-60
NEUT. NO. (MG KOH/GM. OIL)			
ORIGINAL	0.0	0.0	0.0
FINAL	0.0	0.0	0.1
CATALYST WT. LOSS (MG./SQ. CM.)			
M-10 TOOL STEEL	0.04	+0.06	+0.04
52 - 100 STEEL	0.00	+0.04	+0.02
NAVAL BRONZE	0.00	+0.06	0.00

TEST FLUID: A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301).

PRIOR TREATMENT: A 20-HOUR THERMAL STABILITY TEST AT 700°F.
(FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 49A)

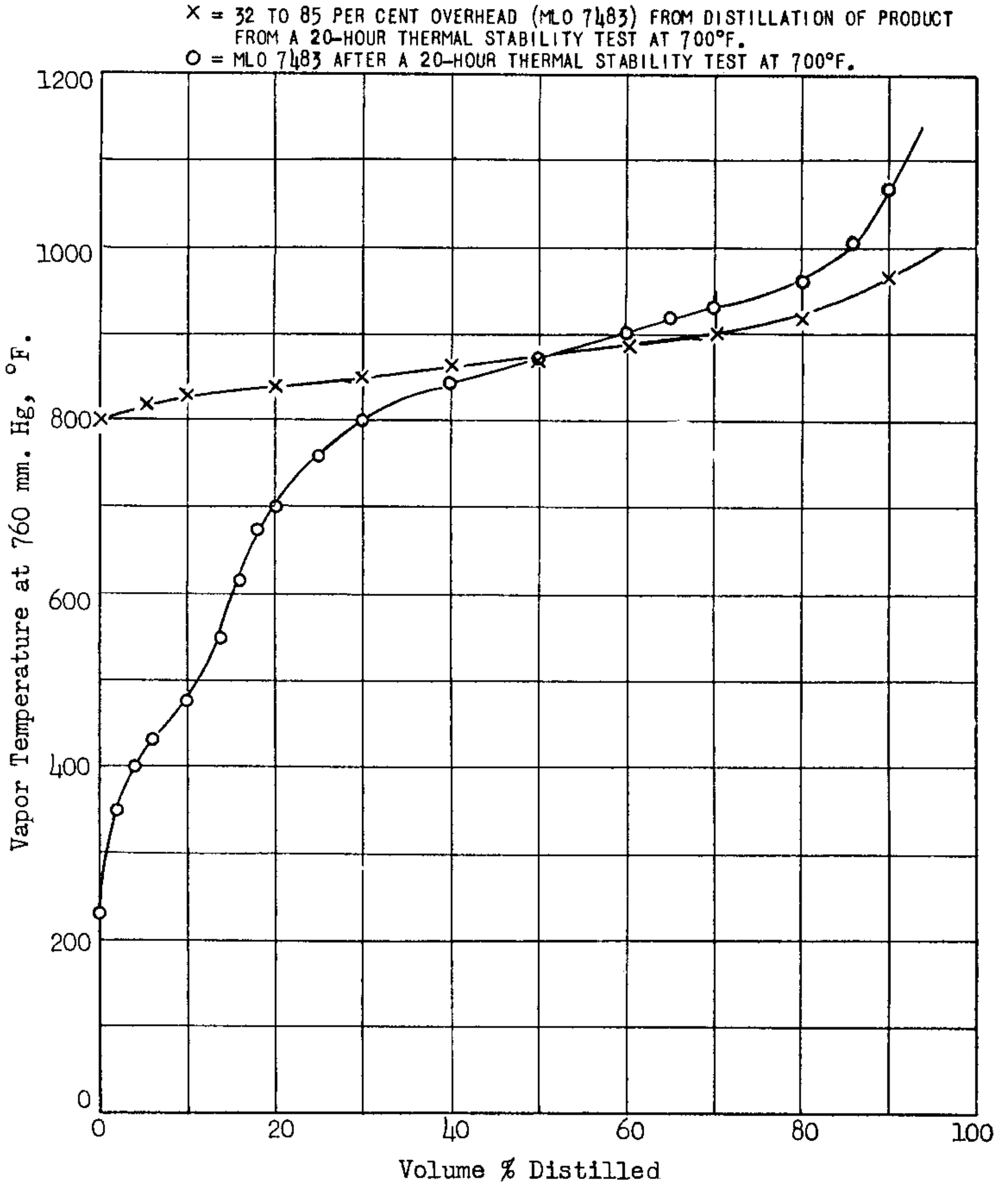
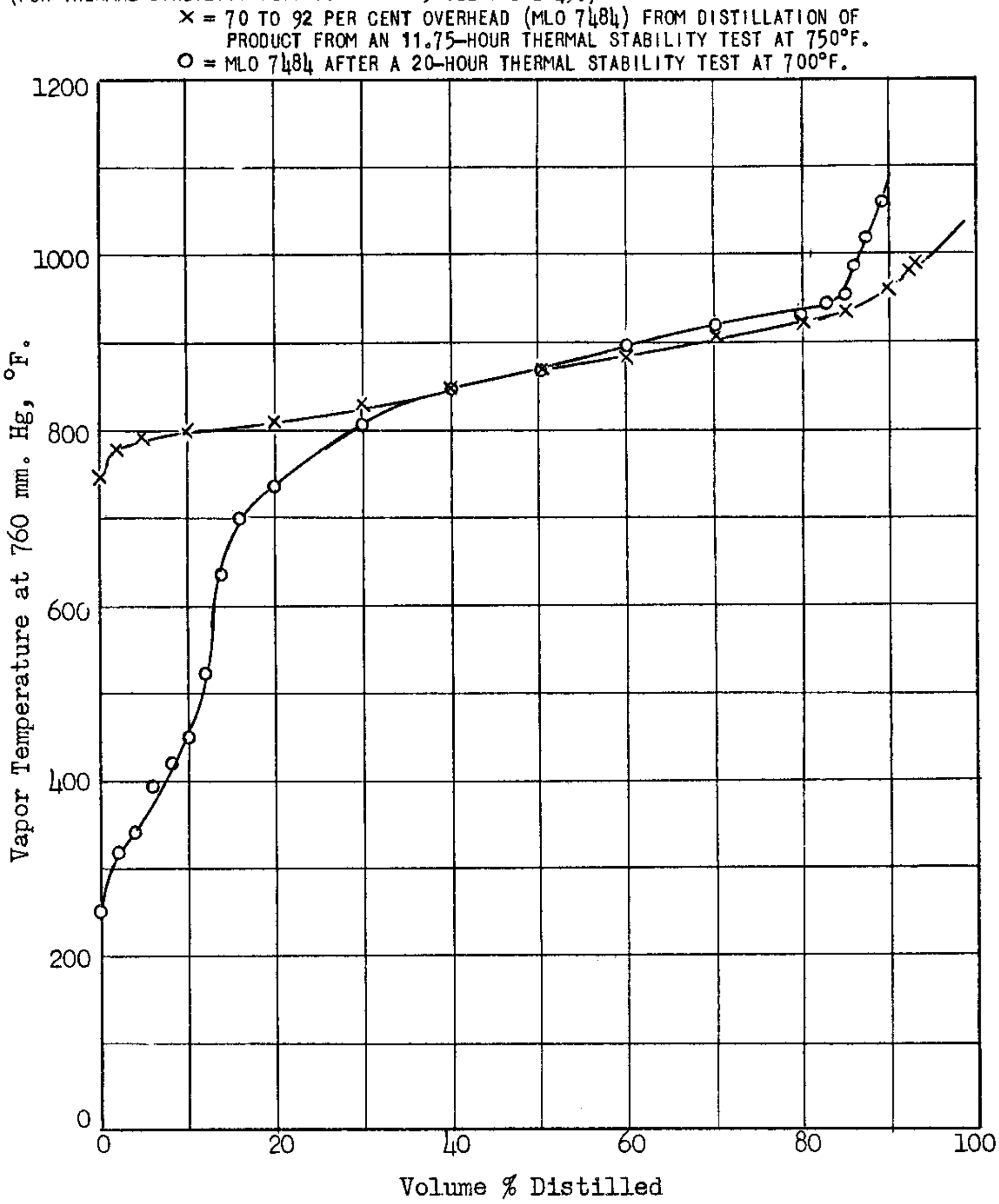


Figure 27. EFFECT OF PRIOR TREATMENT ON THE THERMAL STABILITY OF A PARAFFINIC NEUTRAL



TEST FLUID: A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301).

PRIOR TREATMENT: AN 11.75-HOUR THERMAL STABILITY TEST AT 750°F.
(FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 49.)

Figure 28. EFFECT OF PRIOR TREATMENT ON THE THERMAL STABILITY OF A PARAFFINIC NEUTRAL

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER Hg PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE = 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)

PRODUCTS FROM THERMAL STABILITY TESTS FOR TIME AND TEMPERATURE SHOWN. (FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 42.)

X = 96-HOUR TEST AT 650°F.
O = 20-HOUR TEST AT 700°F.
□ = 2.75-HOUR TEST AT 750°F.

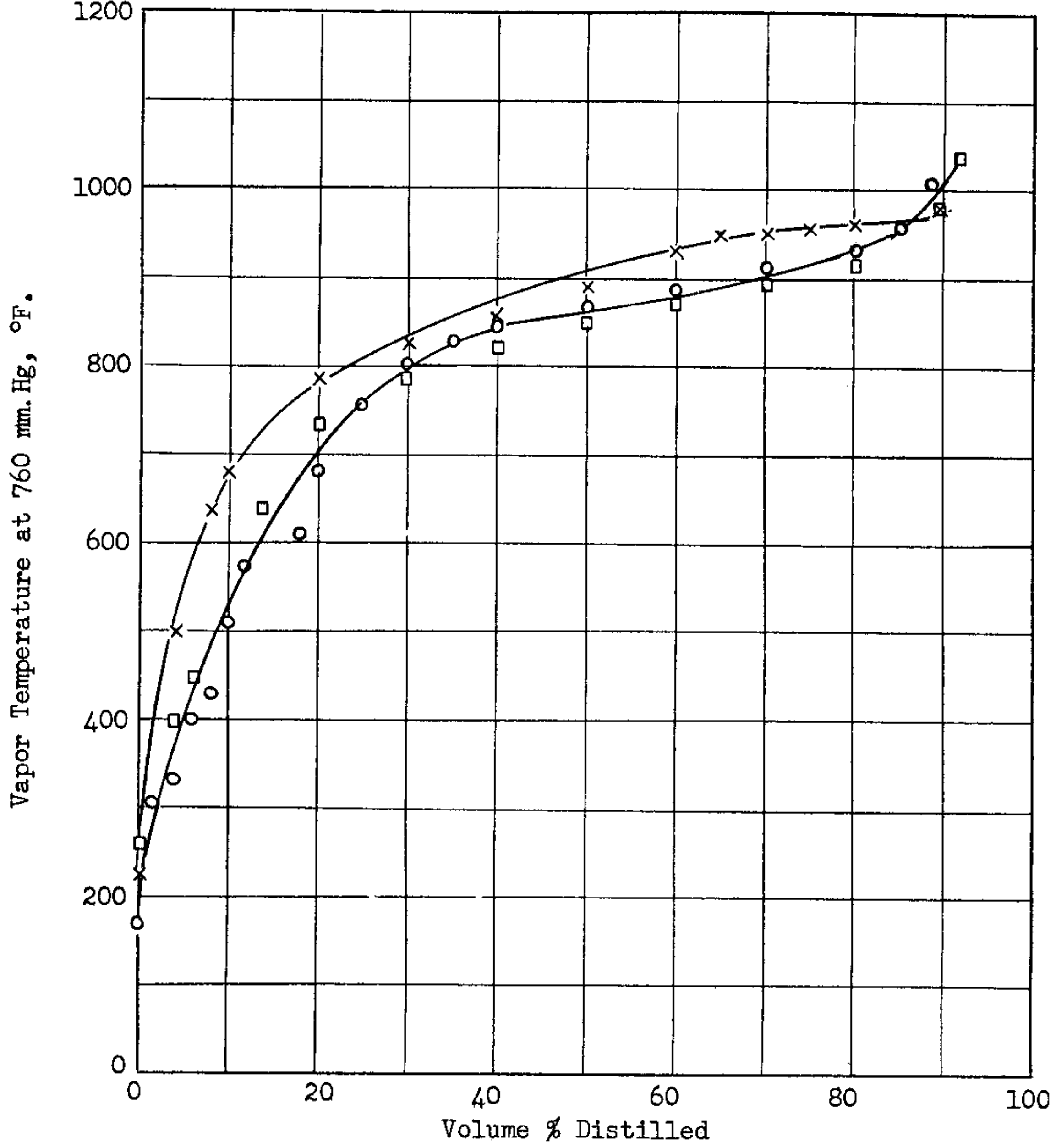


Figure 29. DISTILLATION OF PRODUCTS FROM THERMAL STABILITY TESTS AT VARIOUS TEMPERATURES

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER HG PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE = 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A SUPER-REFINED NAPHTHENIC NEUTRAL (MLO 7357)

PRODUCTS FROM THERMAL STABILITY TESTS FOR TIME AND TEMPERATURE SHOWN. (FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 43.)

× = 103.5-HOUR TEST AT 650°F.
○ = 20-HOUR TEST AT 700°F.
□ = 2.75-HOUR TEST AT 750°F.

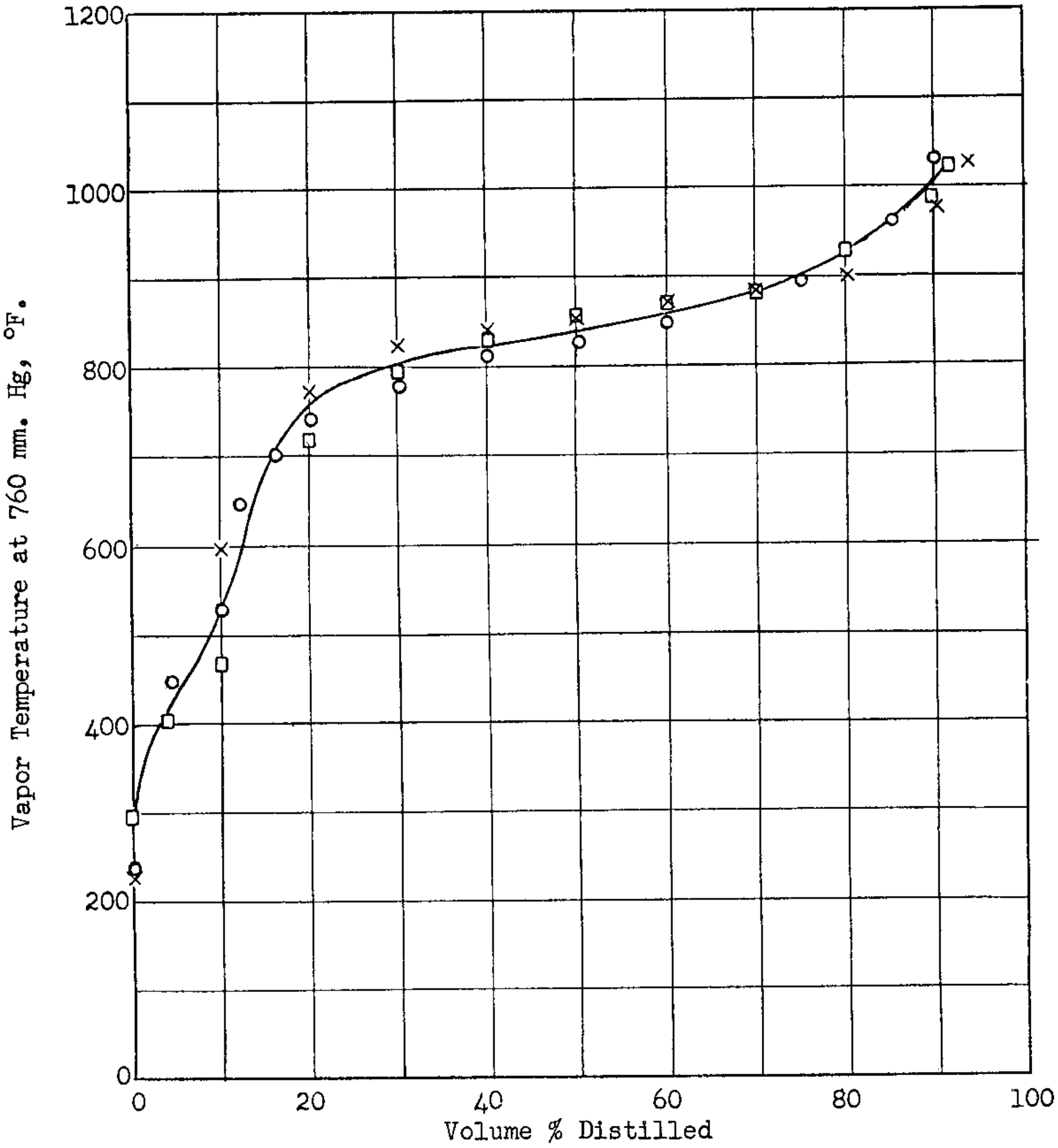


Figure 30. DISTILLATION OF PRODUCTS FROM THERMAL STABILITY TESTS AT VARIOUS TEMPERATURES

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER Hg PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE = 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A SUPER-REFINED PARAFFINIC BRIGHT STOCK (MLO 7289)

PRODUCTS FROM THERMAL STABILITY TESTS FOR TIME AND TEMPERATURE SHOWN (FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 41.)

× = 20-HOUR TEST AT 650°F.
○ = 30-HOUR TEST AT 700°F.
□ = 3.25-HOUR TEST AT 750°F.

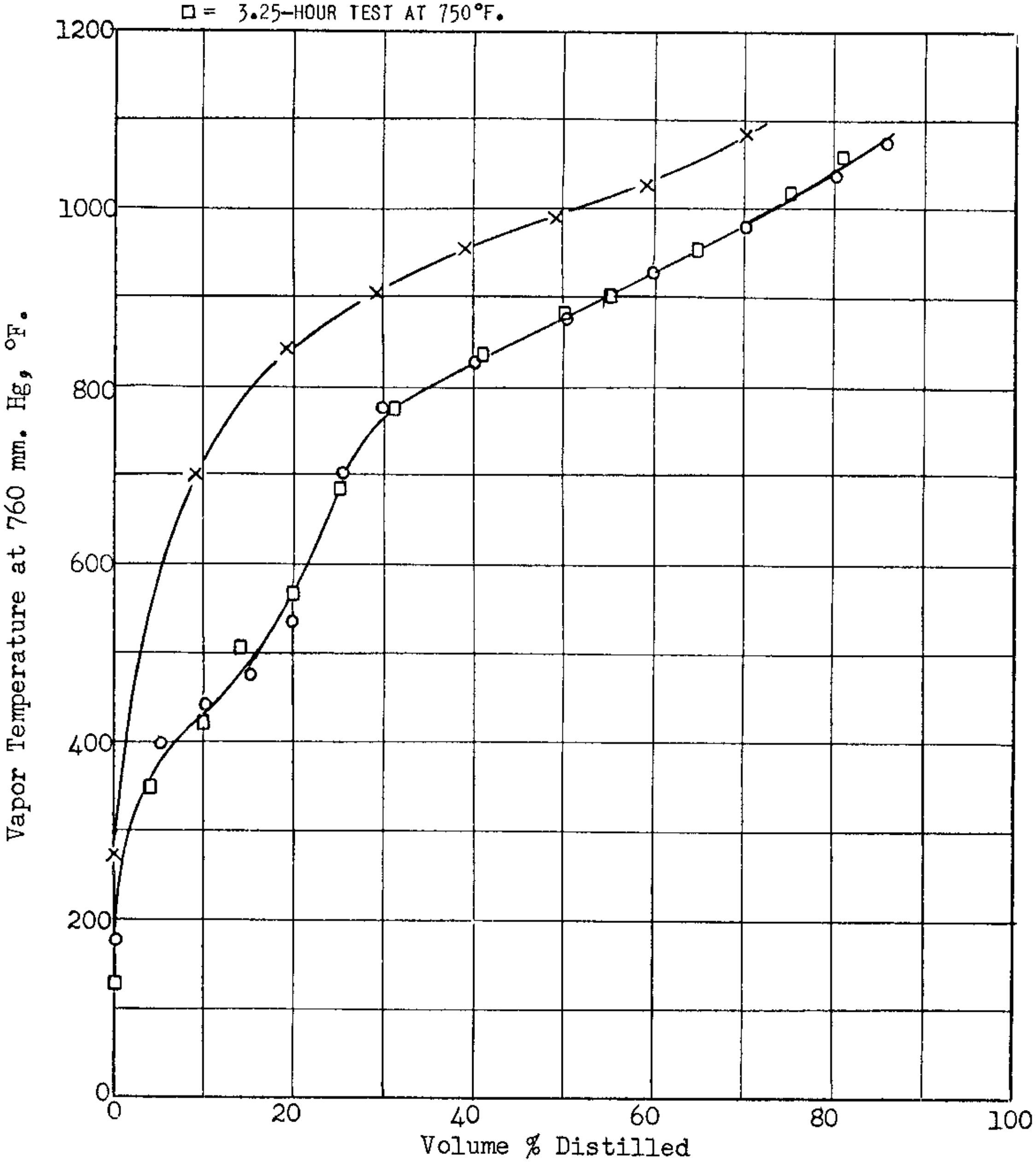


Figure 31. DISTILLATION OF PRODUCTS FROM THERMAL STABILITY TESTS AT VARIOUS TEMPERATURES

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER Hg PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE = 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A PARAFFINIC LIGHT RESIN (MLO 7308)

PRODUCTS FROM THERMAL STABILITY TESTS FOR TIME AND TEMPERATURE SHOWN (FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 41.)

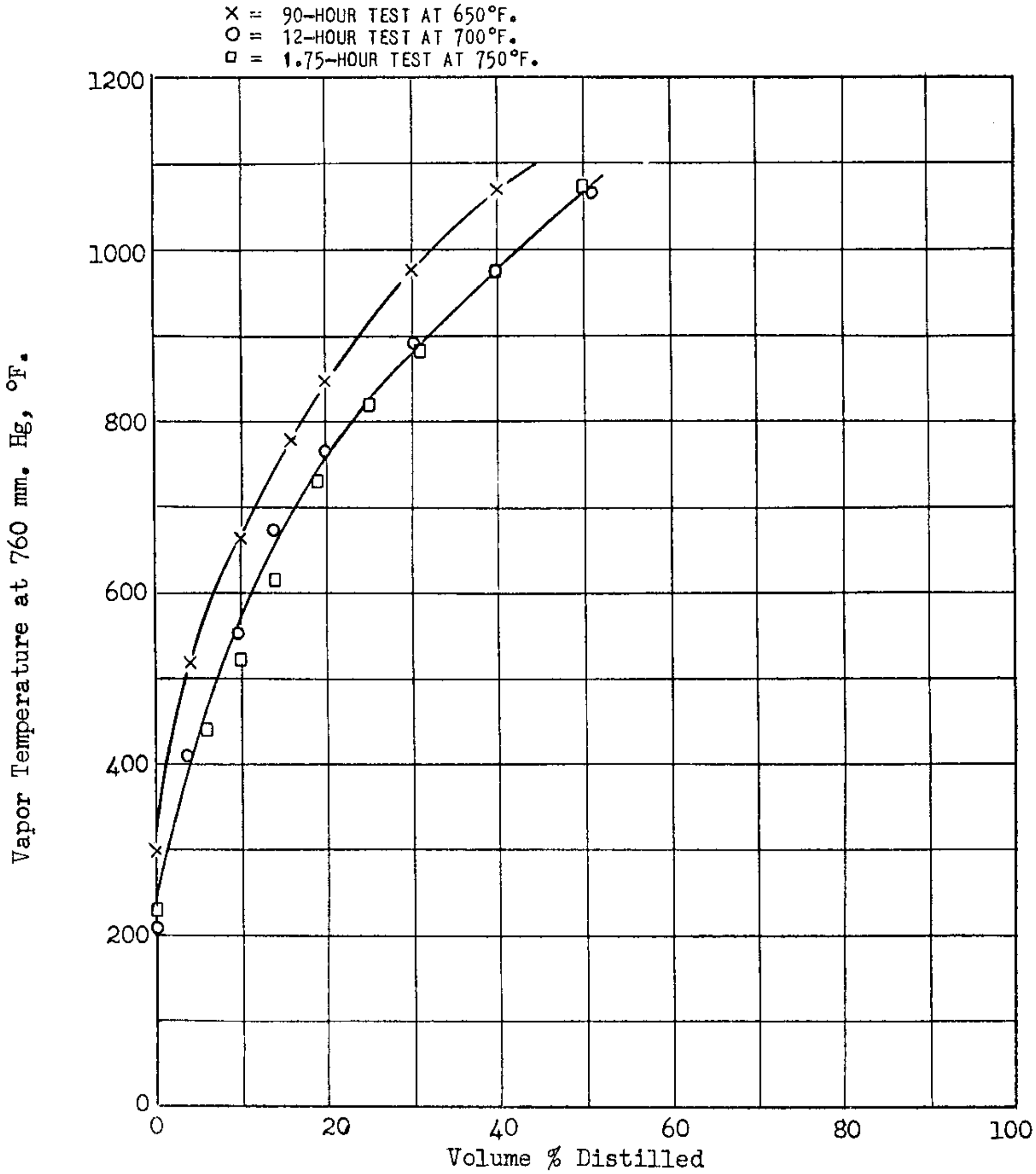


Figure 32. DISTILLATION OF PRODUCTS FROM THERMAL STABILITY TESTS AT VARIOUS TEMPERATURES

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER Hg PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE EXCEEDS 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A PARTIALLY HYDROGENATED AROMATIC HYDROCARBON (MLO 7218-16)

X = ORIGINAL TEST FLUID
O = PRODUCT FROM 18-HOUR THERMAL STABILITY TEST AT 700°F.
(FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 37.)

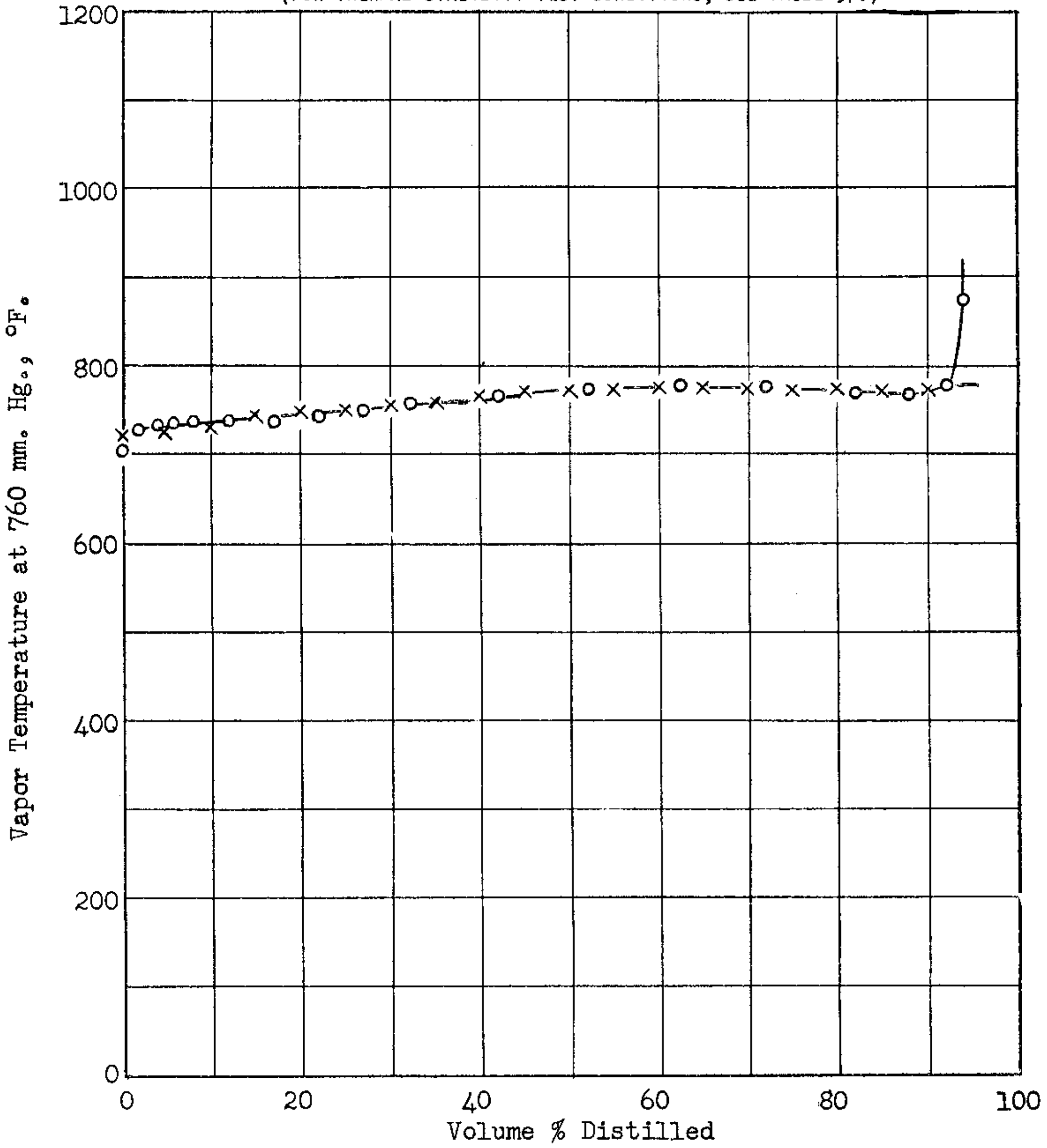


Figure 33. DISTILLATION OF THE PRODUCT FROM A THERMAL STABILITY TEST

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS.

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER HG PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE EXCEEDS 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A PARTIALLY HYDROGENATED AROMATIC HYDROCARBON (MLO 7218-16).
PRODUCTS FROM THERMAL STABILITY TESTS AT 700°F. FOR TIME NOTED. (FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 44.)

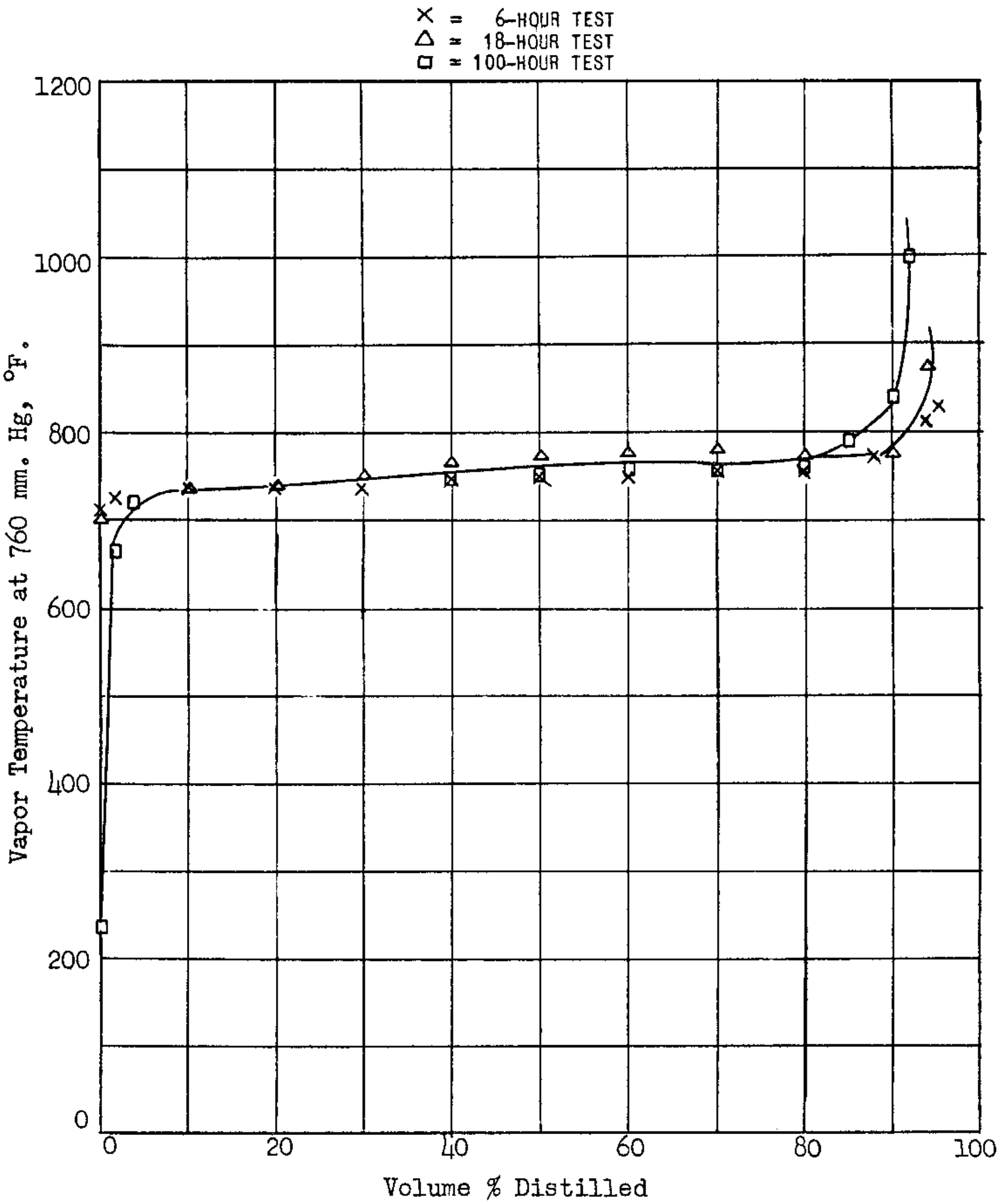


Figure 34. DISTILLATION OF PRODUCTS FROM THERMAL STABILITY TESTS AT DIFFERENT TEST TIME

TEST FLUID: A PARTIALLY HYDROGENATED AROMATIC HYDROCARBON (MLO 7218-16)

THERMAL STABILITY TESTS CONDUCTED IN THE PRL PRESSURE CYLINDER AT 700°F. IN ACCORDANCE WITH TEST CONDITIONS SHOWN ON TABLE 44 FOR TEST TIME NOTED.

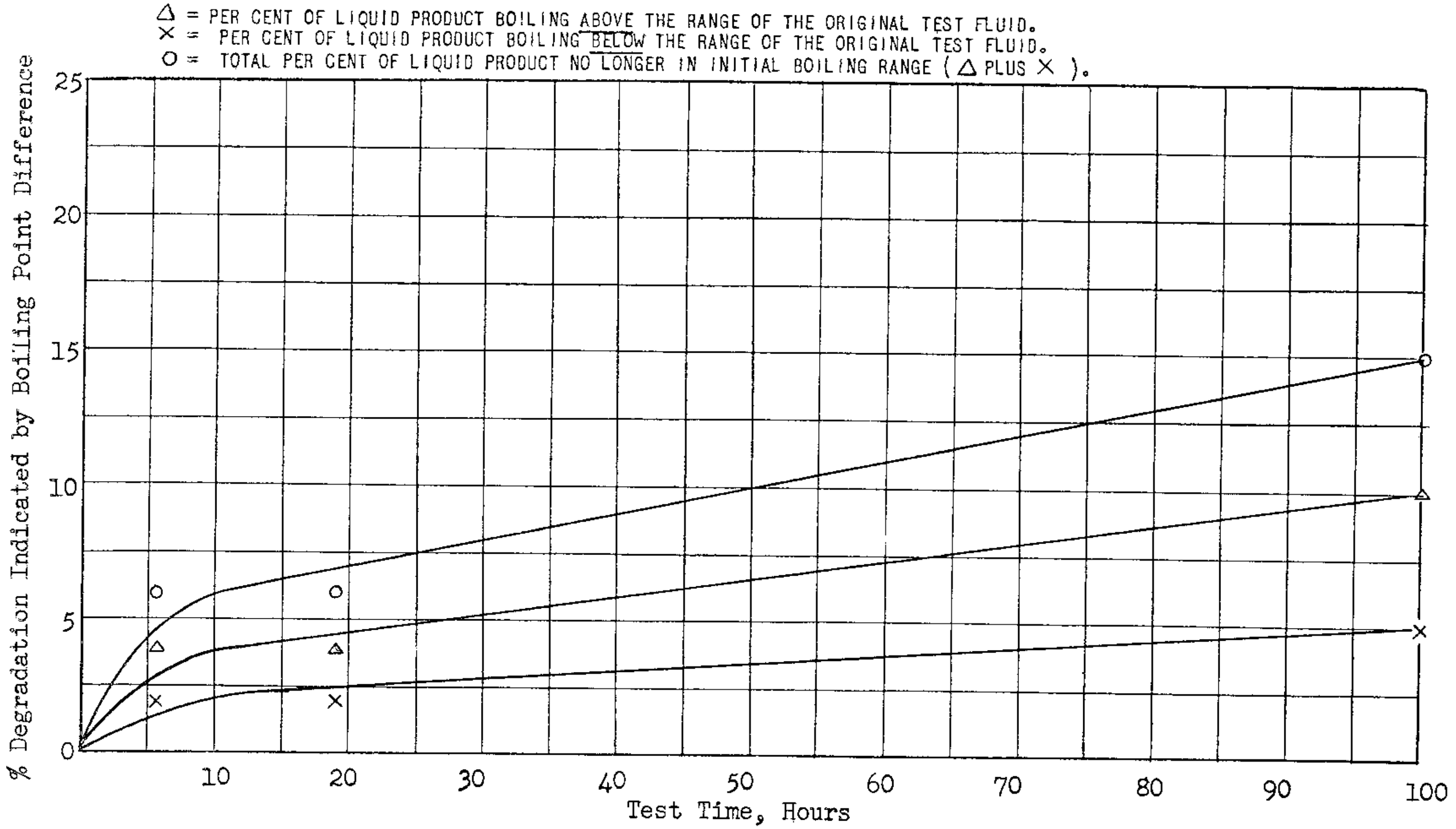


Figure 35. PER CENT DEGRADATION AS INDICATED BY BOILING POINT DIFFERENCES

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER Hg PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE = 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A PARTIALLY HYDROGENATED AROMATIC HYDROCARBON (MLO 7218-16)

PRODUCTS FROM THERMAL STABILITY TESTS FOR TIME AND TEMPERATURE SHOWN (FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 44.)

× = 26-HOUR TEST AT 650°F.
○ = 100-HOUR TEST AT 700°F.
□ = 4.5-HOUR TEST AT 750°F.

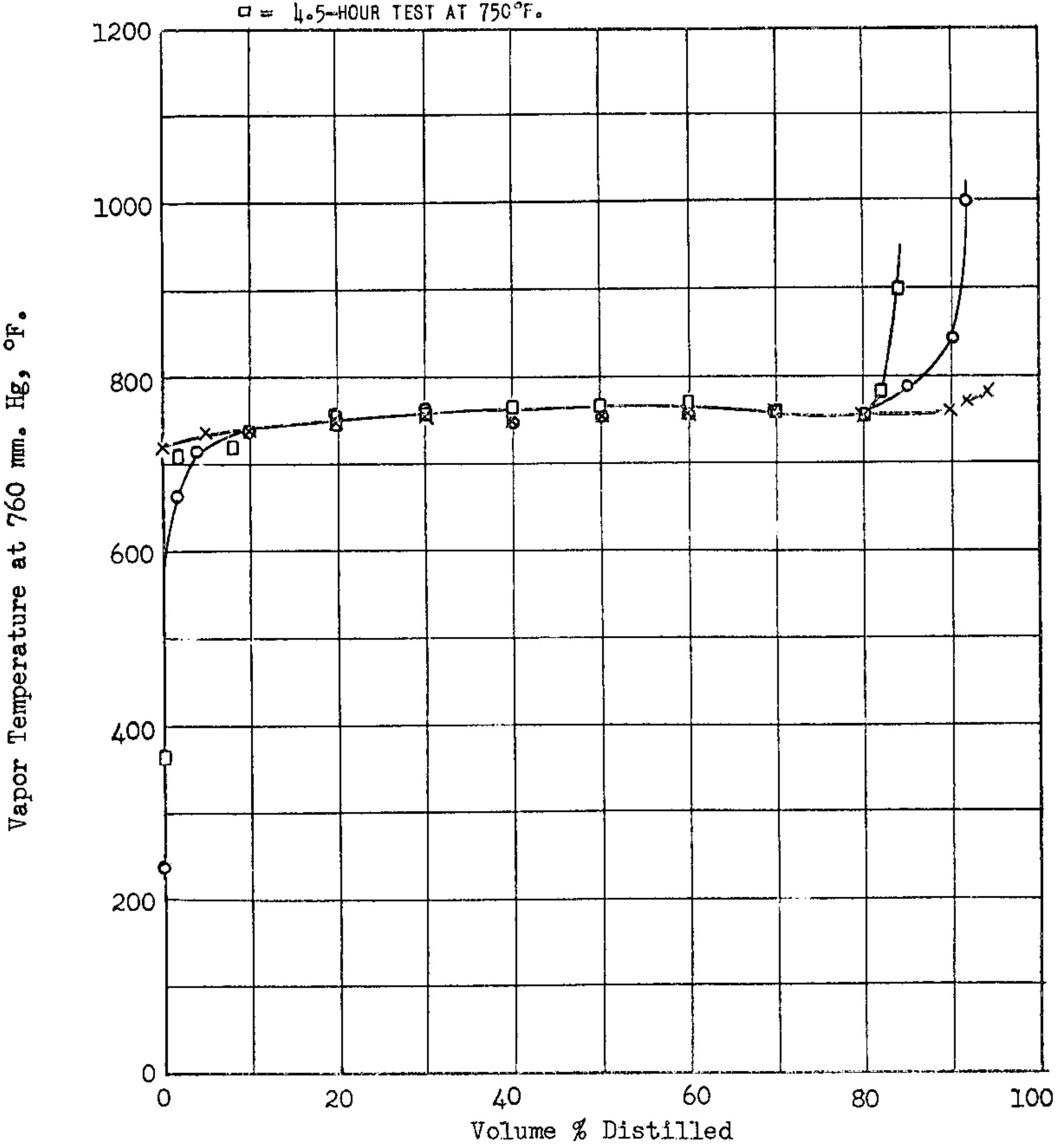


Figure 36. DISTILLATION OF PRODUCTS FROM THERMAL STABILITY TESTS AT VARIOUS TEMPERATURES

Table 50

EFFECT OF TEMPERATURE ON THE THERMAL STABILITY OF A POLYPHENYL ETHER

ALL TESTS CONDUCTED IN THE PRL STAINLESS STEEL PRESSURE CYLINDER.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE AND TEST TIME AS INDICATED; TEST FLUID CHARGED = 20 ML.; TOTAL VOLUME OF CYLINDER = 46 ML.; AND CATALYSTS = A 0.5-INCH DIAMETER BALL BEARING EACH OF M-10 TOOL STEEL, 52 - 100 STEEL, AND NAVAL BRONZE. PRIOR TO THE START OF THE TEST, THE SYSTEM IS PURGED WITH NITROGEN. THE SYSTEM IS THEN SEALED AND THE TEST STARTED. THE NITROGEN PRESSURE IN THE PRESSURE CYLINDER IS ABOUT 48 POUNDS AT 850°F AND 57 POUNDS AT 900°F.

Test Fluid	A Polyphenyl Ether (MLO 7428) (WADC Desig. = MLO 59-142)	
Test Conditions		
Test Time, Hrs.	20	6
Test Temperature, °F	850	900
Decomposition Data		
Gas Formation		
Moles of Gas/Hr. (x 10^3)	0.0496	0.306
Moles of Gas/Mole of Oil/Hr.	0.00073	0.0048
Total Moles Gas/Mole of Oil	0.014	0.025
System Pressure, p.s.i.g.		
Maximum at Test Temp.	92	162
Residual at Room Temp.	5	12
Slope, p.s.i.g./Hr.	3.3	23.2
Fluid Properties		
% Change in Cs. Visc. at 100°F	+38	+75
Neut. No. (mg. KOH/gm. oil)		
Original	0.1	0.1
Final	0.3	1.0
Catalyst Wt. Loss (Mg./Sq. Cm.)		
M-10 Tool Steel	+0.16	+0.08
52 - 100 Steel	+0.12	+0.04
Naval Bronze	+0.02	+0.02

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER HG PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE = 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A POLYPHENYL ETHER (MLO 7428)

X = ORIGINAL TEST FLUID

PRODUCTS FROM THERMAL STABILITY TESTS FOR TIME AND TEMPERATURE SHOWN (FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 50.)

○ = 20-HOUR TEST AT 850°F.
△ = 6-HOUR TEST AT 900°F.

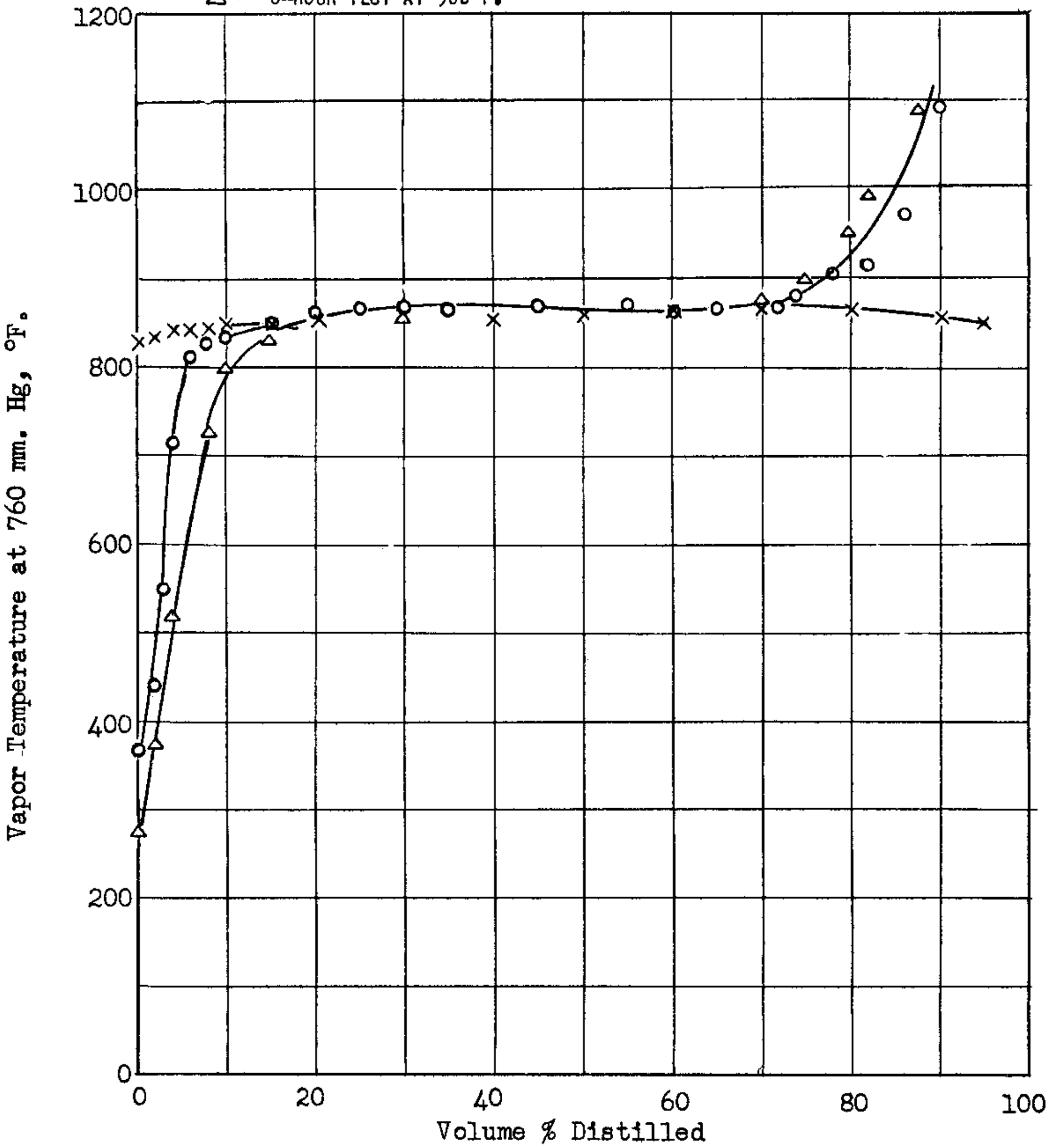


Figure 37. DISTILLATION OF PRODUCTS FROM THERMAL STABILITY TESTS AT VARIOUS TEMPERATURES

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER Hg PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE EXCEEDS 1000°F (NORMAL B. PT.) OR CRACKING OCCURS.

TEST FLUID: A POLYBUTENE OIL (MLO 7123)

× = ORIGINAL TEST FLUID
○ = PRODUCT FROM A 20-HOUR THERMAL STABILITY TEST AT 550°F.
(FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 46.)

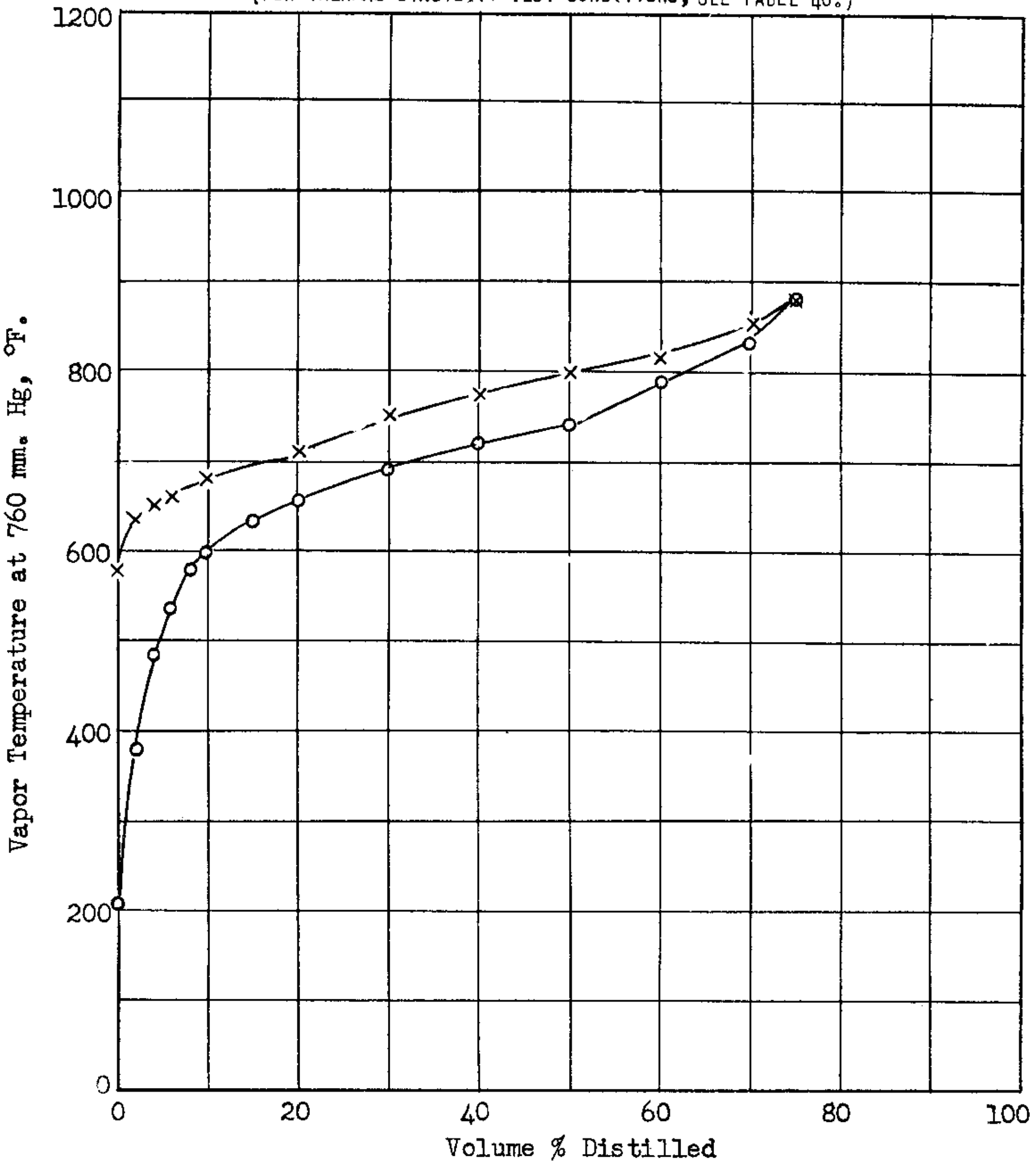


Figure 38. DISTILLATION OF THE PRODUCT FROM A THERMAL STABILITY TEST

DISTILLATIONS CONDUCTED IN A SMALL SCALE VACUUM APPARATUS

PROCEDURE: MATERIAL BOILING BELOW 550°F REMOVED AT ATMOSPHERIC PRESSURE. REMAINDER OF MATERIAL DISTILLED AT LESS THAN 0.1 MILLIMETER Hg PRESSURE. PRODUCT RATE = 0.2 TO 1.0 ML. PER MINUTE. DISTILLATION STOPPED AT 95% OVERHEAD, WHEN VAPOR TEMPERATURE = 1000°F (NORMAL B. PT.), OR CRACKING OCCURS.

TEST FLUID: A POLYBUTENE OIL (MLO 7123)

PRODUCTS FROM THERMAL STABILITY TESTS FOR TIME AND TEMPERATURE SHOWN FOR THERMAL STABILITY TEST CONDITIONS, SEE TABLE 46.

● = 28-HOUR TEST AT 550°F.
Δ = 6-HOUR TEST AT 600°F.
X = 1.25-HOUR TEST AT 650°F.
O = 0.2-HOUR TEST AT 700°F.

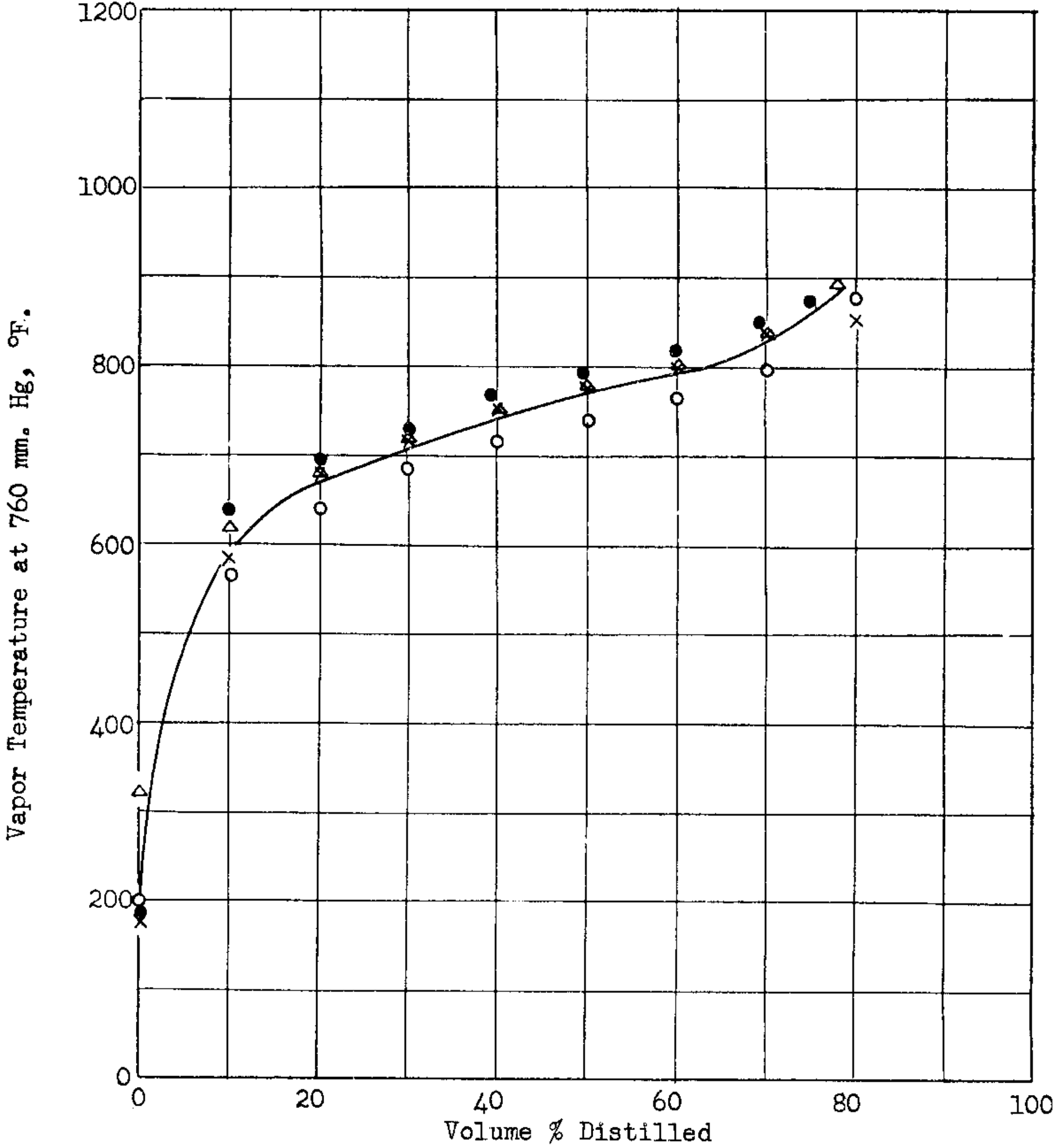


Table 39. DISTILLATION OF PRODUCTS FROM THERMAL STABILITY TESTS AT VARIOUS TEMPERATURES

This Laboratory has begun a program to determine the quantitative effects of 5-10-10 and 5-10-10-PAN combinations in various esters on oxidation stable life, oxidation rate, and oxygen tolerance. The esters used in this study include simple dibasic acid esters as well as neopentyl esters of dibasic acids and neopentyl type alcohols and esters of monobasic acids and di-, tri-, and tetra-functional neopentyl type polyols. Other inhibitors and inhibitor combinations are also being evaluated in this study.

Preliminary stable life studies of several ester types with phenothiazine and 5-10-10 additives alone and in combination with phenyl-alpha-naphthylamine or Primene-81R are shown on Tables 51 and 52 and Figures 40, 41, and 42. The esters used in this study include di-2-ethylhexyl sebacate (MLO 7112), Hercoflex 600 (MLO 7064), Synthetics J-7 (MLO 7023), and a trimethylol propane ester (MLO 7384). Comparative stable life values between the simple dibasic acid ester and the three neopentyl esters of polyols and monobasic acids are typical of those found with a large number of esters using phenothiazine as the inhibitor. That is, the stable life of the neopentyl ester is generally considerably longer than the stable life of the dibasic acid ester. In all cases, there is a gradual build-up of neutralization number to values of two to four within the stable life. That is, this gradual increase in neutralization number is followed in all cases by a distinct increase in the rate of neutralization number change. This rapid increase in acidity is accompanied by rapid changes in viscosity, dirtiness, etc. and is considered to be the end of the stable life or induction period.

The use of 0.5 weight per cent 5-10-10 in esters does not appear to be as effective as 0.5 weight per cent phenothiazine in providing stable life at 347°F. The combination of either PAN or Primene-81R with either phenothiazine or 5-10-10 does appear to have a marked effect on the 347°F oxidative behavior. These effects can best be shown with di-2-ethylhexyl sebacate which has a relatively short stable life with phenothiazine alone. The combination of 5-10-10 or phenothiazine with PAN or Primene-81R appears to extend the stable life at 347°F and, in addition, lowers the neutralization number build-up within the stable life.

The same trends are also shown by either of these inhibitor combinations in the neopentyl esters evaluated. The initial stable life of these neopentyl esters at 347°F is sufficiently long with phenothiazine alone that extremely long tests are required to demonstrate the margin of quality of the inhibitor combination over that of the single inhibitor. The preliminary tests do not yet demonstrate a marked superiority for any one inhibitor system but does suggest the use of a basic (amine) type material in conjunction with phenothiazine or 5-10-10.

The behavior of stable life as a function of test temperature for phenothiazine in di-2-ethylhexyl sebacate is shown in Figure 43. This relationship suggests that increasing the test temperature to 400°F from 347°F may reduce the stable life by a factor of 5 to 10. The stable life range at 400°F should range from one day to about a week based on preliminary test results.

The same esters and additive combinations evaluated for stable life at 347°F have also been evaluated in extended tests at 500°F. The 500°F oxidation tests are evaluated on the basis of comparative values of oxidation rate and oxygen tolerance. A series of 20, 40, and 60-hour oxidation tests at 500°F for di-2-ethylhexyl sebacate and three neopentyl type esters are shown on Tables 53, 54, 55, 56, 57, 58, and 59. These tests include a series of tests without metal catalysts.

The rate of oxygen assimilation (oxidation rate) is tabulated for these tests on Table 60. In the presence of metal catalysts, the oxidation rate for the neopentyl esters is consistently higher for phenothiazine or 5-10-10 alone than for combinations of these additives with PAN or Primene-81R. The oxidation rate for the phenothiazine-inhibited neopentyl esters is approximately 50 per cent higher than the comparable rates for the same esters with 5-10-10 plus PAN or Primene-81R. That is, the neopentyl esters inhibited with 5-10-10 plus PAN or Primene-81R assimilate only as much oxygen in 60 hours as is assimilated in 40 hours by the typical phenothiazine-inhibited ester.

A similar comparison based on Synthetics J-7 oxidations at 500°F without metal catalysts shows less difference in oxidation rate. These data suggest the interdependence of metal catalyst effects, and the presence of the amine (basic) component of the inhibitor package in reducing product acidity and oxidation rate. It has been noted that the 5-10-10-PAN combination is not particularly effective with di-2-ethylhexyl sebacate at 500°F but is effective at 347°F. This again may point up the effect of acidity control by the amine component of the additive package. At 500°F , the di-2-ethylhexyl sebacate is above the threshold of thermal instability and acid number in this test is caused by thermal degradation.

The effect of oxygen tolerance on property change (particularly thickening) is plotted on Figures 44, 45, 46, 47, 48, 49, and 50 for the 500°F oxidation data. In every case, these data show the minimum effect on viscosity change per unit of oxygen assimilated for the esters inhibited by phenothiazine alone. The combination of inhibitors 5-10-10 or phenothiazine with PAN or Primene-81R show more thickeing per unit oxygen assimilated.

These data, in all cases, show that only a relatively small increment of oxygen assimilation is required to change the fluid from the point of 200 to 500 per cent thickening with little or no sludge to the point of infinite thickening and essentially all sludge. That is, the first 80 per cent of the oxygen tolerance of these fluids causes relatively little property change or sludge. It is the last 20 per cent of oxygen input which causes the major deterioration in fluid properties.

These preliminary quantitative oxidation data show several significant trends for the use of 5-10-10-PAN and other similar inhibitor combinations. The use of PAN or Primene-81R with phenothiazine or 5-10-10 ~~does~~ appear to extend the stable life of the esters and reduce the acidity build-up within the stable life. At 500°F in the presence of metal catalysts, the use of PAN or Primene-81R with 5-10-10 or phenothiazine appears to reduce somewhat the rate of oxidation and to lower acidity for neopentyl esters compared with phenothiazine alone. The lower oxidation rate is, in all cases, accompanied by a lowering in neutralization number. The oxygen tolerance at 500°F is lower for 5-10-10 or phenothiazine combined with the PAN or Primene-81R (basic) ingredients than for the fluids containing phenothiazine alone. The overall result of decreased oxidation rate coupled with decreased oxygen tolerance at 500°F. yield a modest improvement in the behavior of neopentyl esters using the combination of 5-10-10-PAN inhibitor over the conventional phenothiazine ester in the 500°F Spec. MIL-L-9236 oxidation and corrosion test. There appear to be some differences between ester types in oxygen tolerance at 500°F. which may result in increasing the apparent advantages of the above inhibitor combinations.

1. Small Volume Oxidation Tests. Many of the materials available for evaluation as hydraulic fluid and lubricant components are research and development samples of limited quantity. In such cases, the completeness of the oxidative evaluation is severely limited by the relatively large volume (100 ml.) of test fluid conventionally used in Spec. MIL-L-7808 and Federal Spec. VV-L-791e type tests. A series of oxidative measurements have been made at 347° and 500°F to establish equivalence between small volume tests and the Spec. MIL-L-7808 type tests.

Studies in the development of a low volume test have been made with a 25 milliliter quantity of test fluid. Under severe oxidative test conditions, 25 milliliters approaches the minimum fluid volume to allow for a reasonable volatility loss, quantitative measure of oil insolubles, and still have enough liquid sample for the determination of viscosity and neutralization number. A volume of 25 milliliters of test fluid is also adequate for stable life testing which requires periodic sampling on a carefully arranged schedule.

This Laboratory has been using the same basic oxidation test equipment for Spec. MIL-L-7808 type tests over the temperature range of 347° to 700°F. The apparatus is shown on Figure 51. Two condensers are shown for use with the same oxidation tube. The water condenser is used at temperatures of 400°F and lower while the air condenser is used at temperatures above 400°F The basic unit with the water condenser was developed for use in Spec. MIL-H-5606 aircraft hydraulic fluid in 1942 and has been used for all conventional bulk oil oxidation studies by this Laboratory. The oxidation tube has an outside diameter of 38 millimeters compared with the tube of 65 millimeters outside diameter currently specified in Federal Spec. VV-L-791e. This size difference is not believed to be critical in producing differences in test severity at 347°F.

At 500°F , where oxidation rates are dependent on air rate, intimacy of air-oil contact, time of air-oil contact, and partial pressure of oxygen, differences in test system geometry cause appreciable differences in test severity using the same air rate, time, temperature, and quantity of test fluid. The effect of test system geometry at 500°F is further emphasized by the small volume tests. These data point up the necessity of quantitative measurements of oxygen assimilation to obtain intra- or inter-laboratory reproducibility.

Table 51

EFFECT OF ADDITIVE COMBINATION ON THE OXIDATION STABILITY OF SEVERAL ESTERS AT 347°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F ; TEST TIME AS INDICATED: AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML., AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM

ADDITIVE SYMBOLS

PTZ = PHENOTHIAZINE
5,10,10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	DI-2-ETHYLHEXYL SEBACATE (MLO 7112)		PENTAERYTHRITOL ESTER (MLO 7064)			DIPENTAERYTHRITOL ESTER (MLO 7023)		
OXIDATION INHIBITOR, WT.%	0.5 PTZ	1.0 5,10,10 +2.0 PAN	0.5 PTZ	1.0 5,10,10 +2.0 PAN	1.0 PTZ + 2.0 PR-81R	0.5 PTZ	1.0 5,10,10 +2.0 PAN	1.0 PTZ + 2.0 PR-81R
TEST TIME, HRS.	261	764	544	790	560	450	790	560
STABLE LIFE, HRS. (1)	240	>764	500	>790	>560	400	>790	>560
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F.	+14	+14	+57	+47	+40	+200	+40	+43
NEUT. NO. (MG. KOH/GM OIL)								
ORIGINAL	0.1	0.1	0.3	0.3	0.1	0.1	0.2	0.1
FINAL	13.6	2.7	5.2	0.4	1.2	10.0	0.5	1.1
ASTM UNION COLOR								
ORIGINAL	1	3	1	3	2	1	1	1
FINAL	>8	>8	>8	>8	>8	>8	>8	>8
WT.% OIL INSOLUBLE MATERIAL	0.3	0.8	0.1	0.1	0.5	0.2	0.1	0.1
FINAL CATALYST CONDITION								
APPEARANCE								
COPPER	DULL	COATED	CORRODED	CORRODED	CORRODED	CORRODED	DULL	CORRODED
STEEL	COATED	COATED	COATED	DULL	COATED	COATED	DULL	COATED
ALUMINUM	COATED	COATED	COATED	BRIGHT	DULL	COATED	BRIGHT	COATED
MAGNESIUM	COATED	COATED	COATED	BRIGHT	DULL	COATED	BRIGHT	DULL
WT. LOSS (MG./SQ. CM.)								
COPPER	0.15	+0.27	0.43	0.26	0.89	1.10	0.16	0.49
STEEL	+0.39	+0.19	+0.12	+0.06	+0.09	+0.18	0.00	+0.15
ALUMINUM	+0.41	+0.60	+0.12	+0.05	+0.06	+0.14	+0.02	+0.16
MAGNESIUM	+0.32	+0.31	+0.09	0.01	+0.02	+0.15	+0.01	+0.07

(1) THE STABLE LIFE OF A FLUID IS TAKEN AS THE POINT WHERE THERE IS A RAPID INCREASE IN NEUTRALIZATION NUMBER WITH TIME.

Table 52

EFFECT OF ADDITIVE COMBINATION ON THE OXIDATION STABILITY OF NEOPENTYL TYPE ESTERS AT 347°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F ; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 100 MLS.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

ADDITIVE SYMBOLS

PTZ = PHENOTHIAZINE
5,10,10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE

PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	A NEOPENTYL TYPE ESTER, MLO 7384 (WADC DESIG. MLO 57-424)					A NEOPENTYL TYPE ESTER, PRL3684
OXIDATION INHIBITOR, WT. %	0.5 PTZ	0.5 5,10,10	1.0 5,10,10 +2.0 PAN	1.0 PTZ +2.0 PR-81R	1.0 5,10,10 +2.0 PR-81R	1.0 5,10,10 +2.0 PAN
TEST TIME, HRS.	840 *	72 *	720	430	432	720
STABLE LIFE, HRS. (1)	>840	<72	>720	>430	>432	>720
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F.	+82	+67	+67	+61	+70	+13
NEUT. NO. (MG. KOH/GM. OIL)						
ORIGINAL	0.2	0.3	0.3	0.1	0.2	0.2
FINAL	3.7	6.1	0.4	1.4	0.9	0.8
ASTM UNION COLOR						
ORIGINAL	0	0	3 1/2	1	1	3 1/2
FINAL	>8	6	>8	>8	>8	>8
WT. % OIL INSOLUBLE MATERIAL	TRACE	TRACE	0.4	0.3	0.1	0.3
FINAL CATALYST CONDITION						
APPEARANCE						
COPPER	DULL	DULL	CORRODED	CORRODED	CORRODED	COATED
STEEL	DULL	DULL	DULL	DULL	DULL	COATED
ALUMINUM	BRIGHT	BRIGHT	BRIGHT	BRIGHT	BRIGHT	COATED
MAGNESIUM	BRIGHT	CORRODED	BRIGHT	CORRODED	BRIGHT	COATED
WT. LOSS (MG./SQ. CM.)						
COPPER	0.33	0.09	0.30	0.99	3.51	+0.59
STEEL	0.00	+0.06	+0.07	+0.02	+0.02	+0.53
ALUMINUM	+0.12	0.19	0.00	0.00	0.01	+0.97
MAGNESIUM	0.16	0.41	+0.02	1.60	0.05	+0.66

* SMALL VOLUME OF OXIDATION TESTS

(1) THE STABLE LIFE OF A FLUID IS TAKEN AS THE POINT WHERE THERE IS A RAPID INCREASE IN NEUTRALIZATION NUMBER WITH TIME.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ±3°F ; TEST TIME AS INDICATED; AIR RATE = 5 ±0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 MLS.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

SYMBOL	TEST FLUID
—●—	0.5 WT.% PHENOTHIAZINE IN DI-2ETHYLHEXYL SEBACATE (MLO 7112)
—○—	1.0 WT.% 5,10,10* (PRL 3702) + 2.0 WT.% PAN** IN DI-2-ETHYLHEXYL SEBACATE (MLO 7112)

* 5-ETHYL-10,10-DIPHENYLPHENAZASILINE

**PHENYL-ALPHA-NAPHTHYLAMINE

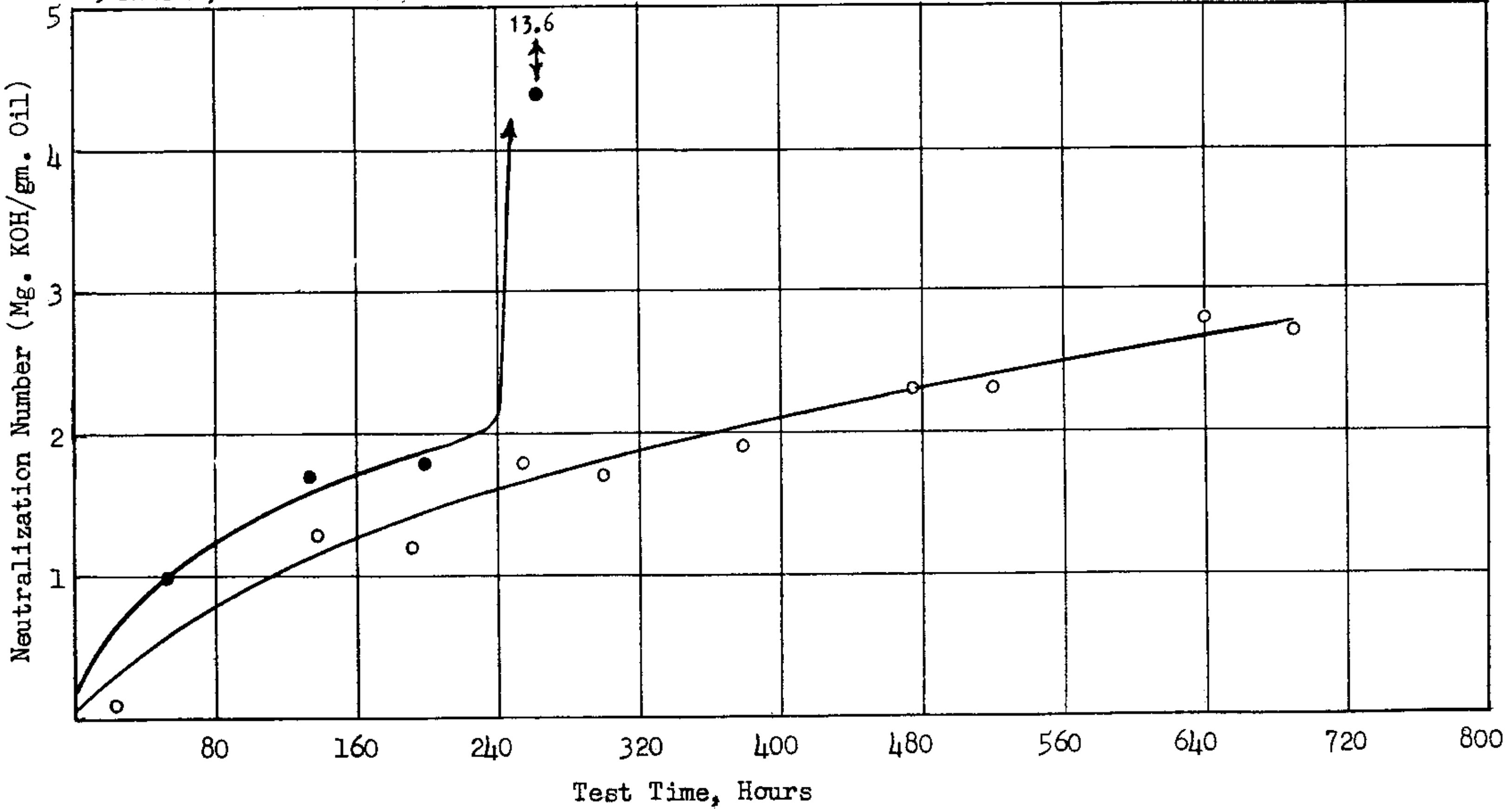


Figure 40. EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION STABILITY OF DI-2-ETHYLHEXYL SEBACATE AT 347°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F ; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 MLS.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

SYMBOL	TEST FLUID
—○—	0.5 WT.% PHENOTHIAZINE IN SYNTHETICS J-7 (MLO 7018)
—●—	0.5 WT.% PHENOTHIAZINE IN HERCOFLEX 600 (PRL 3542)
—△—	1.0 WT.% 5,10,10* (PRL 3702) + 2.0 WT.% PAN** IN HERCOFLEX 600 (MLO 7064)
—▲—	1.0 WT.% PHENOTHIAZINE + 2.0 WT.% PRIMENE-81R IN HERCOFLEX 600 (MLO 7064)
—□—	1.0 WT.% 5,10,10* (PRL 3702) + 2.0 WT.% PAN** IN SNYTHETICS J-7 (MLO 7023)
—■—	1.0 WT.% PHENOTHIAZINE + 2.0 WT.% PRIMENE-81R IN SYNTHETICS J-7 (MLO 7023)

*5-ETHYL-10,10-DIPHENYLPHENAZASILINE **PHENYL-ALPHA-NAPHTHYLAMINE

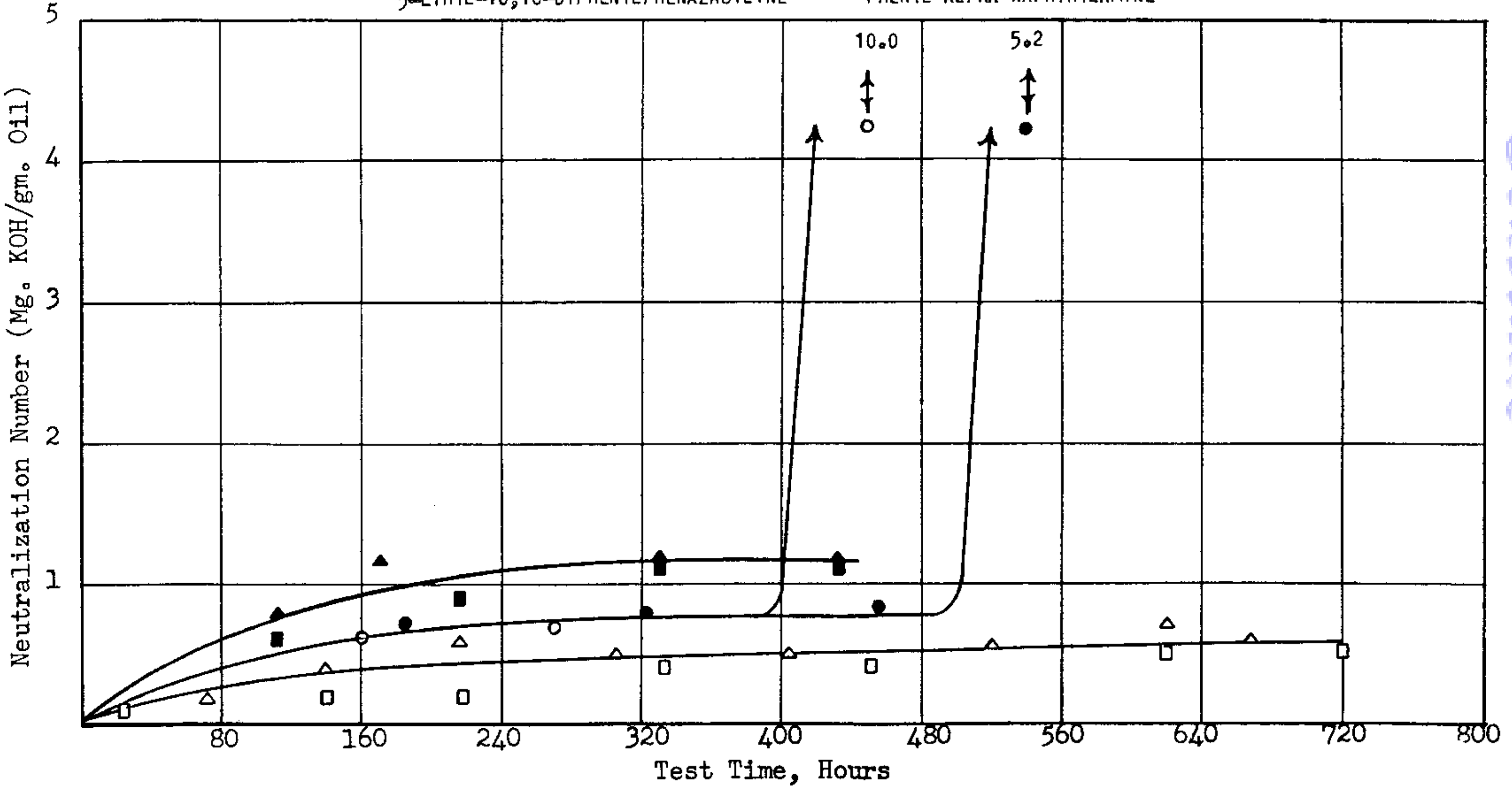


Figure 41. EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION STABILITY OF PENTAERYTHRITOL TYPE ESTERS AT 347°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F ; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 MLS.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

SYMBOL	TEST FLUID
MLO 7384	A NEOPENTYL TYPE ESTER RECEIVED FROM WRIGHT AIR DEVELOPMENT CENTER (WADC DESIG. MLO 57-424)
—○—	0.5 WT.% 5,10,10* (PRL 3679) IN MLO 7384
—●—	0.5 WT.% PHENOTHIAZINE IN MLO 7384
—△—	1.0 WT.% 5,10,10* (PRL 3702) + 2.0 WT.% PAN** IN MLO 7384
—▲—	1.0 WT.% PHENOTHIAZINE + 2.0 WT.% PRIMENE-81R IN MLO 7384
—■—	1.0 WT.% 5,10,10* (PRL 3702) + 2.0 WT.% PRIMENE-81R IN MLO 7384

* 5-ETHYL-10,10-DIPHENYLPHENAZASILINE ** PHENYL-ALPHA-NAPHTHYLAMINE

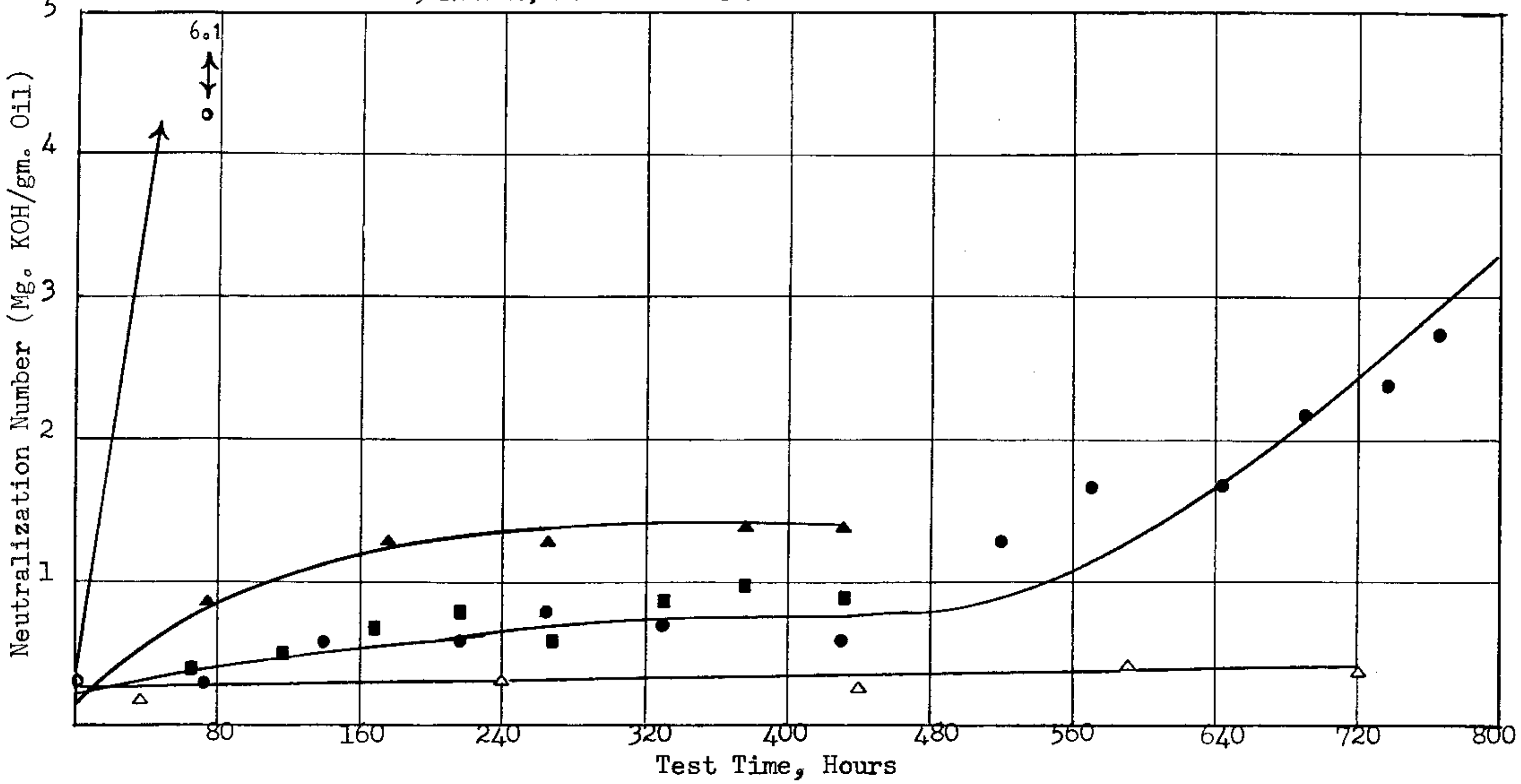
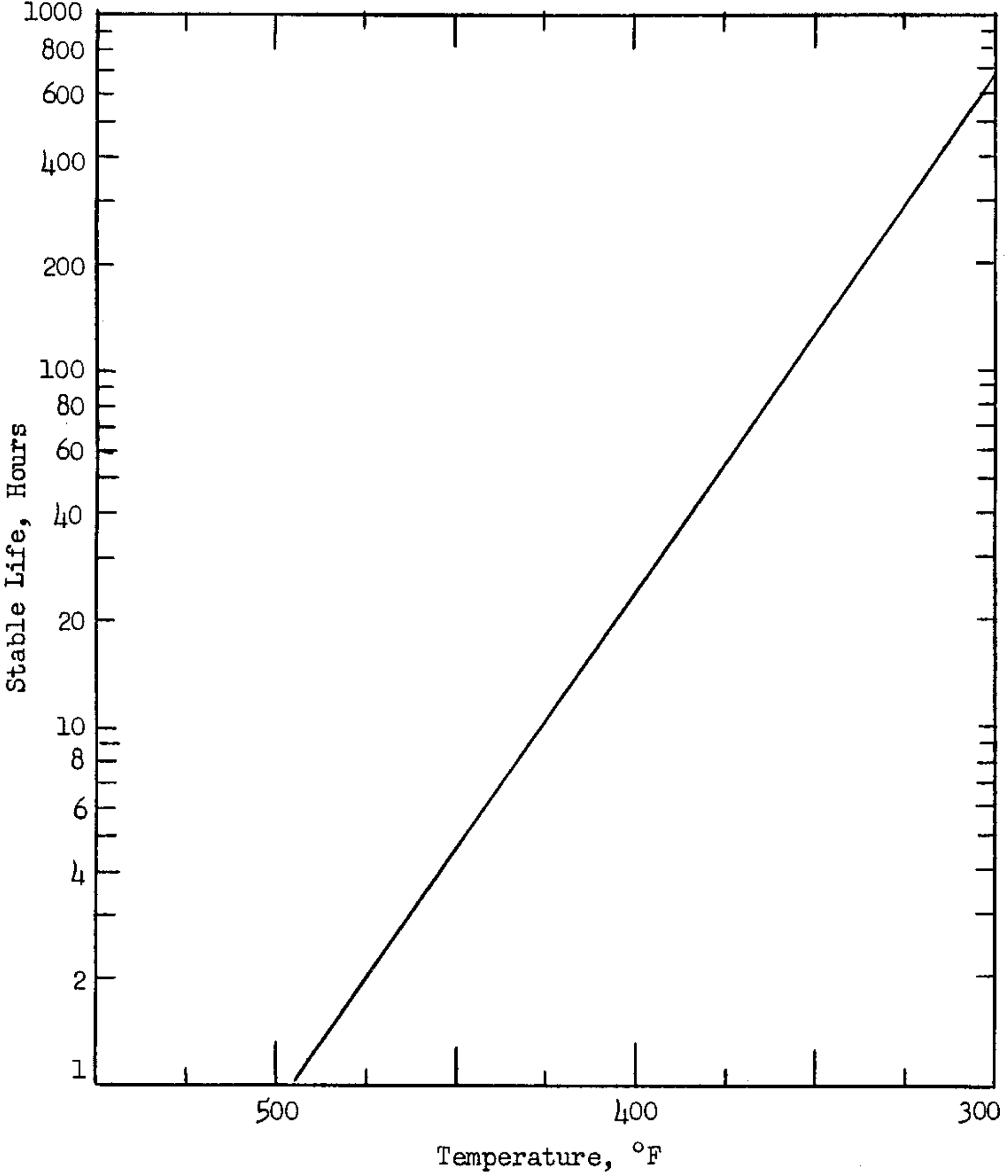


Figure 42. EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION STABILITY OF A NEOPENTYL TYPE ESTER AT 347°F.



TESTS ARE CONDUCTED IN ACCORDANCE WITH THE PROCEDURE AND TECHNIQUES OUTLINED IN SPEC. MIL-L-7808.

TEST FLUID = 0.5 WEIGHT PER CENT PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE.

NOTE: STABLE LIFE IS DEFINED AS THE POINT AT WHICH THERE IS A RAPID INCREASE IN NEUTRALIZATION NUMBER WITH TEST TIME.

Figure 43. EFFECT OF TEST TEMPERATURE ON THE OXIDATION STABILITY OF DI-2-ETHYLHEXYL SEBACATE

Table 53

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF DI-2-ETHYLHEXYL SEBACATE AT 500°F

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500° ± 5°F : TEST TIME = 40 HOURS: AIR RATE = 5 ± 0.5 LITERS PER HOUR TEST FLUID CHARGE = 125 MLS.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM

ADDITIVE SYMBOL
PTZ = PHENOTHIAZINE
5,10,10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE

TEST FLUID	DI-2-ETHYLHEXYL SEBACATE (MLO 7112)					
OXIDATION INHIBITOR, WT.%	0.5 PTZ		0.5 5,10,10		1.0 5,10,10+2.0 PAN	
SAMPLE TIME, HOURS (1)	20	40	20	40	20	40
LIQUID CHARGED, GMS.	-	112	-	112	-	112
APPROX. AMOUNT O_2 SUPPLIED, GMS. (2)	26.2	52.4	26.2	52.4	26.2	52.4
APPROX. AMOUNT O_2 USED, GMS. (2)	7.2	11.5	13.9	25.0	5.8	12.9
MOLS O_2 USED/426 GMS. FLUID CHARGED(3)	0.86	1.72	1.65	2.96	0.69	1.53
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLE MATERIAL, (4) AT 100°F.	+44	+164	+68	+712	+67	+1590
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	15.4	17.1	14.4	20.2	7.0	19.8
WT.% OIL INSOLUBLE MATERIAL	-	0.9	-	1.0	-	2.4
FINAL CATALYST CONDITION						
APPEARANCE						
COPPER	-	CORRODED	-	DULL	-	DULL
STEEL	-	DULL	-	CORRODED	-	CORRODED
ALUMINUM	-	BRIGHT	-	BRIGHT	-	DULL
WT. LOSS (MG./SQ. CM.)						
COPPER	-	0.75	-	0.16	-	0.09
STEEL	-	0.09	-	2.36	-	0.22
ALUMINUM	-	0.00	-	0.02	-	0.00

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 20 AND AT 40 HOURS TEST TIME.

(2) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(3) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYLHEXYL SEBACATE IS 426.

(4) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 54

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF HERCOFLEX 600 AT 500°F (NO CATALYST METALS)

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500° ± 5°F., TEST TIME = 60 HRS.; AIR RATE = 5 ± 0.5 L./HR.; AND FLUID CHARGE = 125 MLS.
NOTE: THERE WERE NO CATALYST METALS PRESENT IN THESE TESTS.

ADDITIVE SYMBOL
- PTZ = PHENOTHIAZINE
- 5, 10, 10 = 5-ETHYL- 10, 10-DIPHENYLPHENAZASILINE
- PAN = PHENYL-ALPHA-NAPHTHYLAMINE
- PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	HERCOFLEX 600, A PENTAERYTHRITOL TYPE ESTER (MLO 7064)										
OXIDATION INHIBITOR, WT.%	1.0 PTZ			1.0PTZ + 2.0 PR-81R		1.0 PTZ + 2.0 PAN			1.0 5,10,10 + 2.0 PAN		
SAMPLE TIME, HRS. (1)	20	40	60	20	40(5)	20	40	60	20	40	60
TEST FLUID CHARGED, GMS.	-	-	123	-	121	-	-	123	-	-	122
APPROX. AMOUNT O_2 SUPPLIED, GMS. (2)	-	-	78.6	-	52.4	-	-	78.6	-	-	78.6
APPROX. AMOUNT O_2 USED, GMS. (2)	4.7	8.9	13.0	3.7	8.3	3.7	8.0	12.9	3.7	7.4	11.5
MOLS O_2 USED/426 GMS. FLUID CHARGED (3)	0.51	0.96	1.41	0.41	0.92	0.40	0.87	1.40	0.40	0.81	1.26
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLE MATERIAL, (4) AT 100°F.	+64	+193	+567	+90	+390	+100	+905	>10,000	+52	+104	+449
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	4.8	10.5	15.1	2.6	10.7	3.0	6.3	11.6	3.0	5.0	8.9
WT.% OIL INSOLUBLE MATERIAL (4)	-	-	0.8	-	2.5	-	-	6.1	-	-	0.8

(1) APPROXIMATELY 25 MILLITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 20 AND AT 40 HOURS TEST TIME.

(2) AMOUNT OXYGEN CONSUMED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HRS.) X O_2 CONTENT (FRACTION) X 1.43 (GMS./LITER). AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(3) MOLS O_2 USED/426 GMS. FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(4) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

(5) AIR TUBE PLUGGED AT 40.5 HOURS.

Table 55

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF HERCOFLEX 600 AT 500°F

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500° ± 5°F ; TEST TIME = 60 HOURS; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGE = 125 MLS.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

ADDITIVE SYMBOL
PTZ = PHENOTHIAZINE
5,10,10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	HERCOFLEX 600, A PENTAERYTHRITOL TYPE ESTER (MLO 7064)											
OXIDATION INHIBITOR, WT.%	0.5 PTZ			1.0 PTZ + 2.0 PR-81R			0.5 5,10,10		1.0 5,10,10 + 2.0 PAN			
SAMPLE TIME, HOURS (1)	20	40	60	20	40	60	20	40	20	40	60	
LIQUID CHARGED, GMS.	-	-	124	-	-	124	-	123	-	-	122	
APPROX. AMOUNT O_2 SUPPLIED, GMS. (2)	26.2	52.4	78.6	26.2	52.4	78.6	26.2	52.4	26.2	52.4	78.6	
APPROX. AMOUNT O_2 USED, GMS. (2)	7.3	11.4	17.1	3.9	10.5	17.0	7.8	15.8	0.57	10.2	12.1	
MOLS O_2 USED/426 GMS. FLUID CHARGED (3)	0.78	1.22	1.84	0.42	1.12	1.82	0.84	1.90	0.62	1.12	1.32	
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLE MATERIAL, (4) AT 100°F.	+66	+268	SOLID (5)	+85	+490	>10,000	+117	SOLID (5)	+59	+298	SOLID (5)	
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	3.7	15.4	11.8	2.5	7.5	11.8	8.8	18.3	2.0	2.7	6.3	
WT.% OIL INSOLUBLE MATERIAL (4)	-	-	SOLID (5)	-	-	3.9	-	SOLID (5)	-	-	SOLID (5)	
FINAL CATALYST CONDITION												
APPEARANCE												
COPPER	-	-	CORRODED	-	-	DULL	-	CORRODED	-	-	CORRODED	
STEEL	-	-	CORRODED	-	-	CORRODED	-	CORRODED	-	-	DULL	
ALUMINUM	-	-	DULL	-	-	DULL	-	DULL	-	-	BRIGHT	
WT. LOSS (MG./SQ. CM.)												
COPPER	-	-	0.32	-	-	0.06	-	0.25	-	-	1.09	
STEEL	-	-	23.90	-	-	0.50	-	12.16	-	-	+0.02	
ALUMINUM	-	-	0.07	-	-	+0.03	-	+0.02	-	-	+0.02	

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM TEST TUBE AT 20 AND AT 40 HOURS TEST TIME.
(2) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.
(3) THE MOLS OF OXYGEN FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.
(4) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.
(5) PRODUCT WAS AN INTIMATE MIXTURE OF OXIDIZED FLUID AND SOLIDS WHICH COULD NOT BE SEPARATED WITHOUT DILUTION.

Table 56

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF SYNTHETICS J-7 AT 500°F. (NO CATALYST METALS)

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500° ± 5°F ; TEST TIME = 60 HRS.; AIR RATE = 5±0.5 L./HR.; AND TEST FLUID CHARGE = 125 MLS.
NOTE: THERE WERE NO CATALYST METALS PRESENT IN THESE TESTS.

ADDITIVE SYMBOL
PTZ = PHENOTHIAZINE
5, 10, 10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	SYNTHETICS J-7, A PENTAERYTHRITOL TYPE ESTER (MLO 7023)											
OXIDATION INHIBITORS, WT.%	1.0 PTZ			1.0 PTZ + 2.0 PR-81R			1.0 PTZ + 2.0 PAN			1.0 5,10,10 + 2.0 PAN		
SAMPLE TIME, HRS. (1)	20	40	60	20	40	60	20	40	60	20	40	60
LIQUID CHARGED, GMS.	-	-	123	-	-	122	-	-	124	-	-	124
APPROX. AMOUNT O_2 SUPPLIED, GMS. (2)	-	-	78.6	-	-	78.6	-	-	78.6	-	-	76.8
APPROX. AMOUNT O_2 USED, GMS. (2)	3.8	7.5	10.9	3.2	6.7	10.1	3.8	7.8	10.7	3.7	6.8	9.6
MOLS O_2 USED/426 GMS. FLUID CHARGED (3)	0.41	0.81	1.18	0.35	0.72	1.10	0.41	0.84	1.15	0.40	0.73	1.03
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLE MATERIAL, (4) AT 100°F	+56	+164	+414	+79	+319	+1085	+98	+469	+5456	+44	+111	+219
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	3.7	7.5	13.7	2.2	5.6	7.2	3.2	4.8	9.1	2.5	4.7	6.7
WT.% OIL INSOLUBLE MATERIAL (4)	-	-	0.6	-	-	1.8	-	-	4.6	-	-	0.7

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM TEST TUBE AT 20 AND AT 40 HOURS TEST TIME.
(2) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L. HR. AT S.T.P.) X TIME (HRS.) X O_2 CONTENT (FRACTION) X 1.43 (GM. LITER).
AMOUNT O_2 CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.
(3) MOLS O_2 ABSORBED FOR 426 GMS. FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.
(4) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM MAPHTHA AND DRIED BEFORE WEIGHING.

Table 57

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF SYNTHETICS J-7 AT 500°F

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500° ± 5°F ; TEST TIME = 60 HRS.; AIR RATE = 5 ± 0.5 LITERS PER HOUR; FLUID CHARGE = 125 MLS.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINIUM

ADDITIVE SYMBOL
PTZ = PHENOTHIAZINE
5,10,10 = 5-EHTYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	SYNTHETICS J-7, A PENTAERYTHRITOL TYPE ESTER (MLO 7023)											
OXIDATION INHIBITOR, WT.%	0.5 PTZ			1.0 PTZ + 2.0 PR-81R			1.0 PTZ + 2.0 PAN			1.0 5,10,10 + 2.0 PAN		
SAMPLE TIME, HOURS (1)	20	40	60	20	40	60	20	40	60	20	40	60
LIQUID CHARGE, GMS.	-	-	123	-	-	122	-	-	124	-	-	125
APPROX. AMOUNT O_2 SUPPLIED, GMS. (2)	26.2	52.4	78.6	26.2	52.4	78.6	26.2	52.4	78.6	26.2	52.4	78.6
APPROX. AMOUNT O_2 USED, GMS. (2)	6.0	10.4	14.5	3.1	6.4	9.7	3.6	7.5	10.2	3.9	7.2	10.1
MOLS O_2 USED/426 GMS. FLUID CHARGED (3)	0.65	1.13	1.57	0.34	0.71	1.06	0.39	0.81	1.12	0.42	0.77	1.07
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLE MATERIAL, (4) AT 100°F.	+51	+283	+1890	+62	+184	+605	+75	+330	+1550	+49	+120	+531
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	13.5	14.0	16.1	1.9	3.2	9.7	1.8	3.9	5.7	1.7	2.3	4.6
WT.% OIL INSOLUBLE MATERIAL (4)	-	-	0.4	-	-	1.3	-	-	2.9	-	-	1.4
FINAL CATALYST CONDITION												
APPEARANCE												
COPPER	-	-	DULL	-	-	CORRODED	-	-	DULL	-	-	CORRODED
STEEL	-	-	CORRODED	-	-	DULL	-	-	DULL	-	-	DULL
ALUMINUM	-	-	BRIGHT	-	-	DULL	-	-	DULL	-	-	BRIGHT
WT. LOSS (MG./SQ. CM.)												
COPPER	-	-	0.09	-	-	0.27	-	-	0.09	-	-	0.56
STEEL	-	-	7.85	-	-	+0.01	-	-	0.02	-	-	0.03
ALUMINUM	-	-	+0.02	-	-	+0.01	-	-	0.01	-	-	0.01

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM TEST TUBE AT 20 AND AT 40 HOURS TEST TIME.
(2) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.
(3) THE MOLS OF OXYGEN FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.
(4) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 58

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF A NEOPENTYL TYPE ESTER AT 500°F

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500° ± 5°F ; TEST TIME = 60 HOURS; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGE = 125 MILLILITERS; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

ADDITIVE SYMBOL
PTZ = PHENOTHIAZINE
5,10,10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE

TEST FLUID	A NEOPENTYL TYPE DIESTER (MLO 7384) (WADC DESIG. MLO 57-424)					
OXIDATION INHIBITOR	0.5 WT.% PTZ			0.5 WT.% 5,10,10		
SAMPLE TIME, HOURS (1)	20	40	60	20	40	60
LIQUID CHARGED, GMS.	-	-	125	-	-	126
APPROX. AMOUNT O_2 SUPPLIED, GMS. (2)	26.2	52.4	78.6	26.2	52.4	78.6
APPROX. AMOUNT O_2 USED, GMS. (2)	7.8	11.8	17.3	5.2	10.4	15.7
MOLS O_2 USED/426 GMS. FLUID CHARGED (3)	0.83	1.26	1.84	0.55	1.11	1.66
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLE MATERIAL, (4) AT 100°F.	+50	+190	+2020	+104	+2410	SOLID(5)
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	8.5	13.0	15.6	9.5	10.3	18.8
WT. % OIL INSOLUBLE MATERIAL (4)	-	-	TRACE	-	-	SOLID(5)
FINAL CATALYST CONDITION						
APPEARANCE						
COPPER	-	-	CORRODED	-	-	BRIGHT
STEEL	-	-	CORRODED	-	-	CORRODED
ALUMINUM	-	-	BRIGHT	-	-	BRIGHT
WT. LOSS (MG./SQ. CM.)						
COPPER	-	-	0.71	-	-	0.07
STEEL	-	-	5.02	-	-	89.50
ALUMINUM	-	-	+0.01	-	-	+0.03

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM TEST TUBE AT 20 AND AT 40 HOURS TEST TIME.

(2) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(3) THE MOLS OF OXYGEN FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(4) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

(5) PRODUCT WAS AN INTIMATE MIXTURE OF OXIDIZED FLUID AND SOLIDS WHICH COULD NOT BE SEPARATED WITHOUT DILUTION.

(CONCLUDED ON NEXT PAGE)

Table 58 (Concluded)

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF A NEOPENTYL TYPE ESTER AT 500°F

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F ; TEST TIME = 60 HOURS; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGE = 125 MLS.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

ADDITIVE SYMBOL
PTZ = PHENOTHIAZINE
5,10,10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	A NEOPENTYL TYPE ESTER (MLO 7384) (WADC DESIG. MLO 57-424)											
OXIDATION INHIBITOR, WT.%	1.0 PTZ + 2.0 PAN			1.0 PTZ + 2.0 PR-81R			1.0 5,10,10 + 2.0 PAN			1.0 5,10,10 + 2.0 PR-81R		
SAMPLE TIME, HOURS (1)	20	40	60	20	40	60	20	40	60	20	40	60
LIQUID CHARGED, GMS.	-	-	124	-	-	124	-	-	125	-	-	122
APPROX. AMOUNT O_2 SUPPLIED, GMS. (2)	26.2	52.4	78.6	26.2	52.4	78.6	26.2	52.4	78.6	26.2	52.4	78.6
APPROX. AMOUNT O_2 USED, GMS. (2)	3.4	12.9	19.0	3.6	8.7	12.7	3.9	7.7	10.8	3.4	6.3	9.8
MOLS O_2 USED/426 GMS. FLUID CHARGED, (3)	0.37	1.38	2.05	0.39	0.93	1.35	0.42	0.82	1.15	0.37	0.69	1.07
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLE MATERIAL, (4) AT 100°F.	+73	+230	+5850	+59	+291	+9340	+42	+92	+284	+37	+77	+180
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	2.2	7.2	15.7	3.1	11.1	17.1	2.1	3.8	7.2	3.2	4.4	13.5
WT.% OIL INSOLUBLE MATERIAL (4)	-	-	2.9	-	-	1.2	-	-	0.5	-	-	0.3
FINAL CATALYST CONDITION												
APPEARANCE												
COPPER	-	-	CORRODED	-	-	CORRODED	-	-	CORRODED	-	-	CORRODED
STEEL	-	-	DULL	-	-	CORRODED	-	-	DULL	-	-	DULL
ALUMINUM	-	-	DULL	-	-	DULL	-	-	BRIGHT	-	-	DULL
WT. LOSS (MG./SQ. CM.)												
COPPER	-	-	0.89	-	-	1.05	-	-	1.05	-	-	0.44
STEEL	-	-	0.18	-	-	4.28	-	-	0.05	-	-	0.02
ALUMINUM	-	-	0.02	-	-	0.05	-	-	+0.02	-	-	0.00

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM TEST TUBE AT 20 AND AT 40 HOURS.
(2) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.
(3) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.
(4) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 59

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF AN EXPERIMENTAL HIGH TEMPERATURE ESTER AT 500°F

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F ; TEST TIME = 60 HOURS; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGE = 125 MLS.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

ADDITIVE SYMBOL
  PTZ = PHENOTHIAZINE
  5,10,10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
  PAN = PHENYL-ALPHA-NAPHTHYLAMINE

TEST FLUID	AN EXPERIMENTAL HIGH TEMPERATURE ESTER (MLO 7385) (WADC DESIG. MLO 58-88)								
OXIDATION INHIBITOR, WT.%	0.5 PTZ			0.5 5,10,10			1.0 5,10,10 + 2.0 PAN		
SAMPLE TIME, HOURS (1)	20	40	60	20	40	60	20	40	60
LIQUID CHARGED, GMS.	-	-	119	-	-	119	-	-	119
APPROX. AMOUNT O_2 SUPPLIED, GMS. (2)	26.2	52.4	78.6	26.2	52.4	78.6	26.2	52.4	78.6
APPROX. AMOUNT O_2 USED, GMS. (2)	5.8	10.5	13.7	5.8	11.0	15.3	4.2	8.3	12.1
MOLS O_2 USED/426 GMS. FLUID CHARGED (3)	0.64	1.17	1.58	0.64	1.23	1.71	0.47	0.93	1.36
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLE MATERIAL, (4) AT 100°F.	+210	+1630	>+10,000	+298	+3240	>+10,000	+343	+2920	>+10,000
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	8.7	16.0	24.3	10.3	20.4	29.7	4.3	9.0	13.0
WT.% OIL INSOLUBLE MATERIAL	-	-	1.4	-	-	2.7	-	-	0.2
FINAL CATALYST CONDITION									
APPEARANCE									
COPPER	-	-	CORRODED	-	-	CORRODED	-	-	CORRODED
STEEL	-	-	DULL	-	-	DULL	-	-	DULL
ALUMINUM	-	-	BRIGHT	-	-	BRIGHT	-	-	BRIGHT
WT. LOSS (MG./SQ. CM.)									
COPPER	-	-	0.38	-	-	0.22	-	-	0.77
STEEL	-	-	0.09	-	-	0.03	-	-	0.01
ALUMINUM	-	-	+0.05	-	-	+0.05	-	-	0.02

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM TEST TUBE AT 20 AND AT 40 HOURS TEST TIME.
(2) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.
(3) THE MOLS OF OXYGEN FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.
(4) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 60

EFFECT OF ADDITIVE COMBINATIONS ON THE RATE OF OXYGEN ASSIMILATION AT 500°F

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500±5°F.; TEST TIME = 40 OR 60 HRS.; AIR RATE = 5 ±0.5 L./HR.; TEST FLUID CHARGE = 125 ML.; AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM. APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TUBE AT 20 AND 40 HOURS TEST TIME TO ALLOW THE DETERMINATION OF PROPERTIES AT THESE INTERVALS.

TEST FLUID (CONCENTRATIONS IN WT.%)	RATE OF OXYGEN ASSIMILATION (MOLS OXYGEN/426 GMS. OIL/HOUR)			
	0 TO 20 HOURS	20 TO 40 HOURS	40 TO 60 HOURS	0 TO 60 HOURS
A NEOPENTYL TYPE ESTER (MLO 7384) (WADC DESIGNATION MLO 57-424)				
+ 0.5 PHENOTHIAZINE	0.041	0.021	0.032	0.032
+ 0.5 5, 10, 10*	0.028	0.028	0.028(1)	0.028
+ 1.0 5, 10, 10* + 2.0 PAN**	0.021	0.020	0.017	0.019
+ 1.0 5, 10, 10* + 2.0 PRIMENE-81R	0.019	0.016	0.019	0.018
+ 1.0 PHENOTHIAZINE + 2.0 PRIMENE-81R	0.020	0.027	0.021(1)	0.022
+ 1.0 PHENOTHIAZINE + 2.0 PAN**	0.019	0.051	0.034(1)	0.034
A PENTAERYTHRITOL TYPE ESTER (MLO 7023) (SYNTHETICS J-7)				
+ 0.5 PHENOTHIAZINE	0.033	0.024	0.022	0.026
+ 1.0 5, 10, 10* + 2.0 PAN**	0.021	0.018	0.015	0.018
+ 1.0 PHENOTHIAZINE + 2.0 PAN**	0.020	0.023	0.016	0.020
+ 1.0 PHENOTHIAZINE + 2.0 PRIMENE-81R	0.017	0.019	0.018	0.018
A PENTAERYTHRITOL TYPE ESTER (MLO 7064) (HERCOFLEX 600)				
+ 0.5 PHENOTHIAZINE	0.039	0.022	0.031(1)	0.031
+ 0.5 5, 10, 10*	0.042	0.053(2)	-	-
+ 1.0 5, 10, 10* + 2.0 PAN**	0.031	0.025	0.010(1)	0.022
+ 1.0 PHENOTHIAZINE + 2.0 PRIMENE-81R	0.021	0.035	0.035(1)	0.030
DI-2-ETHYLHEXYL SEBACATE (MLO 7112)				
+ 0.5 PHENOTHIAZINE	0.043	0.043	-	-
+ 0.5 5, 10, 10*	0.083	0.065	-	-
+ 1.0 5, 10, 10* + 2.0 PAN**	0.035	0.042	-	-

* 5-ETHYL-10,10-DIPHENYLPHENAZASILINE.
** PHENYL-ALPHA-NAPHTHYLAMINE.
(1) AT THE END OF 60 HOURS TEST TIME, THE PRODUCT WAS A MIXTURE OF OXIDIZED FLUID AND SOLIDS WHICH COULD NOT BE SEPARATED WITHOUT DILUTION.
(2) AT THE END OF 40 HOURS TEST TIME, THE PRODUCT WAS A MIXTURE OF OXIDIZED FLUID AND SOLIDS WHICH COULD NOT BE SEPARATED WITHOUT DILUTION.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ±5°F ; TEST TIME = 40 HOURS; AIR RATE = 5 ±0.5 L./HR.; FLUID CHARGE = 125 ML.; AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM. APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST AT 20 HOURS TEST TIME TO ALLOW THE DETERMINATION OF PROPERTIES.

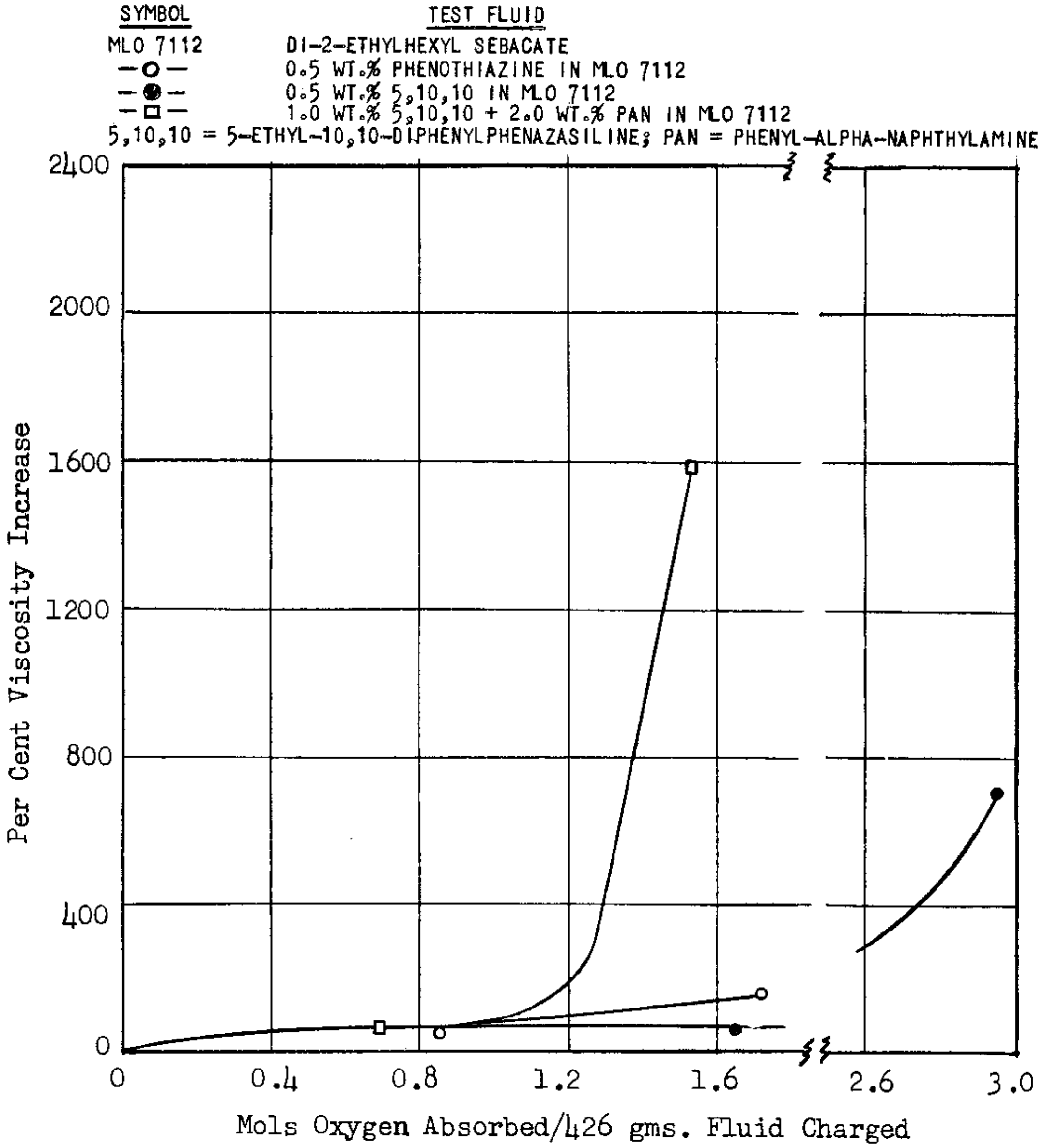


Figure 44. EFFECT OF ADDITIVE COMBINATIONS ON THE OXYGEN TOLERANCE OF DI-2-ETHYLHEXYL SEBACATE AT 500°F

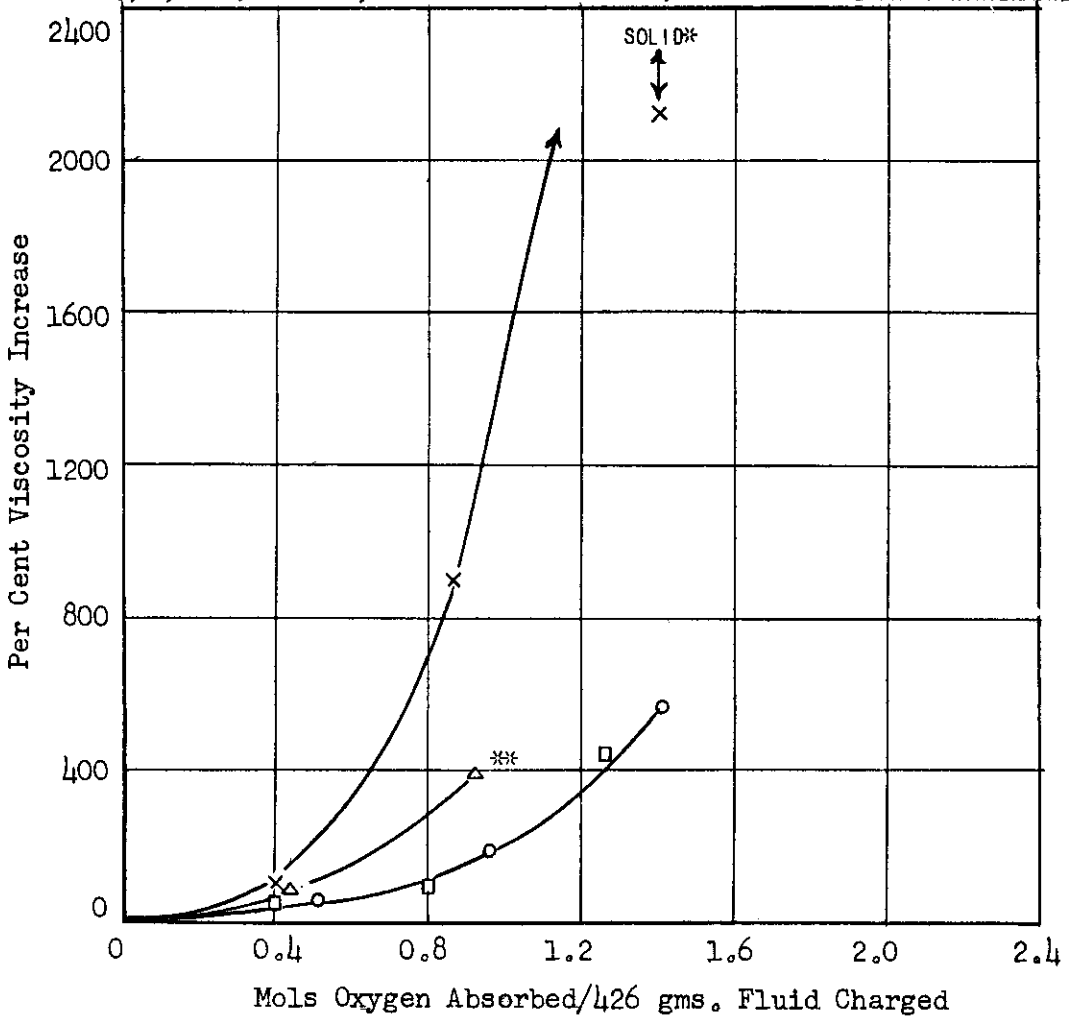
TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± °F ; TEST TIME = 60 HOURS; AIR RATE = 5 ±0.5 L./HR.; AND FLUID CHARGE = 125 MLS. APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST AT 20 AND 40 HOURS TEST TIME TO ALLOW THE DETERMINATIONS OF PROPERTIES AT THESE INTERVALS.

NOTE: THERE WERE NO CATALYST METALS PRESENT IN THESE TESTS.

SYMBOL	TEST FLUID
MLO 7064	HERCOFLEX 600
—O—	1.0 WT.% PHENOTHIAZINE IN MLO 7064
—□—	1.0 WT.% 5,10,10 + 2.0 WT.% PAN IN MLO 7064
—Δ—	1.0 WT.% PHENOTHIAZINE + 2.0 WT.% PRIMENE-81R IN MLO 7064
—X—	1.0 WT.% PHENOTHIAZINE + 2.0 WT.% PAN IN MLO 7064

5,10,10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE; PAN = PHENYL-ALPHA-NAPHTHYLAMINE



* PRODUCT WAS AN INTIMATE MIXTURE OF OXIDIZED FLUID AND SOLIDS WHICH COULD NOT BE SEPARATED WITHOUT DILUTION.

** TEST TERMINATED AT 40 HOURS BECAUSE OF PLUGGED AIR TUBE.

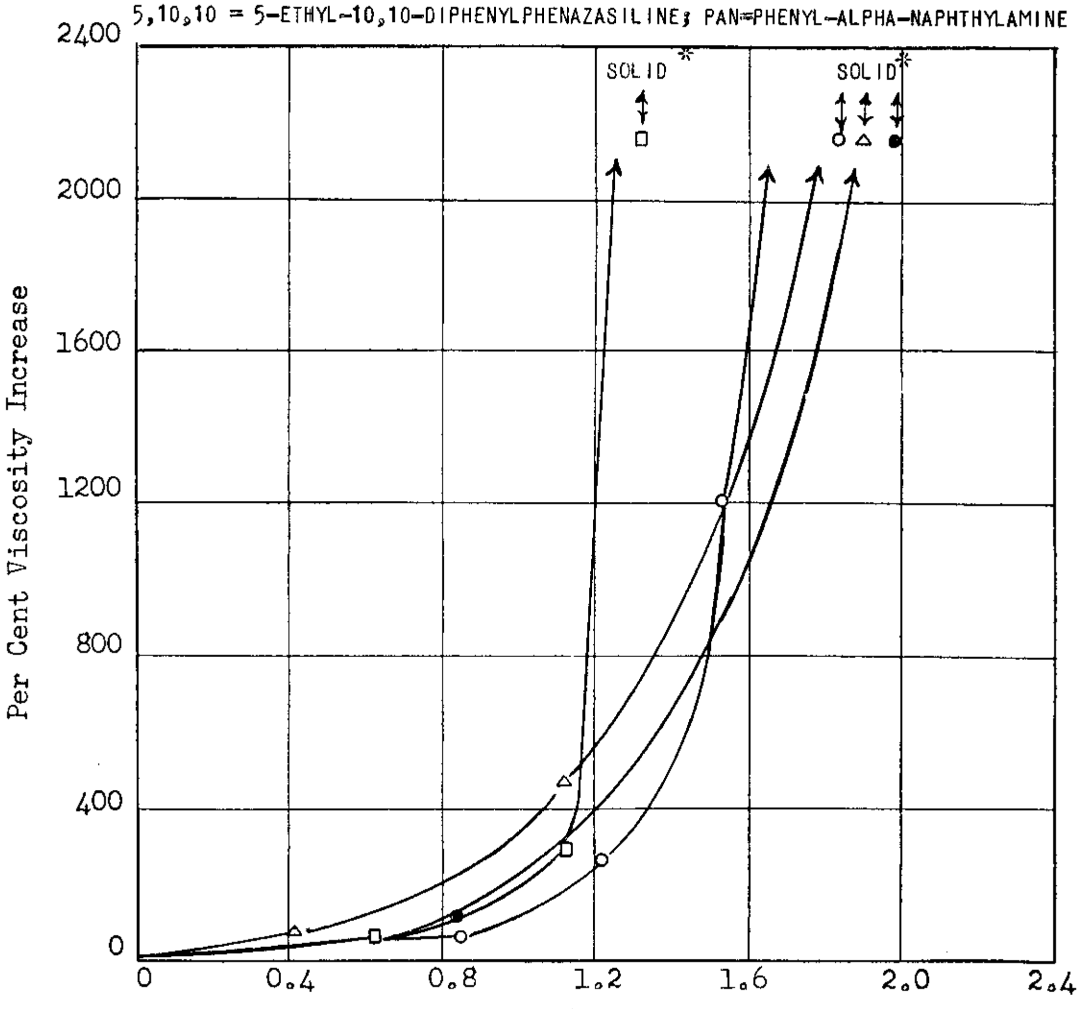
Figure 45. EFFECT OF ADDITIVE COMBINATIONS ON THE OXYGEN TOLERANCE OF HERCOFLEX 600 AT 500°F

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F ; TEST TIME = 60 HOURS; AIR RATE = 5± 0.5 L./HR.; FLUID CHARGE = 125 MLS.; AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM. APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST AT 20 AND AT 40 HOURS TEST TIME TO ALLOW THE DETERMINATION OF PROPERTIES AT THESE INTERVALS.

SYMBOL	TEST FLUID
MLO 7064	HERCOFLEX 600
—○—	0.5 WT.% PHENOTHIAZINE IN MLO 7064
—⊙—	0.5 WT.% 5,10,10 IN MLO 7064
—□—	1.0 WT.% 5,10,10 + 2.0 WT.% PAN IN MLO 7064
—△—	1.0 WT.% PHENOTHIAZINE + 2.0 WT.% PRIMENE-81R IN MLO 7064

5,10,10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE; PAN=PHENYL-ALPHA-NAPHTHYLAMINE



* Product was an intimate mixture of oxidized fluid and solids which could not be separated without dilution.

Figure 46. EFFECT OF ADDITIVE COMBINATIONS ON THE OXYGEN TOLERANCE OF HERCOFLEX AT 500°F

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500±5°F ; TEST TIME = 60 HOURS; AIR RATE = 5 + 0.5 L./HR.; AND FLUID CHARGE = 125 MLS. APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST AT 20 AND 40 HOURS TEST TIME TO ALLOW THE DETERMINATION OF PROPERTIES AT THESE INTERVALS.

NOTE: THERE WERE NO CATALYST METALS PRESENT IN THESE TESTS.

SYMBOL	TEST FLUID
MLO 7023	SYNTHETICS J-7
—○—	1.0 WT.% PHENOTHIAZINE IN MLO 7023
—□—	1.0 WT.% 5,10,10 + 2.0 WT.% PAN IN MLO 7023
—△—	1.0 WT. % PHENOTHIAZINE + 2.0 WT.% PRIMENE-81R IN MLO 7023
—×—	1.0 WT.% PHENOTHIAZINE + 2.0 WT% PAN IN MLO 7023

5,10,10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE; PAN = PHENYL-ALPHA-NAPHTHYLAMINE

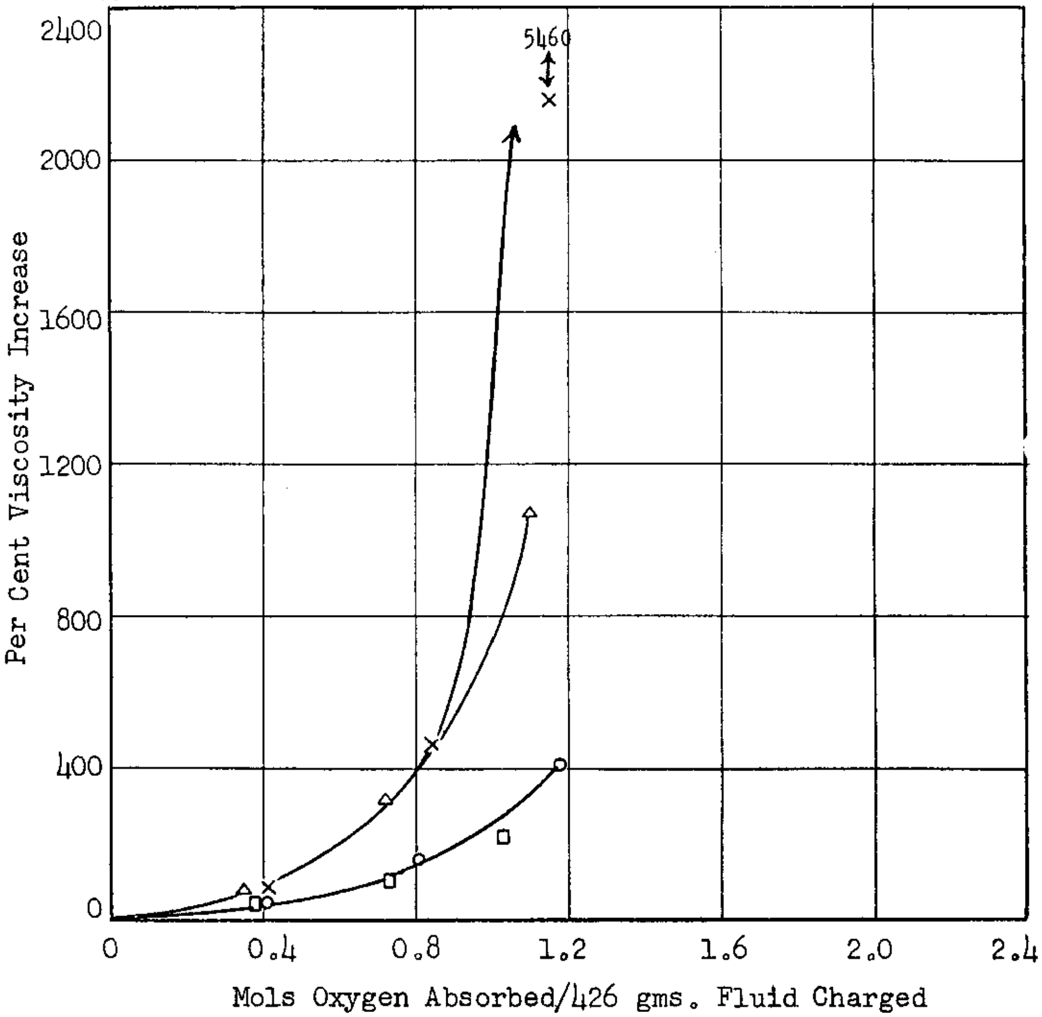


Figure 47. EFFECT OF ADDITIVE COMBINATIONS ON THE OXYGEN TOLERANCE OF SYNTHETICS J-7 AT 500°F

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F ; TEST TIME = 60 HOURS; AIR RATE = 5 ± 0.5 L./HR.; FLUID CHARGE = 125 ML.; AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM. APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST AT 20 AND AT 40 HOURS TEST TIME TO ALLOW THE DETERMINATION OF PROPERTIES AT THESE INTERVALS.

SYMBOL	TEST FLUID
MLO 7023	SYNTHETICS J-7
—○—	0.5 WT.% PHENOTHIAZINE IN MLO 7023
—□—	1.0 WT.% 5,10,10 + 2.0 WT.% PAN IN MLO 7023
—△—	1.0 WT.% PHENOTHIAZINE + 2.0 WT.% PRIMENE-81R IN MLO 7023
—X—	1.0 WT.% PHENOTHIAZINE + 2.0 WT.% PAN IN MLO 7023

5,10,10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE; PAN = PHENYL-ALPHA-NAPHTHYLAMINE

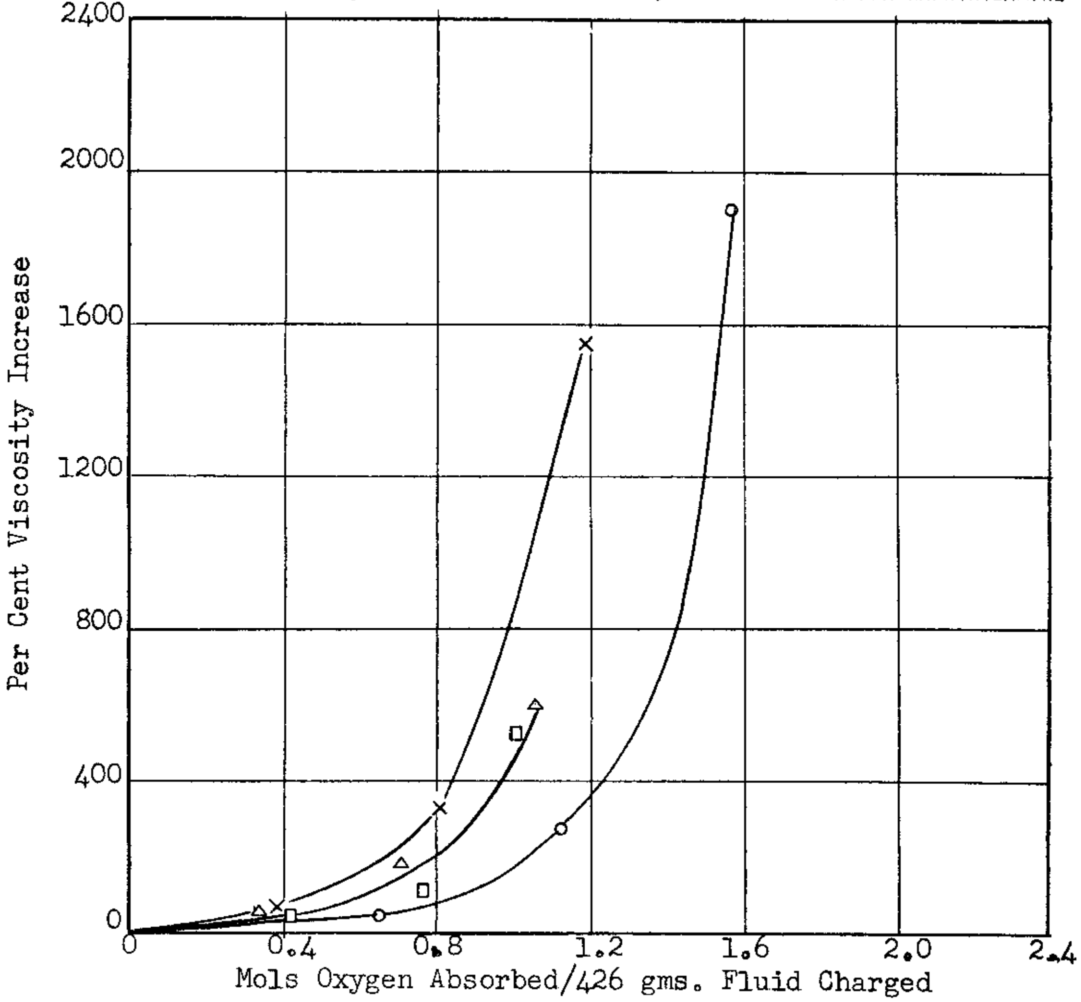


Figure 48. EFFECT OF ADDITIVE COMBINATIONS ON THE OXYGEN TOLERANCE OF SYNTHETICS J-7 AT 500°F

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ±5°F ; TEST TIME = 60 HOURS; AIR RATE = 5 ±0.5 L./HR.; FLUID CHARGE = 125 ML.; AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM. APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST AT 20 AND AT 40 HOURS TEST TIME TO ALLOW THE DETERMINATION OF PROPERTIES AT THESE INTERVALS.

SYMBOL	TEST FLUID
MLO 7384	A NEOPENTYL TYPE ESTER RECEIVED FROM WRIGHT AIR DEVELOPMENT CENTER (WADC DESIG. MLO 57-424)
—○—	0.5 WT.% PHENOTHIAZINE IN MLO 7384
—◐—	0.5 WT.% 5,10,10 IN MLO 7384
—□—	1.0 WT.% 5,10,10 + 2.0 WT.% PAN IN MLO 7384
—▽—	1.0 WT.% 5,10,10 + 2.0 WT.% PRIMENE-81R IN MLO 7384
—△—	1.0 WT.% PHENOTHIAZINE + 2.0 WT.% PRIMENE-81R IN MLO 7384
—X—	1.0 WT.% PHENOTHIAZINE + 2.0 WT.% PAN IN MLO 7384

5,10,10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE; PAN = PHENYL-ALPHA-NAPHTHYLAMINE

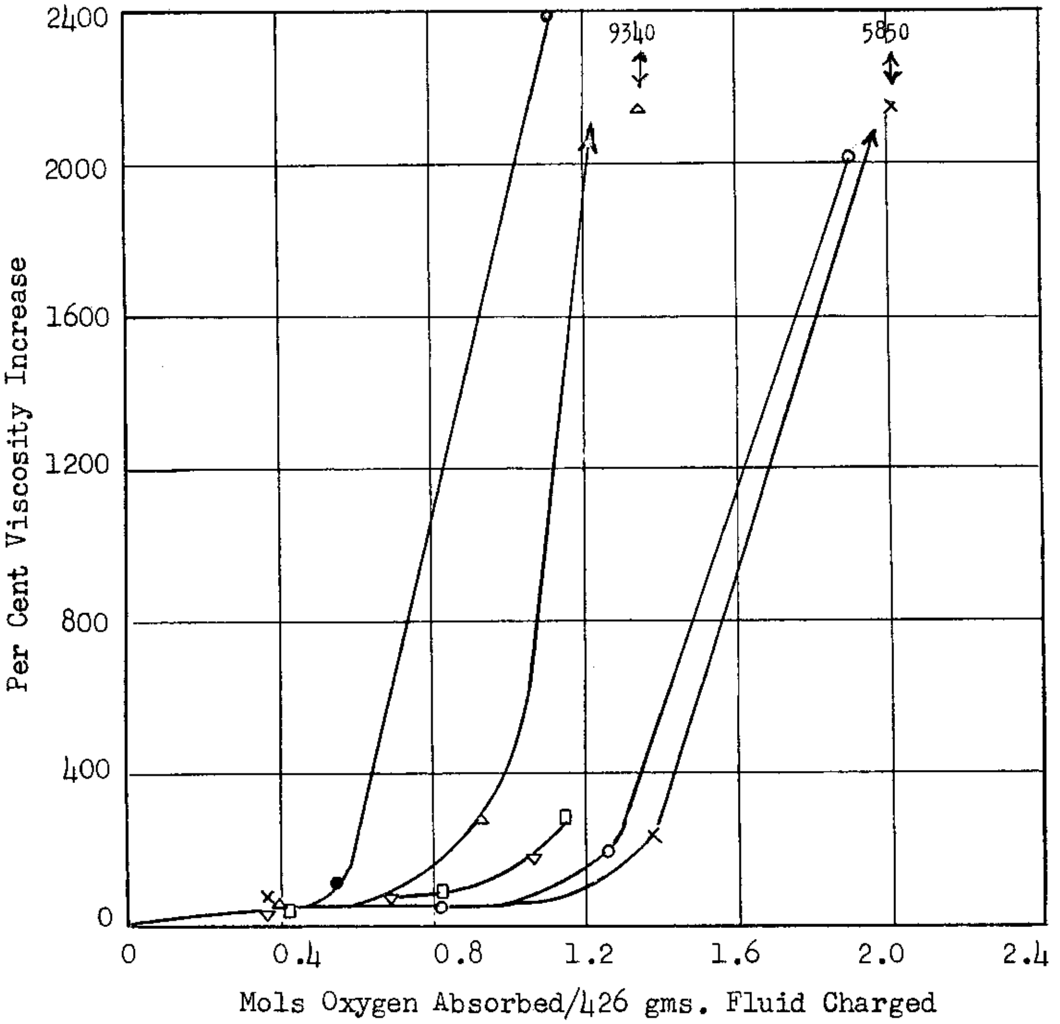


Figure 49. EFFECT OF ADDITIVE COMBINATION ON THE OXYGEN TOLERANCE OF A NEOPENTYL TYPE ESTER AT 500°F

TEST PROCEDURE AND TECHIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITION INCLUDE: TEST TEMPERATURE = 500 +5°F ; TEST TIME = 60 HOURS; AIR RATE = 5 +0.5 L./HR.; FLUID CHARGE = 125 ML.; AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM. APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST AT 20 AND AT 40 HOURS TEST TIME TO ALLOW THE DETERMINATION OF PROPERTIES AT THESE INTERVALS.

SYMBOL	TEST FLUID
MLO 7385	AN EXPERIMENTAL HIGH TEMPERATURE ESTER (WADC DESIG. MLO 58-88)
—○—	0.5 WT.% PHENOTHIAZINE IN MLO 7385
—●—	0.5 WT.% 5,10,10 IN MLO 7385
—□—	1.0 WT.% 5,10,10 + 2.0 PAN IN MLO 7385

5,10,10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE; PAN = PHENYL-ALPHA-NAPHTHYLAMINE

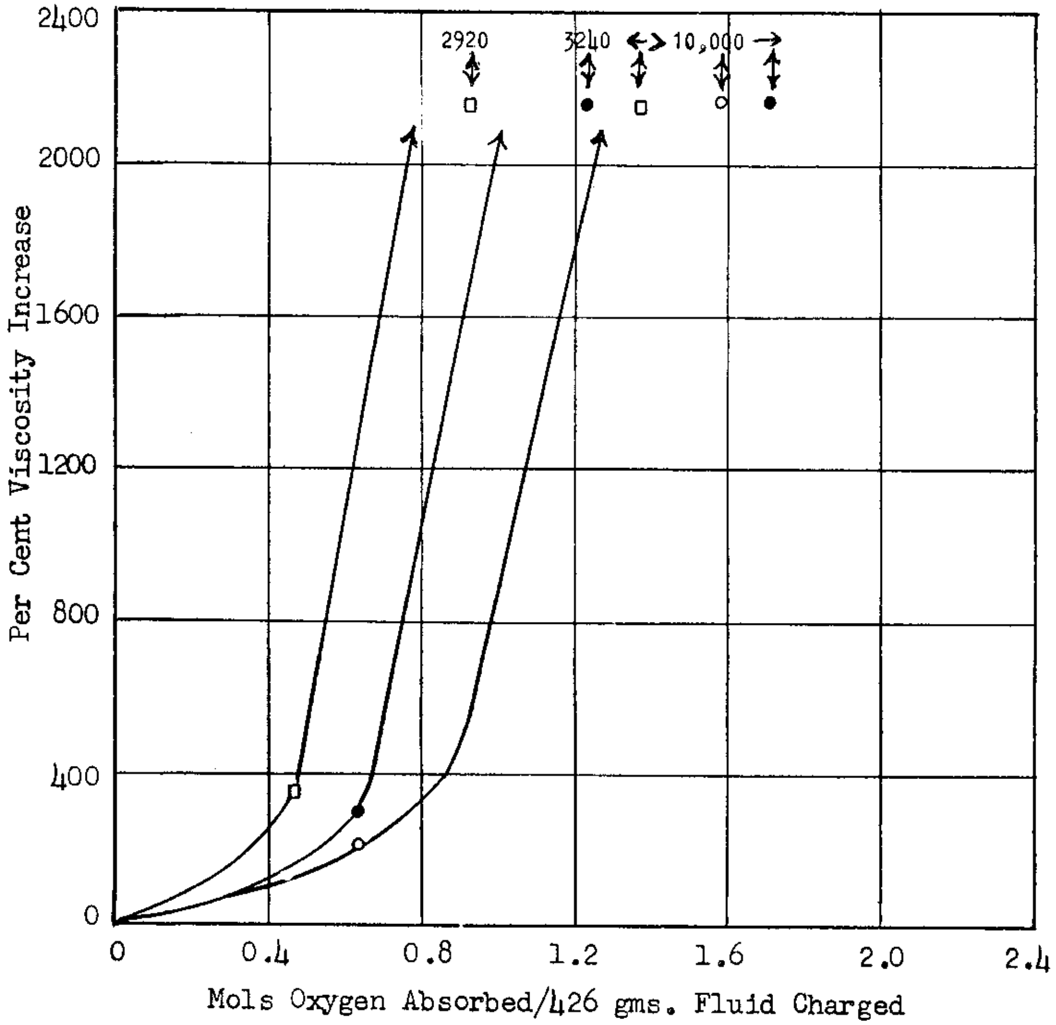


Table 50. EFFECT OF ADDITIVE COMBINATIONS ON THE OXYGEN TOLERANCE OF AN EXPERIMENTAL HIGH TEMPERATURE ESTER AT 500°F

The basic test tube for the 25 milliliter low volume tests is shown on Figure 52. The tube has an outside diameter of 22 millimeters, which will give a fluid height of about 120 millimeters for a 25 milliliter charge. This fluid height is approximately equal to the fluid height for 100 milliliters of test fluid in the 38 millimeter outside diameter tube. The air tube design is the same for both size tubes. The air bubble size is, therefore, basically the same for both the 100 and the 25 milliliter tests. In addition, the air travels in contact with the fluid for the same distance.

A number of mineral oils, hydrocarbons, and esters have been evaluated with several inhibitor types at 347°F to determine the equivalence of a Spec. MIL-L-7808 oxidation test with a small volume test. This equivlence must be established on the basis of equivalent stable life or equivalent deterioration in tests of the same time interval in which the stable life is exceeded.

It has been established that many esters and mineral oils with effective additives exceed the Spec. MIL-L-7808 oxidation test time (72 hours) in stable life by a factor of 2 to 10. Therefore, on the basis of a 72-hour test, substantial differences in test severity could fail to show up because of the stable life of the fluid. Spec. MIL-L-7808 type fluids in conventional and small volume tests at 347°F are compared on Table 61. A similar comparison for mineral oils is shown on Table 62. Two small volume tests are shown. In one case, the test fluid volume and the metal catalysts are reduced to one-quarter of those in the Spec. MIL-L-7808 tests. The air rate is the same for the conventional and the small volume test. In the second set of test conditions test fluid, metal catalysts, and air rate are all reduced to one-quarter of the Spec. MIL-L-7808 test values. In all cases, better agreement is obtained for the small volume test with 1.25 liters of air per hour and the Spec. MIL-L-7808 test than for the small volume test using 5.0 liters of air per hour.

A substantial amount of data are available at this Laboratory to indicate that a change in air rate from 5 to 10 liters per hour does not substantially change the oxidation rate after the stable life or the length of the stable life using Spec. MIL-L-7808 type oxidation test conditions at 347°F. These data have been discussed and presented in various technical reports and theses. A close evaluation of the data on Tables 61 and 62 indicates that, in the current small volume tests, the differences found due to air rate may be attributable primarily to additive volatility and the increased evaporation or entrainment of the additive from the base fluid. This is perhaps illustrated best by Paranox 441-inhibited di-2-ethylhexyl sebacate blends. Paranox 441 is much more volatile than the base stock and has previously shown volatility limitations as an oxidation inhibitor. The two small volume tests show the biggest differences in terms of oil deterioration and in relative volatility of the base stock and inhibitor.

On the basis of these tests, the small volume test chosen for use at 347°F includes the 22 millimeter o.d. test apparatus with the water cooled condenser, a fluid volume of 25 milliliters, a 0.5-inch square of metal sheet for each catalyst, 1.25 liters of air per hour, and the same general test procedures and techniques applied to the conventional 100 milliliter tests.

A comparison of small volume tests and 100 milliliter volume tests at 500°F. has also been made. As is the case for all 500°F. oxidation tests, quantitative measurements of the oxygen assimilated were made. Test results for phenothiazine-inhibited di-2-ethylhexyl sebacate and a hydrogenated polyolefin inhibited with phenyl-alpha-naphthylamine at 500°F. are shown on Tables 63 and 64, respectively. In each case, a range of air rates from 0.6 to 1.5 liters per hour are shown for the low volume test. In both cases, the closest comparison between the conventional 100 milliliter test and the small volume test occurs at about 0.7 liters of air per hour in the small volume test. Agreement is quite good between the oxygen assimilated and the property changes in both the conventional and small volume tests. Curves for property change as a function of oxygen assimilation are shown as Figures 53 and 54. Oxygen absorption as a function of air rate in the small volume tests is shown as Figure 55. These data show dependence of property change on oxygen assimilation.

A number of ester and hydrocarbon fluids have been evaluated with the small volume test for 20 hours at 500°F. These fluids are compared on Tables 65 and 66 with standard 100 milliliter tests of equivalent duration. These data show generally good agreement between the two tests in terms of oxygen assimilation and property changes.

These data indicate the equivalence of the small volume test and the standard 100 milliliter test at 500°F. These small volume tests determined on a quantitative basis will be run for time intervals in excess of 20 hours as well as the 20-hour test. Small volume tests of this type have been used in a subsequent portion of this section.

a. Small Volume Oxidation Tests With Neopentyl Esters. A total of 13 experimental esters obtained from the Food Machinery and Chemical Corporation are discussed in WADC Technical Report 55-30 Part VII. Small volume oxidation tests with these esters at 347° and at 500°F are shown on Tables 67 and 68, respectively. The tests at 347°F are stable life tests. These tests were sampled approximately every three days (72 hours) because of the limited sample size. The large volume stable life tests are generally sampled daily in the critical period of the stable life test. The stable life data on Table 67 may perhaps be clarified by example. The sample of PRL 3688 taken after 713 hours of oxidation still indicated that the fluid was within the induction period but the 766-hour sample indicated the fluid had broken. The stable life is indicated to be between 713 and 766 hours. In the case of PRL 3685, the fluid was still within the stable life after 904 hours. This test was discontinued because the fluid in the test had been depleted by the periodic sampling procedure. In general, these small volume tests adequately define the range of stable life values.

For this stable life comparison, a concentration of 0.5 weight per cent phenothiazine is used in all of the ester fluids. As reference points in discussing stable life, high quality dibasic acid esters, as typified by di-2-ethylhexyl sebacate, give stable life values in the range of 150 to 300 hours, while effective high quality neopentyl esters of tri- and tetra-functional alcohols and monobasic acids give comparable values of the order of 500 to 800 hours. Hercoflex 600 is an example of this latter group. Experimental fluids PRL 3693, PRL 3680, PRL 3681, PRL 3686, and PRL 3687 show stable life values below 72 hours. In all cases, fairly high dirtiness values are obtained and in three of the five cases incipient copper corrosion is noted. In all cases the initial neutralization number is high. All of these data suggest that for these five experimental ester samples, insufficient refining and purification of the ester products contributes to the low value for stable life.

The remaining eight experimental ester samples all show stable life values in the range of the high quality reference esters. The eight experimental esters are believed to encompass the range in compositions to include dibasic acid esters and esters of monobasic acids and di- and tri-functional alcohols. In all cases, the alcohols are believed to be of the neopentyl type. In addition to a satisfactory value for stable life, these experimental esters show good values for cleanliness and corrosion.

Values for a 20-hour small volume oxidation test at 500°F are shown on Table 68 for di-2-ethylhexyl sebacate, Hercoflex 600, and Synthetics J-7 as a basis of comparison for the experimental esters. The 500°F. oxidation values for the experimental esters, in most cases, fall into the expected range of property changes for high quality esters. At 500°F where stable life is too short to be a factor in oxidation and neutralization number buildup is relatively rapid, there is less difference between the behavior of the experimental esters than had been noted at 347°F.

Previous data indicated that these experimental esters exhibit good thermal stability in the range of that shown by high quality neopentyl esters previously evaluated. Preliminary oxidation data also indicate that these experimental esters are competitive with good high quality neopentyl type esters.

Several of the esters with indications of good low temperature fluidity have been used for low temperature viscosity measurements. These data are shown on Table 69. In addition to the measured low temperature viscosities, a column has been added to show the temperature at which a viscosity of 13,000 centistokes is reached. Three of these esters show a potential for -65°F operability in the turbo-jet engine. The PRL 3704 sample has been received recently and the low temperature viscosities have not yet been measured. The extrapolated values are based on cloud and pour values and a viscosity temperature curve paralleling fluid PRL 3688. Test fluids PRL 3688 and PRL 3704 are similar type esters believed to be dibasic acid esters of neopentyl alcohols. Test fluid PRL 3690 is believed to be an ester of a bi-functional neopentyl type alcohol and a monobasic acid.

These data, coupled with the data released by the Wright Air Development Division on the trimethylol propane esters of Celanese and Heyden-Newport, indicate that -65°F. esters of the neopentyl type can in fact be made from mono-, di-, and tri-functional alcohols. A comparison of these three ester types would appear to be particularly desirable in the Spec. MIL-L-9236 lubricant program.

H. OXIDATION STUDIES AT 400°F. Recent developments indicate that neopentyl esters with a well chosen additive package may satisfactorily meet the requirements of Spec. MIL-L-9236. Engine tests reported by the Propulsion Laboratory of the Wright Air Development Division indicate superior engine performance for the Spec. MIL-L-9236 ester formulations at engine "oil-in" temperatures of 400° and 425°F. Data reported in Section G of this report show that several additive combinations, comprising in each case an oxidation inhibitor combined with an amine (basic constituent), have been shown to be more effective than a single inhibitor in providing stable life at 347°F in both conventional and neopentyl esters. Oxidation behavior of the esters is altered at 500°F by the inhibitor combination but to a lesser degree than noted at 347°F.

At 500°F, the additive combinations in both conventional and neopentyl esters show only a small overall improvement in oxidative behavior over the single oxidation inhibitor. The slight overall improvement in oxidation results from a modest reduction in rate of oxidation at 500°F which is partially offset by a somewhat lower oxygen tolerance for the additive combination. The quantitative oxidation differences noted in these studies were not sufficient to preclude the use of conventional dibasic acid esters as Spec. MIL-L-9236 fluids nor were the quantitative oxidation properties at 500°F sufficiently different to predict adequately large differences in operating time in a turbo-jet engine. The increased stable life at 347°F for the additive combination in esters is more nearly of the order of magnitude required to explain the differences in esters noted in the engine tests.

A series of tests at 400°F. have been conducted with esters to determine the effectiveness of additives at this intermediate temperature. The relative effects from stable life and oxygen tolerance should be established. Data are available to show that esters and mineral oils, for example, differ in their response to additives to provide stable life and oxygen tolerance level.

A 50°F change in oxidation test temperature from 347° to 400°F has a very substantial effect on stable life. A typical relationship between stable life and test temperature is shown in Figure 43 for a good quality Spec. MIL-L-7808 type fluid. The stable life of the fluid is considered to be the point at which there is a rapid increase in neutralization number with test time. These data show a reduction in stable life from 150 hours at 347°F to about 25 hours at 400°F.

Stable life tests at 400°F for di-2-ethylhexyl sebacate blends are shown in Table 70 and Figure 56. The stable life with phenothiazine antioxidant fits the stable lifetime relationships shown in Figure 43. The oxygen assimilated during the stable life tests is shown on Figure 56. These data show that in the case of the phenothiazine-inhibited di-2-ethylhexyl sebacate, the increase in neutralization number results in an increase in rate

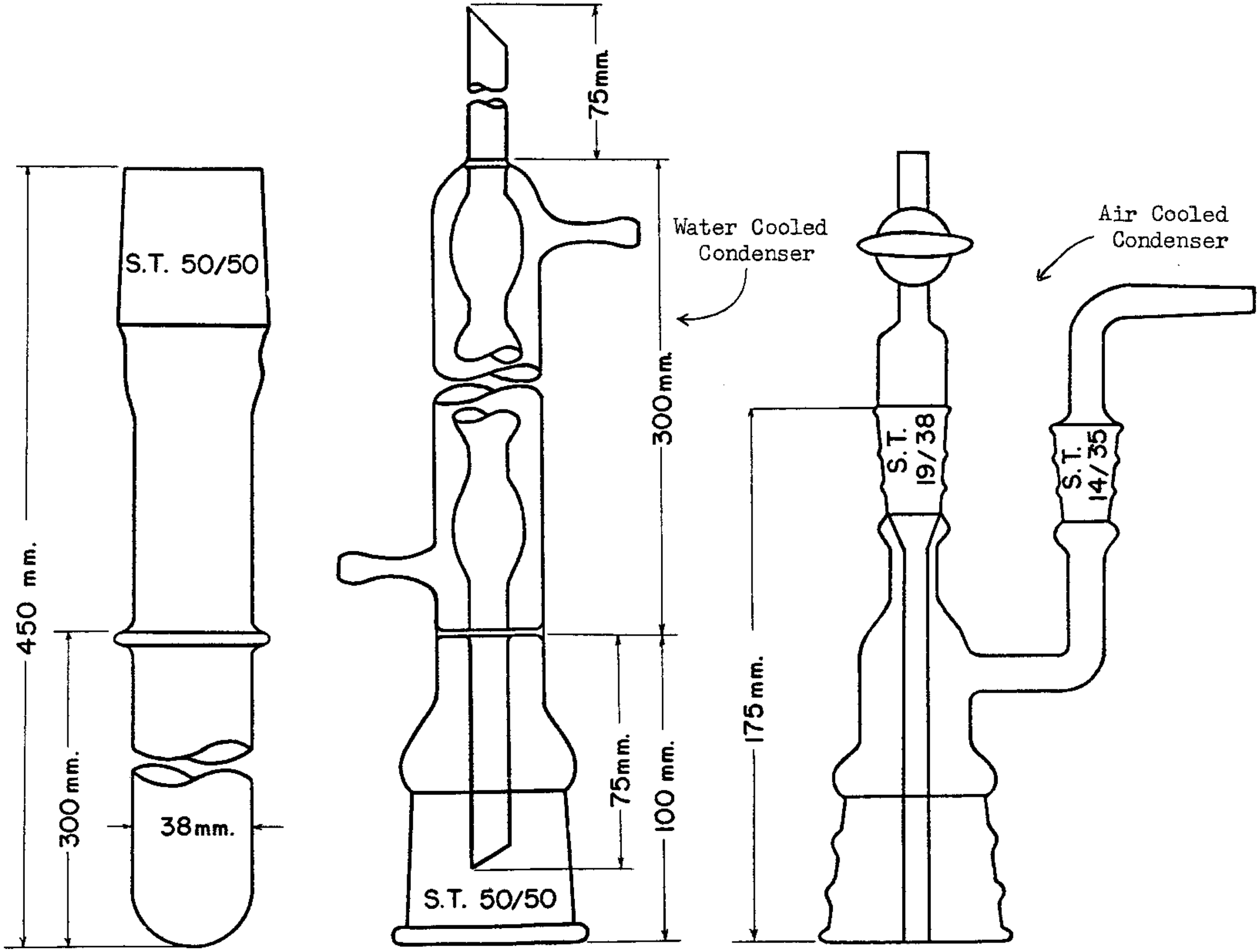


Table 51. TUBE AND CONDENSERS FOR SPEC. MIL-L-7808 TYPE OXIDATION TEST

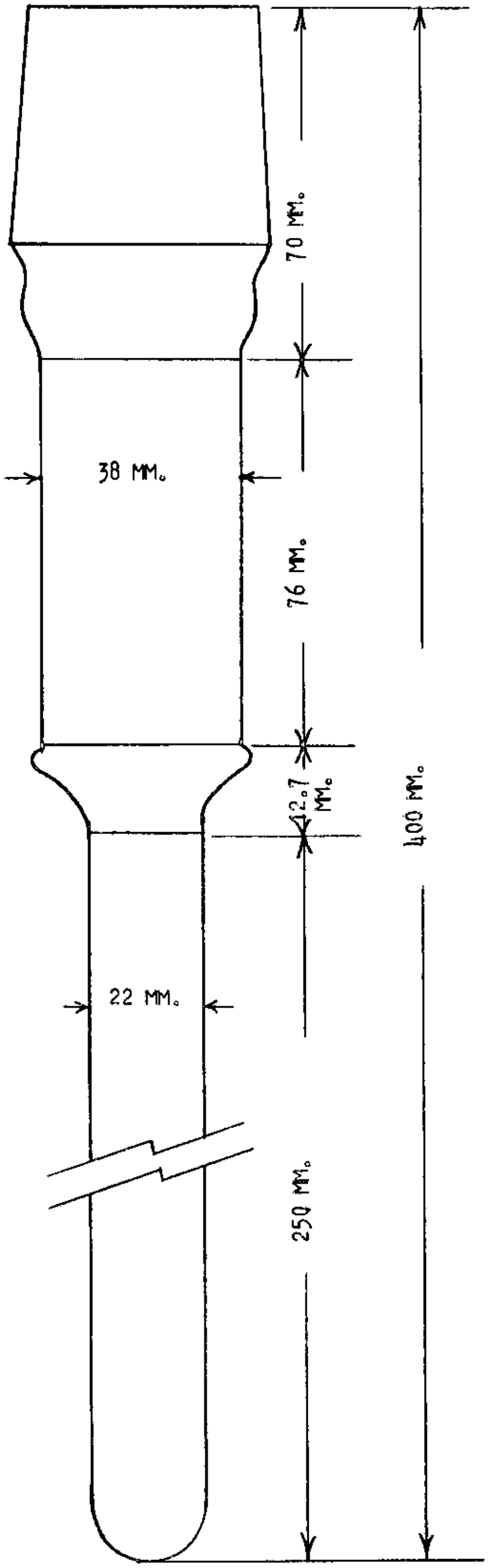


Figure 52. TUBE FOR SMALL VOLUME OXIDATION TEST

Table 61

A COMPARISON OF SMALL VOLUME AND STANDARD OXIDATION TEST PROCEDURES AT 347°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L- 7808.

TEST CONDITIONS INCLUDE: STANDARD TEST – TEST TEMPERATURE = 347 ± 3°F ; TEST FLUID CHARGE = 100 ML.; AIR RATE AND TEST TIME AS INDICATED; AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

SMALL VOLUME TEST – TEST TEMPERATURE = 347° ± 3°F ; TEST FLUID CHARGE = 25 ML.; AIR RATE AND TEST TIME AS INDICATED; AND CATALYST = A 0.5-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

TEST FLUID	<---- DI-2-ETHYLHEXYL SEBACATE (MLO 7112) ---------------->								SYNTHETIC OIL (MLO 7302)*		
OXIDATION INHIBITOR, WT.%	0.5 PHENOTHIAZINE		5.0 PARANOX 441				0.5 AGE RITE HIPAR		-		
TEST TYPE	STANDARD	SMALL VOLUME	STANDARD	SMALL VOLUME			STANDARD	SMALL VOLUME	STANDARD	SMALL VOLUME	
AIR RATE, L./HR.	5	5	5	5	5	1.25	5	5	5	5	1.25
TEST TIME, HRS.	260	335	113	67	48	94	260	192	112	67	118
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F.	+14	+2	+19	+93	+34	+23	+21	+13	+37	+104	+41
NEUT. NO. (MG. KOH/GM. OIL)											
ORIGINAL	0.1	0.1	0.3	0.3	0.3	0.3	0.1	0.1	0.0	0.0	0.0
FINAL	13.6	1.7	6.8	17.6	11.7	7.8	13.7	4.4	10.1	21.3	11.3
ASTM UNION COLOR											
ORIGINAL	1	1	2	2	2	2	4	4	1	1	1
FINAL	>8	>8	>8	>8	>8	>8	>8	>8	>8	>8	>8
WT.% OIL INSOLUBLE MATERIAL	0.3	TRACE	TRACE	5.8	TRACE	TRACE	0.2	TRACE	TRACE	0.1	TRACE
FINAL CATALYST CONDITION											
APPEARANCE											
COPPER	DULL	COATED	DULL	CORRODED	DULL	CORRODED	CORRODED	DULL	CORRODED	CORRODED	CORRODED
STEEL	DULL	COATED	DULL	DULL	COATED	DULL	DULL	DULL	DULL	DULL	DULL
ALUMINUM	DULL	COATED	BRIGHT	BRIGHT	DULL	DULL	DULL	BRIGHT	BRIGHT	DULL	BRIGHT
MAGNESIUM	BRIGHT	COATED	BRIGHT	CORRODED	BRIGHT	BRIGHT	DULL	BRIGHT	BRIGHT	BRIGHT	DULL
WT. LOSS (MG./SQ. CM.)											
COPPER	0.13	+0.88	0.16	8.59	0.19	2.31	0.53	0.09	0.29	4.25	0.81
STEEL	0.05	+0.11	+0.02	+0.06	+0.13	0.00	+0.05	0.13	0.00	+0.09	0.00
ALUMINUM	0.10	+0.12	+0.02	0.00	+0.09	0.19	+0.09	+0.03	+0.02	+0.06	0.00
MAGNESIUM	0.00	+1.34	-0.01	16.16	+0.06	0.19	0.12	+0.06	0.69	0.25	0.09

* A COMMERCIALLY PREPARED SYNTHETIC HIGH TEMPERATURE LUBRICANT FORMULATION.

Table 62

A COMPARISON OF SMALL VOLUME AND STANDARD OXIDATION TEST PROCEDURES AT 347°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: STANDARD TEST: TEST TEMPERATURE = 347 ± 3°F ; TEST FLUID CHARGE = 100 ML.; AIR RATE AND TEST TIME AS INDICATED; AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

SMALL VOLUME TEST: TEST TEMPERATURE = 347 ± 3°F ; TEST FLUID CHARGE = 25 ML.; AIR RATE AND TEST TIME AS INDICATED; AND CATALYST = A 0.5-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

OXIDATION INHIBITOR, WT.%	<------ 1.0 PHENYL-ALPHA-NAPHTHYLAMINE ------->				
TEST FLUID	A HYDROGENATED POLYOLEFIN (MLO 7124)		A NAPHTHENIC WHITE OIL (MLO 7273)		
TEST TYPE	STANDARD	SMALL VOLUME	STANDARD	SMALL VOLUME	
AIR RATE, L./HR.	5	5	5	5	1.25
TEST TIME, HRS.	283	286	168	113	165
STABLE LIFE, HRS. (1)	263	258	137	88	128
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F.	+7	+5	+41	+74	+23
NEUT. NO. (MG. KOH/GM. OIL)					
ORIGINAL	0.1	0.1	0.1	0.1	0.1
FINAL	3.4	3.4	2.3	3.3	2.1
ASTM UNION COLOR					
ORIGINAL	3	2	2	2	2
FINAL	>8	7	>8	8	8
WT.% OIL INSOLUBLE MATERIAL	0.3	2.2	0.1	0.1	0.2
FINAL CATALYST CONDITION					
APPEARANCE					
COPPER	DULL	DULL	DULL	BRIGHT	DULL
STEEL	DULL	DULL	DULL	DULL	DULL
ALUMINUM	DULL	DULL	DULL	BRIGHT	BRIGHT
MAGNESIUM	DULL	BRIGHT	DULL	BRIGHT	BRIGHT
WT. LOSS (MG./SQ. CM.)					
COPPER	0.15	0.06	0.01	+0.03	0.22
STEEL	0.06	+0.09	+0.03	0.03	+0.12
ALUMINUM	0.05	0.00	+0.02	0.00	+0.16
MAGNESIUM	0.02	0.13	+0.05	+0.03	0.00

(1) STABLE LIFE IS DEFINED AS THE POINT AT WHICH THERE IS A RAPID INCREASE IN NEUTRALIZATION NUMBER WITH TEST TIME.

Table 63

EFFECT OF AIR RATE ON SMALL VOLUME OXIDATION TESTS AT 500°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: STANDARD TEST: TEST TEMPERATURE = 500 ±5°F ; TEST TIME = 20 HOURS; AIR RATE = 5 ±0.5 L./HR.; TEST FLUID CHARGE = 100 MLS.; AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

SMALL VOLUME TEST: TEST TEMPERATURE = 500 ±5°F ; TEST TIME = 20 HOURS; AIR RATE AS INDICATED; TEST FLUID CHARGE = 25 MLS.; AND CATALYST=A 0.5 INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

TEST FLUID	0.5 WT.% PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE (MLO 7112)							
TEST TYPE	STANDARD	←---SMALL VOLUME---→						
AIR RATE, LITERS PER HOUR	5.0	1.5	1.25	0.8	0.7	0.7	0.6	0.6
LIQUID CHARGED, GM.	91	22	22	23	23	23	24	24
LIQUID LOSS, WT.%	7	13	9	13	0	2	9	0
APPROX. AMOUNT O_2 SUPPLIED, GMS.(1)	26.2	8.0	6.6	4.20	3.68	3.68	3.15	3.15
APPROX. AMOUNT O_2 USED, GMS.(1)	5.8	2.45	2.1	1.68	1.58	1.24	1.20	1.10
MOLS O_2 USED/426 GMS. FLUID (2)	0.86	1.48	1.27	0.97	0.91	0.75	0.68	0.62
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLE MATERIAL,(3) AT 100°F	+44	+290	+112	+54	+43	+39	+27	+26
NEUT. NO (MG. KOH/GM. OIL)								
ORIGINAL	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
FINAL	15.4	21.8	20.4	15.7	16.1	13.7	9.6	11.9
WT.% OIL INSOLUBLE MATERIAL(3)	0.1	1.3	0.9	0.4	0.7	0.3	0.1	0.7
FINAL CATALYST CONDITION								
APPEARANCE								
COPPER	DULL	DULL	CORRODED	DULL	DULL	DULL	DULL	DULL
STEEL	DULL	DULL	COATED	COATED	COATED	COATED	COATED	COATED
ALUMINUM	BRIGHT	DULL	DULL	DULL	BRIGHT	DULL	BRIGHT	DULL
WT. LOSS (MG./SQ. CM.)								
COPPER	0.10	+0.03	0.50	0.16	0.03	0.13	+0.06	0.00
STEEL	0.07	0.22	+0.91	+1.25	+2.06	+1.44	+2.28	+0.97
ALUMINUM	0.00	0.09	0.00	+0.06	+0.13	0.09	0.13	+0.16

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYLHEXYL SEBACATE IS 426.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 64

EFFECT OF AIR RATE ON SMALL VOLUME OXIDATION TESTS AT 500°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808

TEST CONDITIONS INCLUDE: STANDARD TEST: TEST TEMPERATURE = 500 ± 5°F ; TEST TIME = 20 HOURS; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGE = 100 MLS; AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL AND ALUMINUM.

SMALL VOLUME TEST: TEST TEMPERATURE = 500 ± 0.5°F ; TEST TIME = 20 HOURS; AIR RATE AS INDICATED; TEST FLUID CHARGE = 25 ML.; AND CATALYST = A 0.5-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM

TEST FLUID	1.0 WT.% PHENYL-ALPHA-NAPHTHYLAMINE IN A HYDROGENATED POLYOLEFIN (MLO 7124)									
TEST TYPE	STANDARD		<- - - - SMALL VOLUME - - - ->							
AIR RATE; LITERS PER HOUR	5.0		1.5	1.25	1.25	0.8	0.7	0.7	0.6	0.6
LIQUID CHARGED, GMS.	81	81	20	20	21	20	19	20	20	22
LIQUID LOSS, WT.%	9	10	10	0	7	8	0	0	10	9
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	26.2	26.2	8.0	6.6	6.6	4.20	3.68	3.68	3.15	3.15
APPROX. AMOUNT O_2 USED, GMS. (1)	5.0	4.3	1.90	2.10	2.10	1.70	1.70	1.64	0.94	1.35
MOLS O_2 USED/426 GMS. FLUID (2)	0.80	0.72	1.20	1.40	1.33	1.13	1.19	1.09	0.63	0.82
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLE MATERIAL,(3) AT 100°F	+1	+6	-12	+5	-3	+2.	-7	-6	-3	-7
NEUT. NO. (MG. KOH/GM. OIL)										
ORIGINAL	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
FINAL	2.0	2.3	4.2	5.0	3.8	3.3	2.8	2.9	1.9	2.0
WT.% OIL INSOLUBLE MATERIAL (3)	1.1	1.3	1.3	1.4	2.1	1.8	2.4	0.8	1.1	0.9
FINAL CATALYST CONDITION										
APPEARANCE										
COPPER	DULL	DULL	BRIGHT	BRIGHT	DULL	DULL	DULL	BRIGHT	COATED	DULL
STEEL	DULL	DULL	DULL	DULL	DULL	DULL	DULL	DULL	DULL	DULL
ALUMINUM	DULL	DULL	DULL	DULL	DULL	DULL	DULL	BRIGHT	DULL	DULL
WT. LOSS (MG./SQ. CM.)										
COPPER	+0.05	+0.07	0.00	+0.09	+0.03	0.06	0.03	+0.06	+0.13	+0.06
STEEL	+0.05	+0.06	0.06	0.03	+0.06	+0.03	+0.19	+0.09	+0.03	0.03
ALUMINUM	+0.07	+0.07	0.03	0.09	+0.03	+0.03	0.22	0.13	0.00	+0.06

(1) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF OXYGEN FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ±5°F ; TEST TIME = 20 HOURS; TEST FLUID CHARGE = 25 ML.; AND CATALYST = A 0.5-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

NOTE: DATA OBTAINED FROM A SERIES OF TESTS CONDUCTED AT AIR RATES OVER THE RANGE OF 0.6 TO 1.5 LITERS PER HOUR.

TEST FLUID: 0.5 WT.% PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE (MLO 7112)

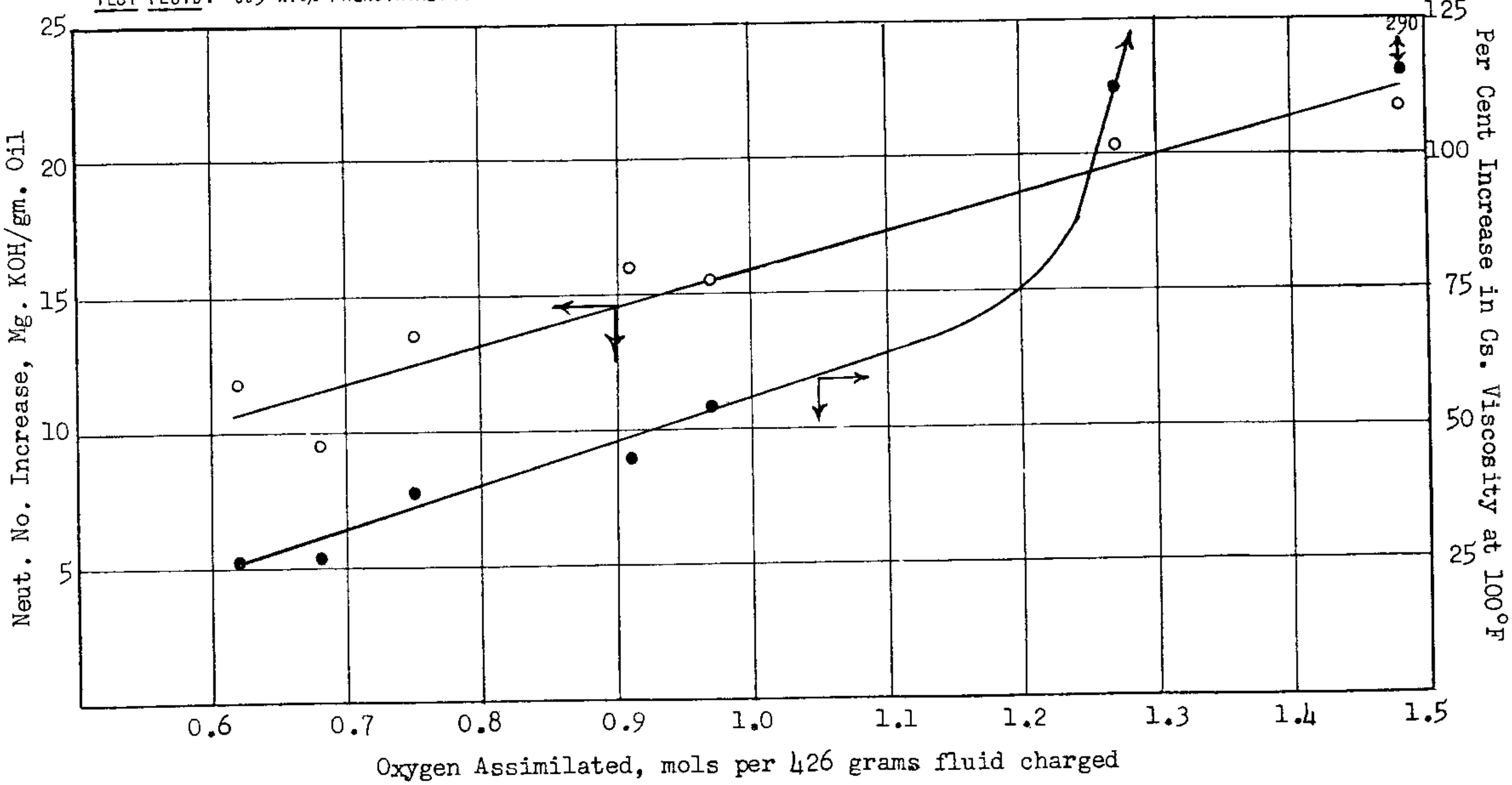


Figure 53. EFFECT OF OXYGEN ASSIMILATION ON PROPERTY CHANGE IN SMALL VOLUME OXIDATION TEST AT 500°F

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F ; TEST TIME = 20 HOURS; TEST FLUID CHARGE = 25 ML.; AND CATALYST = A 0.5-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

NOTE: DATA OBTAINED FROM A SERIES OF TESTS CONDUCTED AT AIR RATES OVER THE RANGE OF 0.6 TO 1.5 LITERS PER HOURS.

TEST FLUID = 1.0 WT.% PHENYL-ALPHA-NAPHTHYLAMINE IN A HYDROGENATED POLYOLEFIN (MLO 7124)

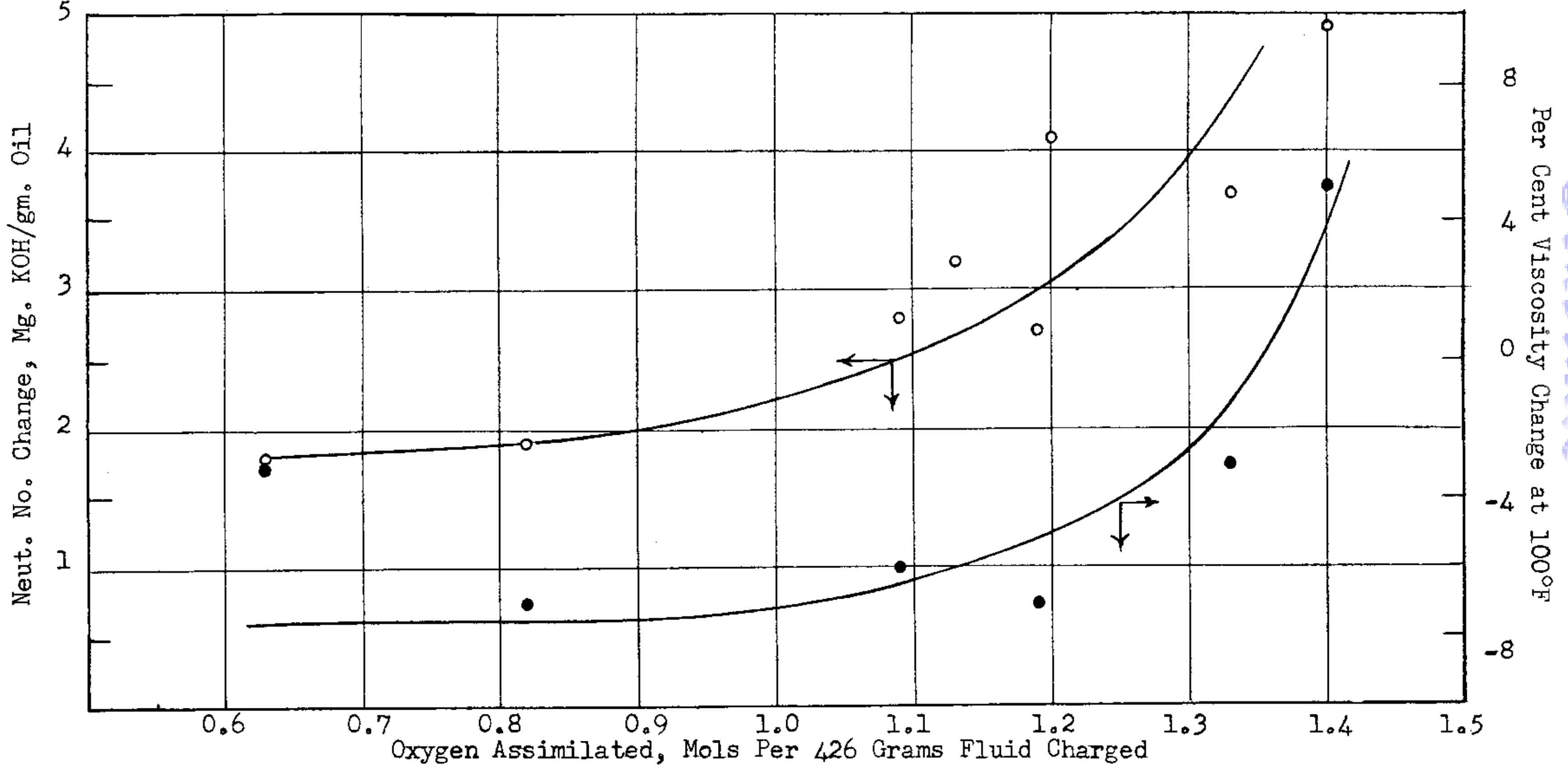


Figure 54. EFFECT OF OXYGEN ASSIMILATION ON PROPERTY CHANGE IN SMALL VOLUME OXIDATION TEST AT 500°F

TEST PROCEDURE AND TECHNIQUE IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F ; TEST TIME = 20 HOURS; AIR RATE AS INDICATED; TEST FLUID CHARGE = 25 ML.; AND CATALYST = A 0.5-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

SYMBOL	TEST FLUID
—○—	1.0 WT.% PHENYL-ALPHA-NAPHTHYLAMINE IN A HYDROGENATED POLYOLEFIN (MLO 7124)
—●—	0.5 WT.% PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE (MLO 7112)

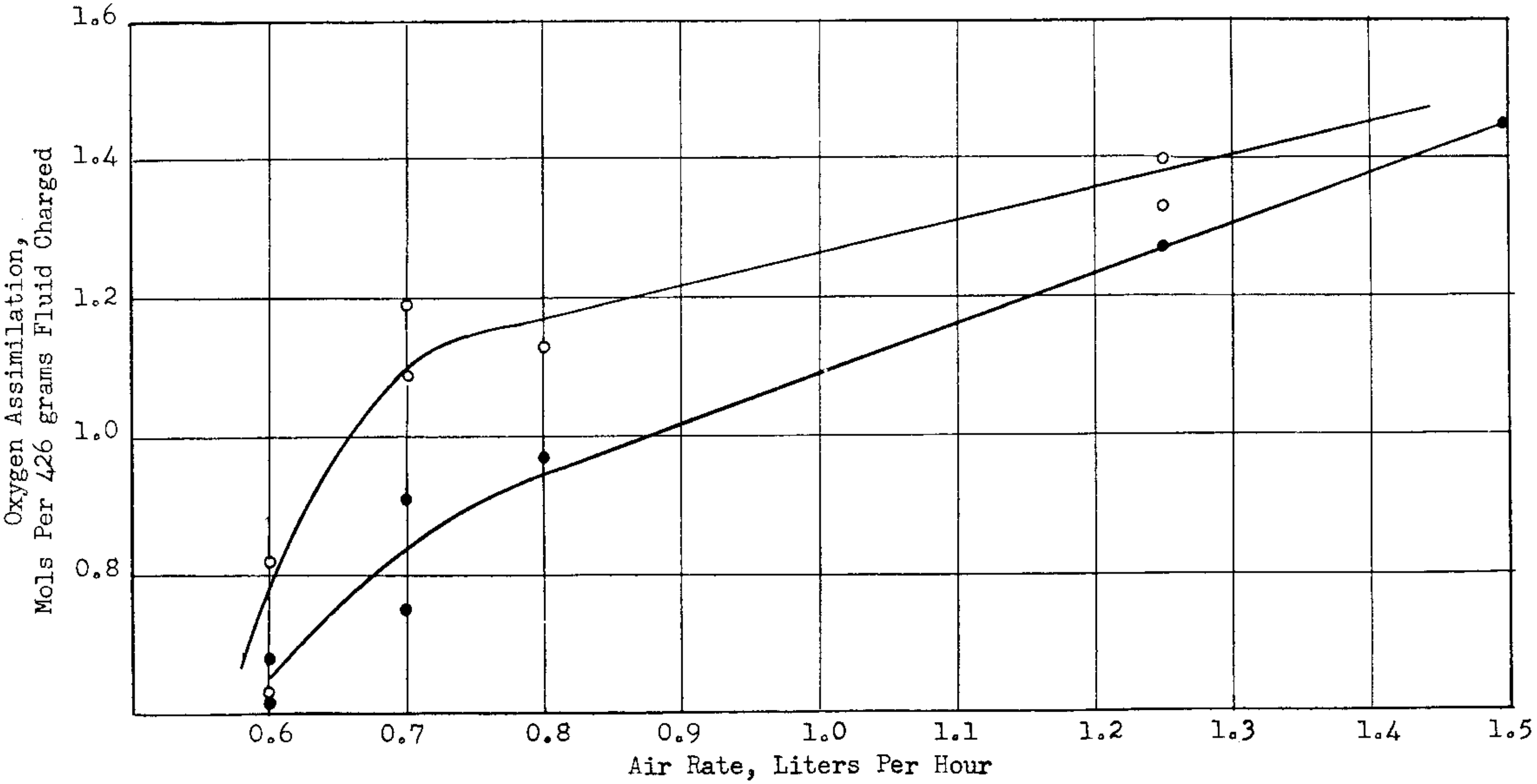


Figure 55. OXYGEN ASSIMILATION AT VARIOUS AIR RATES IN SMALL VOLUME OXIDATION TEST AT 500°F

Table 65

COMPARISON OF STANDARD AND SMALL VOLUME OXIDATION TESTS AT 500°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: STANDARD TEST: TEST TEMPERATURE = 500 ±5°F ; TEST TIME = 20 HOURS; AIR RATE = 5 ±0.5 L./HR.; TEST FLUID CHARGED = 100 ML.; AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

SMALL VOLUME TEST: TEST TEMPERATURE = 500 ±5°F.; TEST TIME 20 HOURS; AIR RATE = 0.7 ±0.1 L./HR.; TEST FLUID CHARGED = 25 ML.; AND CATALYST = A 0.5-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

OXIDATION INHIBITOR	<- - - - - - - - - -	- - - - - - - - - 0.5 WT.% PHENOTHIAZINE	- - - - - - - - -	- - - - - - - - -	- - - - - - - - -	- - - - - - - - - ->	
TEST FLUID	DI-2-ETHYLHEXYL SEBACATE (MLO 7112)			HERCOFLEX 600 (MLO 7064)		HERCULES SYN. J-7 (MLO 7023)	
TEST TYPE	STANDARD	SMALL VOLUME		STANDARD	SMALL VOLUME	STANDARD	SMALL VOLUME
LIQUID CHARGED, GMS.	91	23	23	98	24	98	24
LIQUID LOSS, WT.%	7	0	2	9	6	4	2
APPROX. AMOUNT O_2 SUPPLIED, GMS.(1)	26.2	3.68	3.68	26.2	3.68	26.2	3.68
APPROX. AMOUNT O_2 USED, GMS. (1)	5.8	1.58	1.24	5.6	1.20	4.7	0.75
MOLS O_2 USED/426 GMS. FLUID (2)	0.86	0.91	0.75	0.76	0.67	0.65	0.42
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLE MATERIAL,(3) AT 100°F.	+44	+43	+39	+66	+55	+51	+49
NEUT. NO (MG. KOH/GM. OIL)							
ORIGINAL	0.1	0.1	0.1	0.2	0.1	0.1	0.1
FINAL	15.4	15.7	16.1	3.7	5.2	13.5	3.6
WT.% OIL INSOLUBLE MATERIAL (3)	0.1	0.4	0.7	TRACE	TRACE	TRACE	TRACE
FINAL CATALYST CONDITION							
APPEARANCE							
COPPER	DULL	DULL	DULL	DULL	DULL	DULL	DULL
STEEL	DULL	COATED	COATED	DULL	DULL	COATED	DULL
ALUMINUM	BRIGHT	BRIGHT	DULL	DULL	DULL	DULL	DULL
WT. LOSS (MG./SQ. CM.)							
COPPER	0.10	0.03	0.13	0.06	0.00	0.12	0.00
STEEL	0.07	+2.06	+1.44	0.02	0.00	+0.57	0.00
ALUMINUM	0.00	+0.13	0.09	+0.01	0.03	+0.02	+0.03

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYLHEXYL SEBACATE IS 426.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING NAPHTHA AND DRIED BEFORE WEIGHING.

Table 66

COMPARISON OF STANDARD AND SMALL VOLUME OXIDATION TESTS AT 500°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE; STANDARD TEST: TEST TEMPERATURE = 500 ± 5°F ; TEST TIME = 20 HOURS; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGE = 100 ML.; AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

SMALL VOLUME TEST: TEST TEMPERATURE = 500 ± 5°F ; TEST TIME = 20 HOURS; AIR RATE = 0.7 ± 0.1 L./HR.; TEST FLUID CHARGE = 25 ML.; AND CATALYST = A 0.5-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

OXIDATION INHIBITOR	<- - - 1.0 WEIGHT PER CENT PHENYL-ALPHA-NAPHTHAMINE- - - - ->					
TEST FLUID	A HYDROGENATED POLYOLEFIN (MLO 7124)				A NAPHTHENIC WHITE OIL (MLO 7273)	
TEST TYPE	<- - STANDARD - ->		SMALL VOLUME		STANDARD	SMALL VOLUME
LIQUID CHARGED, GMS.	81	81	19	20	86	22
LIQUID LOSS, WT.%	9	10	0	0	0	2
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	26.2	26.2	3.68	3.68	26.2	3.68
APPROX. AMOUNT O_2 USED, GMS. (1)	5.0	4.3	1.70	1.64	4.0	0.73
MOLS O_2 USED/426 GMS. FLUID (2)	0.80	0.72	1.19	1.09	0.62	0.45
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	+1	+6	-7	-6	+70	+40
NEUT. NO. (MG. KOH/GM. OIL)						
ORIGINAL	0.1	0.1	0.1	0.1	0.0	0.1
FINAL	2.0	2.3	2.8	2.9	2.9	1.7
WT.% OIL INSOLUBLE MATERIAL (3)	1.1	1.3	2.4	0.8	0.2	0.1
FINAL CATALYST CONDITION						
APPEARANCE						
COPPER	DULL	DULL	DULL	BRIGHT	DULL	DULL
STEEL	DULL	DULL	DULL	DULL	DULL	DULL
ALUMINUM	DULL	DULL	DULL	BRIGHT	DULL	DULL
WT. LOSS (MG./SQ. CM.)						
COPPER	+0.05	+0.07	0.03	+0.06	0.02	0.00
STEEL	+0.05	+0.06	+0.19	+0.09	0.01	0.03
ALUMINUM	+0.07	+0.07	0.13	0.13	0.02	0.01

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2-ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 67

OXIDATION AND CORROSION CHARACTERISTICS OF SOME NEOPENTYL TYPE ESTERS AT 347°F

TESTS CONDUCTED IN SMALL VOLUME APPARATUS

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F ; TEST TIME AS INDICATED; AIR RATE = 1.25 ± 0.1 LITERS PER HOUR; TEST FLUID CHARGE = 25 MLS.; AND CATALYSTS = A 0.5-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

COMPARISON DATA: STABLE LIFE OF DI-2-ETHYLHEXYL SEBACATE = APPROXIMATELY 300 HOURS
STABLE LIFE OF HERCOFLEX 600 (PENTAERYTHRITOL TYPE ESTER) = 500 TO 700 HOURS

NOTE: ALL FLUIDS CONTAIN 0.5 WT. % PHENOTHIAZINE.
TEST FLUIDS OBTAINED FROM THE FOOD MACHINERY AND CHEMICAL CORPORATION

TEST FLUID								
PRL DESIGNATION	PRL 3685	PRL 3688	PRL 3684	PRL 3690	PRL 3682	PRL 3689	PRL 3695	PRL 3683
FMC DESIGNATION	111	112	110	114	108	113	115	109
TEST TIME, HOURS	904	766	503	476	306	355	239	167
STABLE LIFE, HOURS	>904	>713 <766	>425 <503	>401 <476	>257 <306	>239 <355	>186 <239	>118 <167
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+4	+48	+31	+82	+28	+94	+30	+20
NEUT. NO. (MG. KOH/GM. OIL)								
ORIGINAL	0.1	0.0	0.0	0.1	0.0	0.1	0.0	0.0
FINAL	2.5	16.3	4.5	9.2	5.2	20.4	9.1	5.5
ASTM UNION COLOR								
ORIGINAL	1	1	1	1	1	1	1	1
FINAL	7	>8	>8	>8	>8	>8	>8	>8
WT. % OIL INSOLUBLE MATERIAL	TRACE	TRACE	0.2	0.2	0.2	0.3	0.3	0.2
FINAL CATALYST CONDITION								
APPEARANCE								
COPPER	COATED	COATED	DULL	DULL	DULL	DULL	DULL	DULL
STEEL	COATED	COATED	DULL	COATED	COATED	COATED	DULL	DULL
ALUMINUM	COATED	COATED	DULL	COATED	DULL	COATED	DULL	DULL
MAGNESIUM	COATED	DULL	DULL	COATED	DULL	COATED	DULL	DULL
WT. LOSS (MG./SQ.CM.)								
COPPER	+0.59	+0.41	+0.25	0.02	+0.03	+0.28	0.18	+0.19
STEEL	+0.75	+0.56	+0.09	+0.20	+0.34	+0.59	+0.06	+0.22
ALUMINUM	+0.78	+0.53	+0.19	+0.15	+0.16	+0.59	+0.28	+0.28
MAGNESIUM	+0.78	+0.19	+0.44	+0.16	+0.28	+0.53	+0.03	+0.22

(CONCLUDED ON THE NEXT PAGE)

Table 67 (Concluded)

OXIDATION AND CORROSION CHARACTERISTICS OF SOME NEOPENTYL TYPE ESTERS AT 347°F

TESTS CONDUCTED IN SMALL VOLUME APPARATUS

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F ; TEST TIME AS INDICATED; AIR RATE = 1.25 ± 0.1 LITERS PER HOUR; TEST FLUID CHARGE = 25 MLS.; AND CATALYSTS = A 0.5 - INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

COMPARISON DATA: STABLE LIFE OF DI-2-ETHYLHEXYL SEBACATE = APPROXIMATELY 300 HOURS
STABLE LIFE OF HERCOFLEX 600 (PENTAERYTHRITOL TYPE ESTER) = 500 TO 700 HOURS

NOTE: ALL FLUIDS CONTAIN 0.5 WT. % PHENOTHIAZINE.
TEST FLUIDS OBTAINED FROM THE FOOD MACHINERY AND CHEMICAL CORPORATION

TEST FLUID					
PRL DESIGNATION	PRL 3693	PRL 3680	PRL 3681	PRL 3686	PRL 3687
FMC DESIGNATION	105	106	107	107B	107C
TEST TIME, HOURS	72	72	72	72	72
STABLE LIFE, HOURS	<72	<72	<72	<72	<72
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+19	+23	+27	+36	+30
NEUT. NO. (MG. KOH/GM. OIL)					
ORIGINAL	0.3	0.4	0.5	0.7	0.4
FINAL	5.9	7.8	5.3	6.9	7.6
ASTM UNION COLOR					
ORIGINAL	1	1	1	1	1
FINAL	>8	>8	>8	>8	>8
WT. % OIL INSOLUBLE MATERIAL	0.5	0.7	0.8	0.8	1.2
FINAL CATALYST CONDITION					
APPEARANCE					
COPPER	DULL	CORRODED	DULL	DULL	DULL
STEEL	DULL	DULL	DULL	DULL	DULL
ALUMINUM	DULL	DULL	DULL	DULL	DULL
MAGNESIUM	DULL	DULL	DULL	DULL	DULL
WT. LOSS (MG./SQ.CM.)					
COPPER	0.16	1.72	0.44	0.03	0.00
STEEL	0.00	+0.32	+0.09	+0.19	+0.31
ALUMINUM	+0.06	+0.03	+0.06	+0.19	+0.16
MAGNESIUM	+0.13	0.09	0.06	+0.28	+0.28

Table 68

OXIDATION AND CORROSION CHARACTERISTICS OF SOME NEOPENTYL ESTERS AT 500°F

TESTS CONDUCTED IN SMALL VOLUME APPARATUS

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F ; TEST TIME = 20 HOURS; AIR RATE = 0.7 ± 0.1 L./HR.; TEST FLUID CHARGE = 25 MLS.; AND CATALYSTS = A 0.5 - INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

TEST FLUIDS OBTAINED FROM THE FOOD MACHINERY AND CHEMICAL CORPORATION.

NOTE: ALL TEST FLUIDS CONTAIN 0.5 WT. % PHENOTHIAZINE.
TEST FLUIDS MLO 7112 = DI-2-ETHYLHEXYL SEBACATE; MLO 7064 = HERCOFLEX 600; MLO 7023 = SYNTHETICS J - 7

TEST FLUID: PRL DESIGNATION FMC DESIGNATION	MLO 7112 -	MLO 7064 -	MLO 7023 -	PRL 3681 107	PRL 3686 107B	PRL 3695 115	PRL 3687 107C
LIQUID CHARGED, GMS.	23	24	24	22	22	23	22
LIQUID LOSS, WT. %	2	6	2	7	0	0	2
APPROX. AMT. O_2 SUPPLIED, GMS.(1)	3.68	3.68	3.68	3.68	3.68	3.68	3.68
APPROX. AMT. O_2 USED, GMS.(1)	1.24	1.20	0.75	0.58	0.72	0.83	0.84
MOLS O_2 USED/426 GMS. FLUID(2)	0.75	0.67	0.42	0.35	0.47	0.48	0.51
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLE MATERIAL,(3) AT 100°F	+39	+55	+49	+47	+42	+26	+38
NEUT. NO. (MG. KOH/GM. OIL)							
ORIGINAL	0.1	0.1	0.1	0.5	0.7	0.0	0.4
FINAL	13.7	5.2	3.6	5.1	4.0	3.2	3.8
WT. % OIL INSOLUBLE MATERIAL	0.3	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE
FINAL CATALYST CONDITION							
APPEARANCE							
COPPER	DULL	DULL	DULL	DULL	DULL	DULL	DULL
STEEL	COATED	DULL	DULL	DULL	DULL	DULL	DULL
ALUMINUM	DULL	DULL	DULL	BRIGHT	BRIGHT	BRIGHT	BRIGHT
WT. LOSS (MG./SQ.CM.)							
COPPER	0.13	0.00	0.00	0.31	0.09	0.09	0.22
STEEL	+1.44	0.00	0.00	0.06	0.06	0.13	+0.03
ALUMINUM	0.09	0.03	+0.03	0.13	0.06	0.00	+0.06

(1) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF OXYGEN FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

(CONCLUDED ON NEXT PAGE)

Table 68 (Concluded)

OXIDATION AND CORROSION CHARACTERISTICS OF SOME NEOPENTYL ESTERS AT 500°F

TESTS CONDUCTED IN SMALL VOLUME APPARATUS

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F ; TEST TIME = 20 HOURS; AIR RATE = 0.7 ± 0.1 L./HR.; TEST FLUID CHARGE = 25 MLS.; AND CATALYSTS = A 0.5 - INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

TEST FLUIDS OBTAINED FROM THE FOOD MACHINERY AND CHEMICAL CORPORATION.
NOTE: ALL TEST FLUIDS CONTAIN 0.5 WT. % PHENOTHIAZINE.
TEST FLUIDS MLO 7112 = DI-2-ETHYLHEXYL SEBACATE; MLO 7064 = HERCOFLEX 600; MLO 7023 = SYNTHETICS J - 7

TEST FLUID: PRL DESIGNATION FMC DESIGNATION	PRL 3693 105	PRL 3680 106	PRL 3684 110	PRL 3689 113	PRL 3688 112	PRL 3683 109	PRL 3682 108	PRL 3685 111	PRL 3690 114
LIQUID CHARGED, GMS.	22	22	24	24	22	24	23	22	23
LIQUID LOSS, WT. %	9	2	6	2	9	6	2	0	2
APPROX. AMT. O_2 SUPPLIED, GMS.(1)	3.68	3.68	3.68	3.68	3.68	3.68	3.68	3.68	3.68
APPROX. AMT. O_2 USED, GMS.(1)	0.83	1.06	1.17	1.21	1.15	1.30	1.35	1.54	2.47
MOLS O_2 USED/ 426 GMS. FLUID(2)	0.52	0.64	0.65	0.67	0.70	0.72	0.78	0.93	1.43
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLE MATERIAL,(3) AT 100°F	+48	+58	+48	+34	+54	+52	+69	+41	+72
NEUT. NO. (MG. KOH/GM. OIL)									
ORIGINAL	0.3	0.4	0.0	0.1	0.0	0.0	0.0	0.1	0.1
FINAL	6.2	9.6	7.7	5.3	13.2	8.7	10.5	13.0	15.8
WT. % OIL INSOLUBLE MATERIAL	0.8	0.1	0.3	TRACE	0.4	0.2	0.7	0.2	0.2
FINAL CATALYST CONDITION									
APPEARANCE									
COPPER	DULL	DULL	DULL	DULL	DULL	CORRODED	DULL	DULL	DULL
STEEL	DULL	DULL	DULL	DULL	CORRODED	DULL	DULL	DULL	DULL
ALUMINUM	BRIGHT	BRIGHT	DULL	DULL	DULL	BRIGHT	BRIGHT	DULL	DULL
WT. LOSS (MG./SQ.CM.)									
COPPER	0.22	0.41	0.28	0.06	0.06	0.56	0.47	0.28	0.22
STEEL	0.06	0.03	+0.06	+0.03	0.56	0.03	0.25	0.34	+0.03
ALUMINUM	+0.09	0.00	0.03	+0.06	+0.03	+0.06	0.00	0.19	0.00

(1) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF OXYGEN FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 69

LOW TEMPERATURE PROPERTIES OF SOME NEOPENTYL TYPE ESTERS

FLUIDS RECEIVED FROM THE FOOD MACHINERY AND CHEMICAL CORPORATION

TEST FLUID		CENTISTOKE VISCOSITY AT				CLOUD POINT, °F	POUR POINT, °F	TEMP., °F AT WHICH FLUID ATTAINS 13,000 CS.
PRL DESIG.	FMC DESIG.	210°F	100°F	-40°F	-65°F			
PRL 3704	116	3.63	14.6	(2,600)	(13,000)	BELOW -75	BELOW -75	(-65)
PRL 3690	114	2.87	11.4	2,230	17,600	-60	BELOW -75	-62
PRL 3688	112	3.46	14.3	3,510	28,600	BELOW -75	BELOW -75	-57
PRL 3693	105	5.11	26.1	10,600	94,400	-74	-75	-43
PRL 3684	110	4.65	22.2	SOLID	-	-20	-50	-
PRL 3685	111	3.81	14.9	SOLID	-	-	+3*	-

* THIS FLUID WAS SUPERCOOLED TO -20°F ON WARMING, SOLIDS SEPARATED OUT AT +3°F

of oxidation. The combination of 5-10-10 and phenyl-alpha-naphthylamine (PAN) as an inhibitor for di-2-ethylhexyl sebacate shows a somewhat different behavior in the stable life tests. The neutralization number increases steadily but without a sharp break point. The oxygen assimilated during this stable life ranges from 2 to 5 per cent of the available oxygen. Oxygen assimilation values for the phenothiazine-inhibited di-2-ethylhexyl sebacate are of the order of 9 to 12 per cent following the break point in the stable life curve.

It would appear that the principal effect of the inhibitor combination in the ester base stock is to reduce the oxygen assimilation and thereby extend the so called stable life period. Preliminary quantitative oxygen assimilation data at 347°F show a small but measurable rate of oxygen assimilation during the induction period or stable life of the inhibited esters. In the case of the 400°F stable life test with 5-10-10 and PAN in di-2-ethylhexyl sebacate, the production of sludge is relatively high despite the relatively low rate of oxidation. This behavior appears to be consistent with the behavior at 500°F where a reduced oxidation rate but relatively poor oxygen tolerance values are noted.

Stable life tests at 400°F have been conducted with three neopentyl esters using phenothiazine and combinations of inhibitors. These data are presented on Table 71 and Figures 57, 58, 59, 60, and 61. The three neopentyl esters evaluated include a pentaerythritol ester Hercoflex 600 (MLO 7064), a dipentaerythritol ester Synthetics J-7 (MLO 7023), and a trimethylol propane ester (MLO 7384). In fluids MLO 7064 and MLO 7023, the effect of phenothiazine alone and a combination of 5-10-10 or phenothiazine with phenyl-alpha-naphthylamine are compared. In both esters the phenothiazine inhibitor is less effective in controlling neutralization number and oxygen assimilation than is the combination of inhibitors. The neutralization number exhibits a typical induction period for the neopentyl esters with the combination inhibitors. It is noteworthy that the oxygen assimilation rate does not follow the neutralization number curve for the case of the combination inhibitors. The oxygen assimilation rate remains low for the entire test period suggesting the continued effect of the additive combination on oxidation rate after the apparent induction period.

The effects of phenothiazine-PAN, and 5-10-10-PAN combinations are compared in the MLO 7023 neopentyl ester. The effects of these two oxidation inhibitor combinations, as shown on Table 71 and Figures 59 and 60, are essentially identical from the aspects of oxidation rate and property changes.

A comparison of the additive combination 5-10-10 and PAN in MLO 7023, MLO 7064 and MLO 7384 suggests the same overall effectiveness of the inhibitor combination and only very minor property differences due to the specific ester structure. In general, previous studies of ester oxidation have shown similarities for esters of similar structures. On this basis, oxygen tolerance at 500°F appears to be of the same order of magnitude for the neopentyl esters and the dibasic acid esters. At 347°F, the stable life values of the neopentyl esters appear to be somewhat longer than the comparable values for the dibasic acid esters. These preliminary stable life data at 400°F indicate that there may be differences between the dibasic acid esters and neopentyl esters evaluated similar to those noted at 347°F.

Three tests shown on Table 71 have been conducted at 400°F without metal catalysts. These tests show that oxidation does occur at about the same rate without metal catalysts. Property changes such as viscosity and sludge may be intensified by the presence of metal while in some cases neutralization number may be reduced by the presence of metal. It is important to note that the complete removal of metals would not drastically change the lubricant life picture in this 400°F temperature range.

1. <u>A 400°F Oxidation Test Procedure</u>. The preliminary 400°F stable life tests indicate significant trends in oxidation but do not show readily definable stable life values. For these reasons, comparative tests emphasizing property changes in a given time are preferred to stable life tests. A 168-hour test described in WADC TR 55-30 part VII has been used for this 400°F evaluation. The procedure is a modification of the Spec. MIL-L-7808 type oxidation tests used by this Laboratory. The test is conducted at a test temperature of 400°F and an air rate of five liters per hour in the presence of copper, steel, aluminum, and magnesium catalysts. A fluid charge of 125 milliliters is used. A 25-milliliter sample is taken after 72 and after 120 hours test time and the remaining 75 milliliters is used for the final property evaluations after 168 hours. Using this procedure, a single test yields data indicative of the extent of oxidation for three test times.

Tests of the extended 168-hour type at 400°F for di-2-ethylhexyl sebacate (MLO 7112) and a trimethylol propane ester (MLO 7427) are shown in Tables 72, 75, and 76. Each ester has been evaluated with phenothiazine alone and with combinations of phenothiazine or 5-10-10 with Primene 81R or PAN. In both esters, the phenothiazine-PAN and 5-10-10-PAN combinations appear to be about equal in effectiveness and superior to phenothiazine alone or phenothiazine and Primene 81R. A consistent problem in these 400°F. tests is the corrosion of magnesium. Magnesium corrosion problems have been noted in all ester oxidation studies conducted at temperatures in excess of 347°F.

The 400°F. oxidation tests have been repeated for esters MLO 7112 and MLO 7427 without magnesium. The results of these tests are shown in Tables 73 and 77. A comparison of the data show some indication that fluids showing excessive magnesium corrosion exhibit improved oxidation characteristics when the magnesium is removed from the system. In cases where only moderate magnesium corrosion was noted, the absence of magnesium did not materially improve the properties of the oxidized fluid. The properties affected by the presence of magnesium are viscosity change and sludge formation. The esters containing phenothiazine alone and combinations of phenothiazine and Primene 81R show a sensitivity to the presence of the magnesium.

The oxidation tests using steel, copper, and aluminum metal catalysts show the increased effectiveness of the additive combinations over phenothiazine alone in both ester base stocks. In the MLO 7112 ester, the additive combination acts primarily to lower sludge formation. The primary change noted in MLO 7427 ester for the combined inhibitors compared with phenothiazine is in the viscosity increase value.

One of the limitations of this extended oxidation test at 400°F is the lack of sludge values on the intermediate (72- and 120-hour) samples. Several of the samples shown on Tables 72 through 76 have been evaluated for sludge in the intermediate as well as the terminal sample. The sludge values from Table 73 plotted as a function of time indicate that several trends may be found. Several examples of three trends may be observed from these measurements which show (1) a steady rate of sludge formation throughout the test, (2) a low rate of sludge formation followed by a high rate of sluding (induction period curve), and (3) a high rate of sluding followed by a period of essentially no additional sludge formation. The fluids are well stirred during the oxidation which should result in a representative sample. However, sludges which coat the walls and metal specimens or those that settle rapidly are not adequately represented in the two preliminary samples.

Before a true picture of the sludging may be obtained, it will be necessary to run a series of cocurrent oxidation tests so that sludge values in all cases will be determined on the terminal samples. This additional testing is of increasing importance in view of the relatively small differences noted between ester types and additive combinations.

2. Effect of Dispersant Acryloid and Dialkyl Acid Phosphite Lubricity Additives on 400°F. Oxidation Tests. A dispersant Acryloid has been shown to be effective at 347° and 500°F in reducing the sludge in oxidation tests. The effects of a dispersant Acryloid on MLO 7112 and MLO 7427 containing various inhibitor combinations are shown on Tables 74 and 78, respectively. The comparisons with fluids not containing Acryloid are shown on Tables 73 and 77. Generally, the use of a dispersant Acryloid increases the copper corrosion value somewhat and decreases the sludge value. The viscosity change is significantly affected, resulting in a decrease or very little increase in all cases. The viscosity decrease is primarily a thermal effect. Data are presented in Table 79 illustrating the thermal effect on viscosity, neutralization number, metal corrosion, and sludge for a 168-hour test at 400°F under a nitrogen atmosphere. These data show a viscosity change pattern similar to that shown by the 400°F oxidation test on the same fluid composition.

The use of a dialkyl acid phosphite has proven beneficial in increasing load carrying ability of the ester fluids in gear testers. The dialkyl acid phosphites, in some cases, cause increased oxidative deterioration in ester fluids. This is particularly true of 500°F oxidation tests. The results on Tables 74 and 78 at 400°F in the presence of a dispersant Acryloid illustrate this adverse effect on fluid dirtiness by the dialkyl acid phosphite. It should be noted that one exception to the increased dirtiness trend in the presence of the dialkyl acid phosphite is the test results for the blend of MLO 7112 containing phenothiazine-Primene 81R-dispersant Acryloid and dialkyl acid phosphite. This composition, in fact, remained as clean in the 168-hour test as any of the MLO 7112 fluid formulations tested without the dialkyl acid phosphite.

As noted in Table 74, these results have been confirmed by a check determination. In addition, the MLO 7427 blend containing phenothiazine-Primene 81R-dispersant Acryloid and dialkyl acid phosphite shows evidence of low sludge values in the 72- and 120-hour samples. The sludge value after 168 hours is high indicating a rapid change in product character after an induction period in which only minor changes occurred. These data tend to confirm the 347° and 500°F data for various ester and additive combinations. That is, specific additive combinations may substantially alter the properties of the ester base stock.

Data for a second trimethylol propane ester are presented in Tables 80 and 81. These data compare directly with data for MLO 7427 trimethylol propane ester shown on Tables 75 and 78. A critical comparison of the two trimethylol propane esters indicates less dirtiness but more viscosity increase for MLO 7384 than for MLO 7427. The incremental improvement of the additive combinations over phenothiazine alone appears to be somewhat less for the MLO 7384 than for MLO 7427. The effect of dispersant Acryloid in reducing sludge in finished formulations is greater in MLO 7384 than in MLO 7427.

Data at 400°F with various additives in a dipentaerythritol ester MLO 7023 are shown in Table 82. These data indicate a similarity in oxidative behavior for MLO 7023 and the two trimethylol propane esters. There is more indication of viscosity increase and less sludge noted for the neopentyl esters prepared from monobasic acids than have been found in the dibasic acid esters.

3. Small Volume 400°F. Oxidation Tests. In several cases, the quantities of experimental esters were insufficient to conduct 400°F oxidation tests with a number of additives. The small volume test described in Section G-1 of this report for use at 347° and 500°F has been tailored to fit the severity of tests at 400°F. The small volume test uses a small tube to duplicate the fluid height for 25 milliliters charge in the small volume test with 100 milliliters of fluid in the conventional 347° or 500°F test. On this basis, an air rate of 1.25 liters per hour is used in the small volume test along with a one-half-inch square each of steel, copper, and aluminum metal catalysts. Data comparing the conventional and small volume tests at 400°F are shown on Table 83. Comparisons are shown between conventional and small volume tests which indicate that, in general, the small volume tests are somewhat more severe than the larger volume tests. However, good general agreement is indicated. The correlations between tests with and without magnesium is also good.

I. PANEL COKER STUDIES. The development of the controlled atmosphere panel coker is described in WADC TR 55-30 part V. The use of the controlled atmosphere panel coker substantially enhances the value of the panel coker to predict high temperature dirtiness for a wide variety of fluid types. Techniques for quantitatively measuring the oxygen assimilated in the controlled atmosphere panel coker are described in WADC TR 55-30 part VII. The quantitative evaluation of oxygen assimilation provides some insight into the mechanism of oxidation on or in the vicinity of hot metal surfaces.

Table 70

OXIDATION STABILITY OF SOME ESTERS AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 100 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

ADDITIVE DESIGNATIONS:
PTZ = PHENOTHIAZINE
5-10-10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE

TEST FLUID	DI-2-ETHYLHEXYL SEBACATE (MLO 7112)		TRIMETHYLOL PROPANE ESTER (MLO 7384)
OXIDATION INHIBITOR, WT. %	0.5 PTZ	1.0 5-10-10 + 2.0 PAN	1.0 5-10-10 + 2.0 PAN
TEST TIME, HRS.	48	162	185
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+19	+16	+85
NEUT. NO. (MG. KOH/GM. OIL)			
ORIGINAL	0.1	0.1	0.3
FINAL	14.2	7.1	6.0
ASTM UNION COLOR			
ORIGINAL	2	3-1/2	2
FINAL	>8	>8	>8
WT. % OIL INSOLUBLE MATERIAL	1.0	6.3	1.3
FINAL CATALYST CONDITION			
APPEARANCE			
COPPER	CORRODED	CORRODED	CORRODED
STEEL	DULL	COATED	DULL
ALUMINUM	COATED	COATED	BRIGHT
MAGNESIUM	DULL	CORRODED	CORRODED
WT. LOSS (MG./SQ. CM.)			
COPPER	0.32	0.45	0.39
STEEL	0.05	0.15	0.02
ALUMINUM	+0.12	0.16	+0.02
MAGNESIUM	0.09	19.17	13.87

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

OXYGEN ABSORBED: AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

TEST FLUIDS: ○ AND ● = DI-2-ETHYLHEXYL SEBACATE (MLO 7112) + 0.5 WT.% PHENOTHIAZINE.
△ AND ▲ = DI-2-ETHYLHEXYL SEBACATE (MLO 7112) + 1.0 WT.% 5-10-10 + 2.0 WT.% PHENYL-ALPHA-NAPHTHYLAMINE.

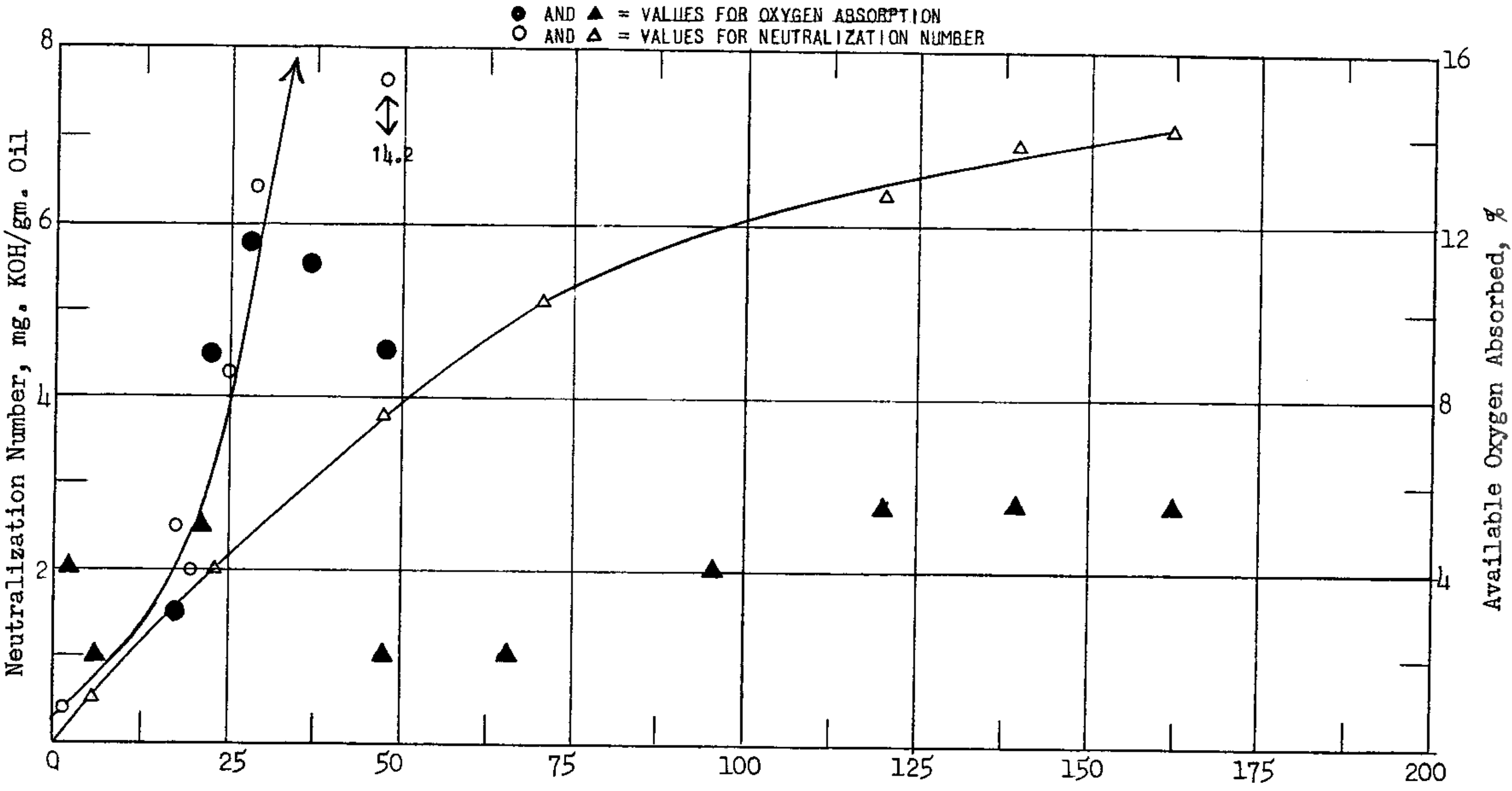


Figure 56. OXIDATION STABILITY AS A FUNCTION OF TEST TIME AT 400°F

Table 71

OXIDATION STABILITY OF SOME ESTERS AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400° ± 4°F ; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 100 ML.; AND CATALYSTS, WHERE INDICATED = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

ADDITIVE DESIGNATIONS:
PTZ = PHENOTHIAZINE
5-10-10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE

TEST FLUID	<- - - - - - A DIPENTAERYTHRITOL ESTER (MLO 7023) - - - - - >					<-A PENTAERYTHRITOL ESTER (MLO 7064)->		
OXIDATION INHIBITOR, WT. %	<- 0.5 PTZ ->		1.0 PTZ + 2.0 PAN		1.0 5-10-10 + 2.0 PAN	<- 0.5 PTZ ->		1.0 5-10-10 + 2.0 PAN
TEST TIME, HOURS	95	214	357	386	408	95	162	408
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+55	+226	+123	+395	+321	+78	+194	+313
NEUT. NO. (MG. KOH/GM. OIL)								
ORIGINAL	0.1	0.1	0.0	0.0	0.2	0.1	0.1	0.3
FINAL	12.7	5.0	5.1	5.6	4.9	14.5	11.3	8.1
ASTM UNION COLOR								
ORIGINAL	2	2	3-1/2	3-1/2	3-1/2	2	2	3-1/2
FINAL	>8	>8	>8	>8	>8	>8	>8	>8
WT. % OIL INSOLUBLE MATERIAL	0.2	0.6	0.1	1.0	0.4	0.1	0.5	3.0
FINAL CATALYST CONDITION								
APPEARANCE								
COPPER	-	CORRODED	-	CORRODED	CORRODED	-	CORRODED	CORRODED
STEEL	-	DULL	-	COATED	DULL	-	DULL	DULL
ALUMINUM	-	DULL	-	COATED	BRIGHT	-	COATED	BRIGHT
MAGNESIUM	-	DULL	-	COATED	BRIGHT	-	CORRODED	CORRODED
WT. LOSS (MG./SQ. CM.)								
COPPER	-	3.81	-	0.60	0.63	-	11.18	1.50
STEEL	-	0.05	-	+0.44	+0.03	-	+0.02	0.05
ALUMINUM	-	+0.03	-	+0.52	0.03	-	+0.10	+0.04
MAGNESIUM	-	+0.01	-	+0.61	0.01	-	0.32	10.02

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

OXYGEN ABSORBED: AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

TEST FLUID: ○ AND ● = A PENTAERYTHRITOL ESTER (MLO 7064) + 0.5 WT.% PHENOTHIAZINE
△ AND ▲ = A PENTAERYTHRITOL ESTER (MLO 7064) + 1.0 WT.% 5-10-10 + 2.0 PHENYL-ALPHA-NAPHYLAMINE
○ AND △ = VALUES FOR NEUTRALIZATION NUMBER
● AND ▲ = VALUES FOR OXYGEN ABSORPTION

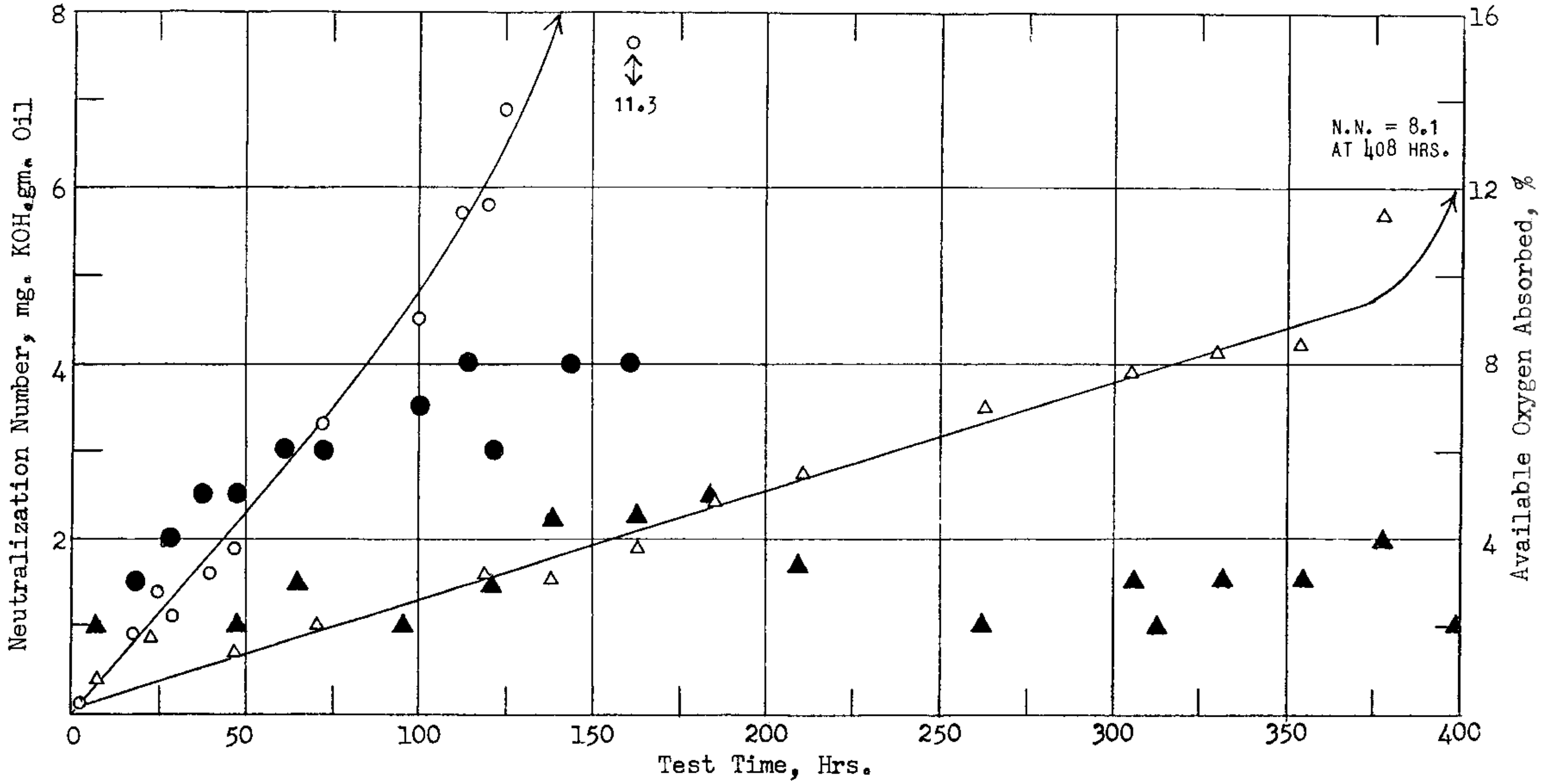


Figure 57. OXIDATION STABILITY AS A FUNCTION OF TEST TIME AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

OXYGEN ABSORBED: AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

TEST FLUID: A DIPENTAERYTHRITOL ESTER (MLO 7023) + 0.5 WT.% PHENOTHIAZINE

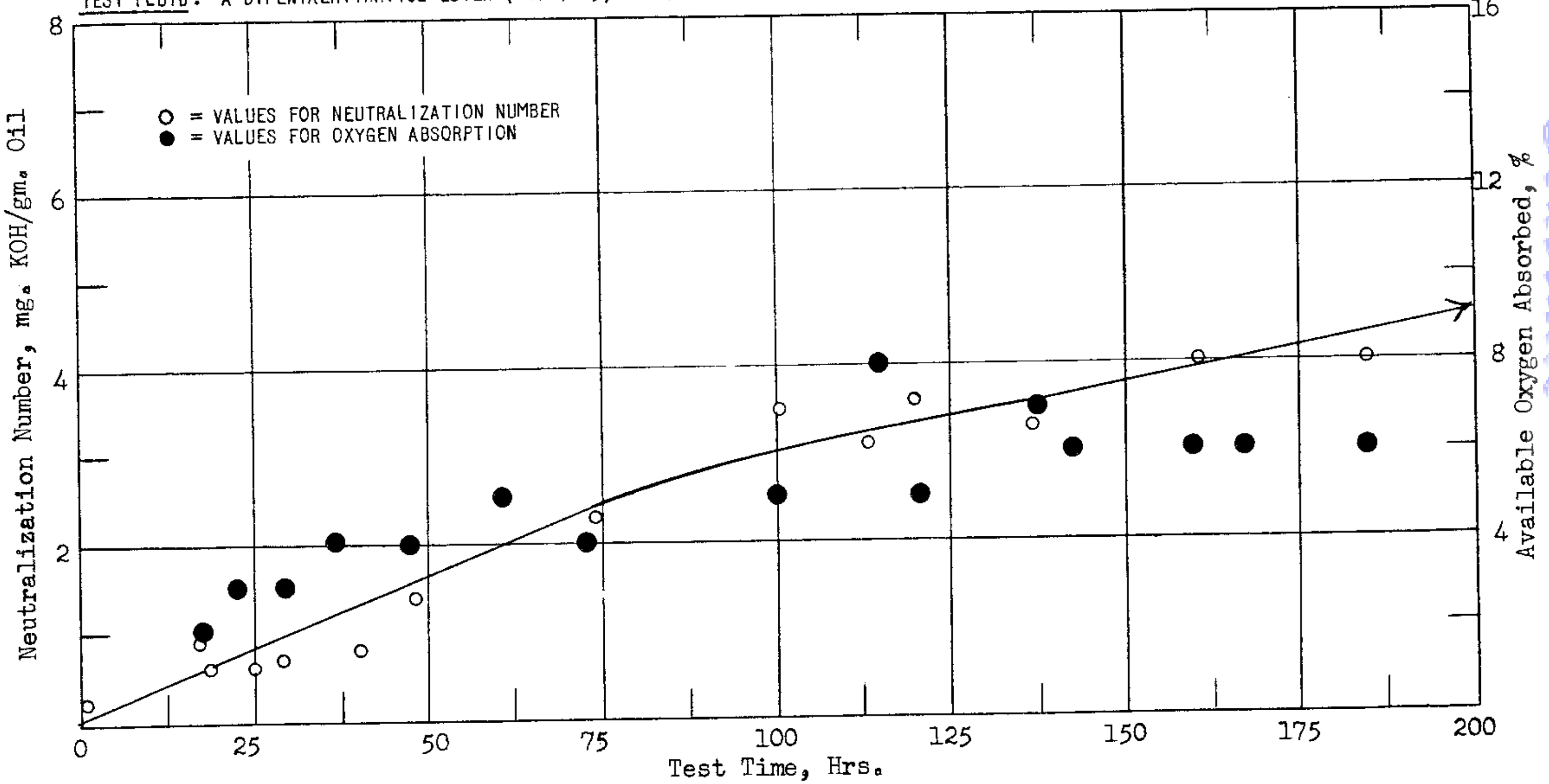


Figure 58. OXIDATION STABILITY AS A FUNCTION OF TEST TIME AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

OXYGEN ABSORBED: AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

TEST FLUID: A DIPENTAERYTHEITOL ESTER (MLO 7023) + 1.0 WT.% PHENOTHIAZINE + 2.0 WT.% PHENYL-ALPHA-NAPHTHYLAMINE

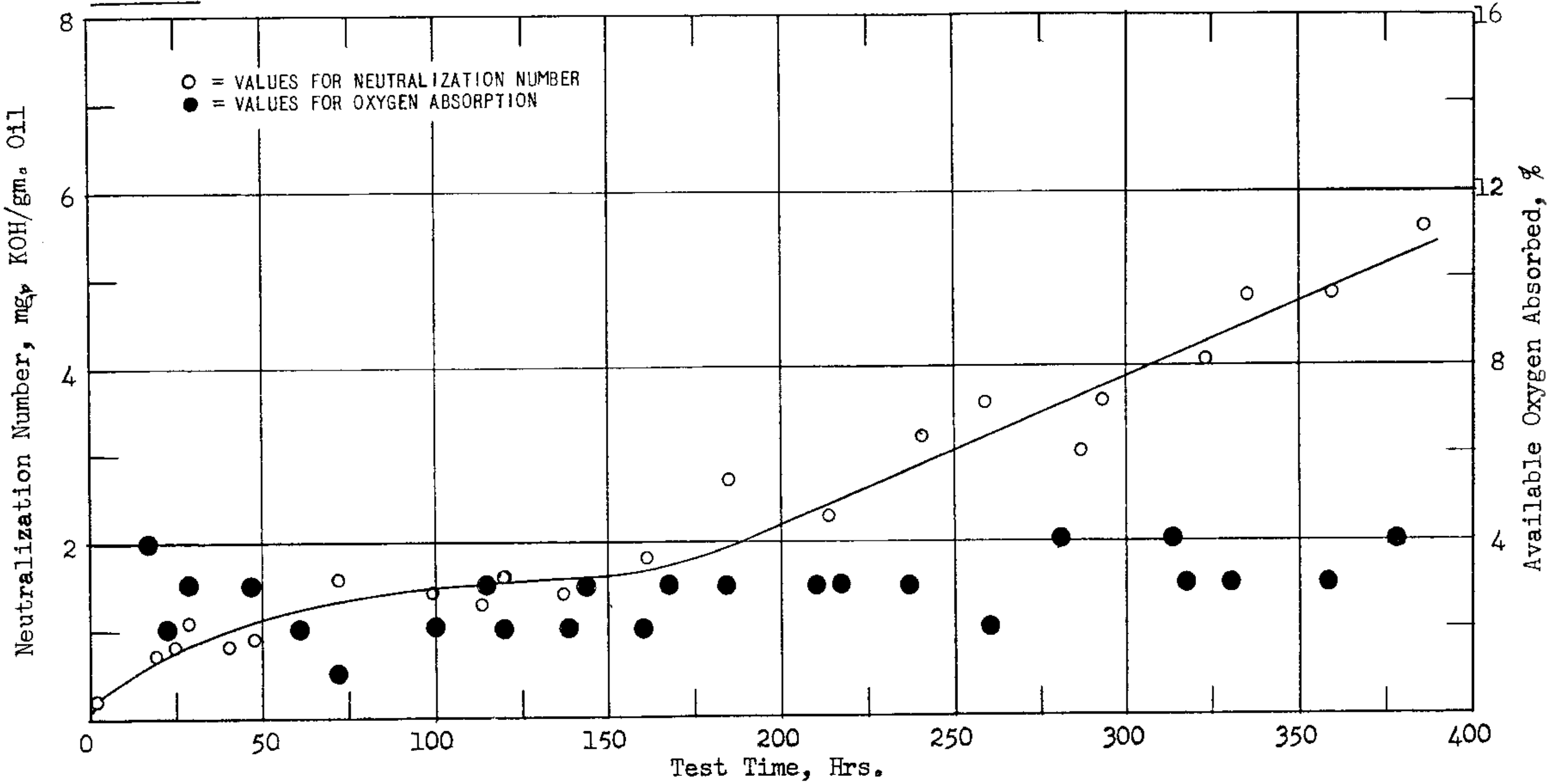


Figure 59. OXIDATION STABILITY AS A FUNCTION OF TEST TIME AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

OXYGEN ABSORBED: AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

TEST FLUID: A DIPENTAERYTHRITOL ESTER (MLO 7023) + 1.0 WT.% 5-10-10 + 2.0 WT.% PHENYL-ALPHA-NAPHTHYLAMINE

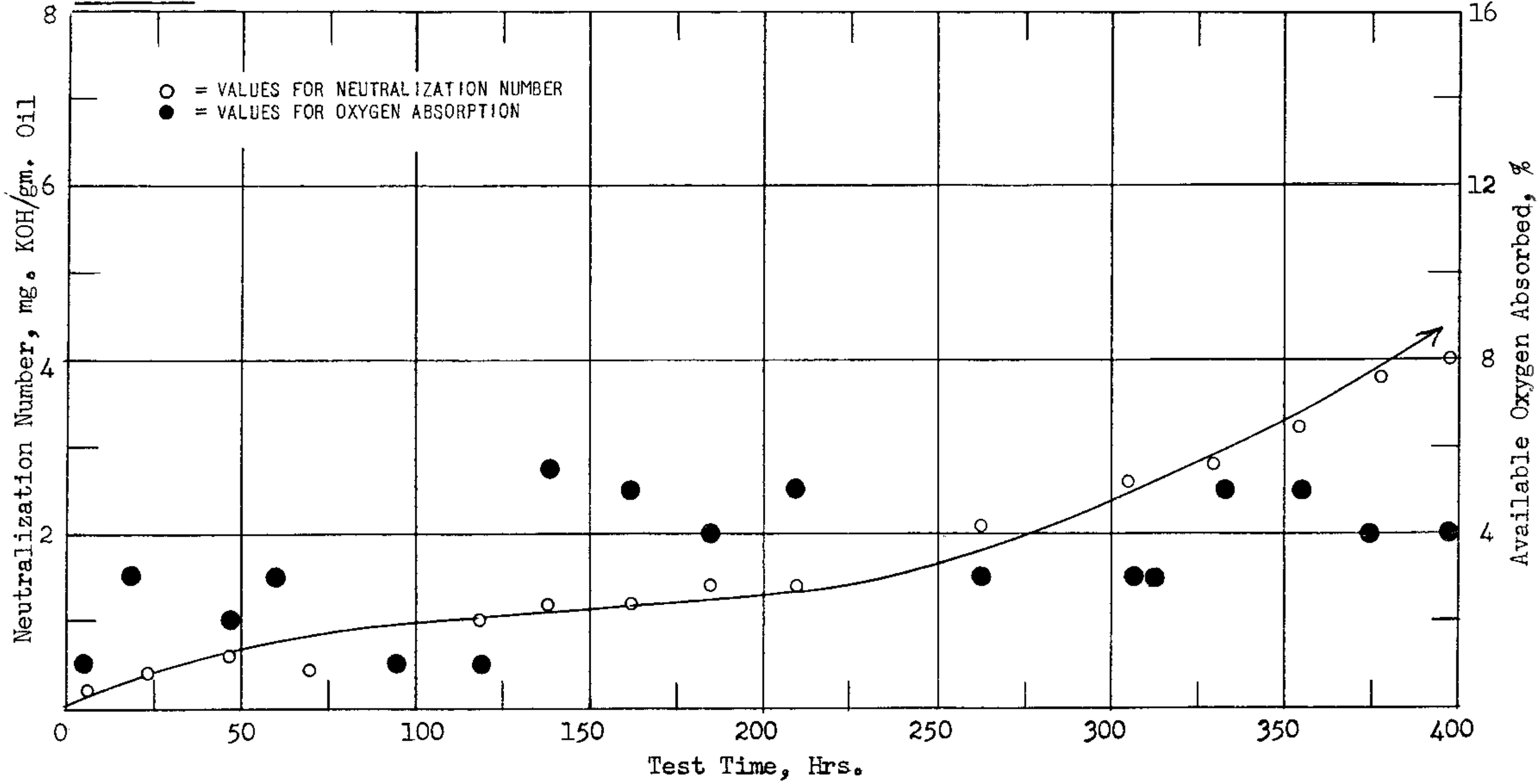


Figure 60. OXIDATION STABILITY AS A FUNCTION OF TEST TIME AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

OXYGEN ABSORBED: AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

TEST FLUID: A TRIMETHYLOL PROPANE ESTER (MLO 7384) + 1.0 WT.% 5-10-10 + 2.0 WT.% PHENYL-ALPHA-NAPHTHYLAMINE.

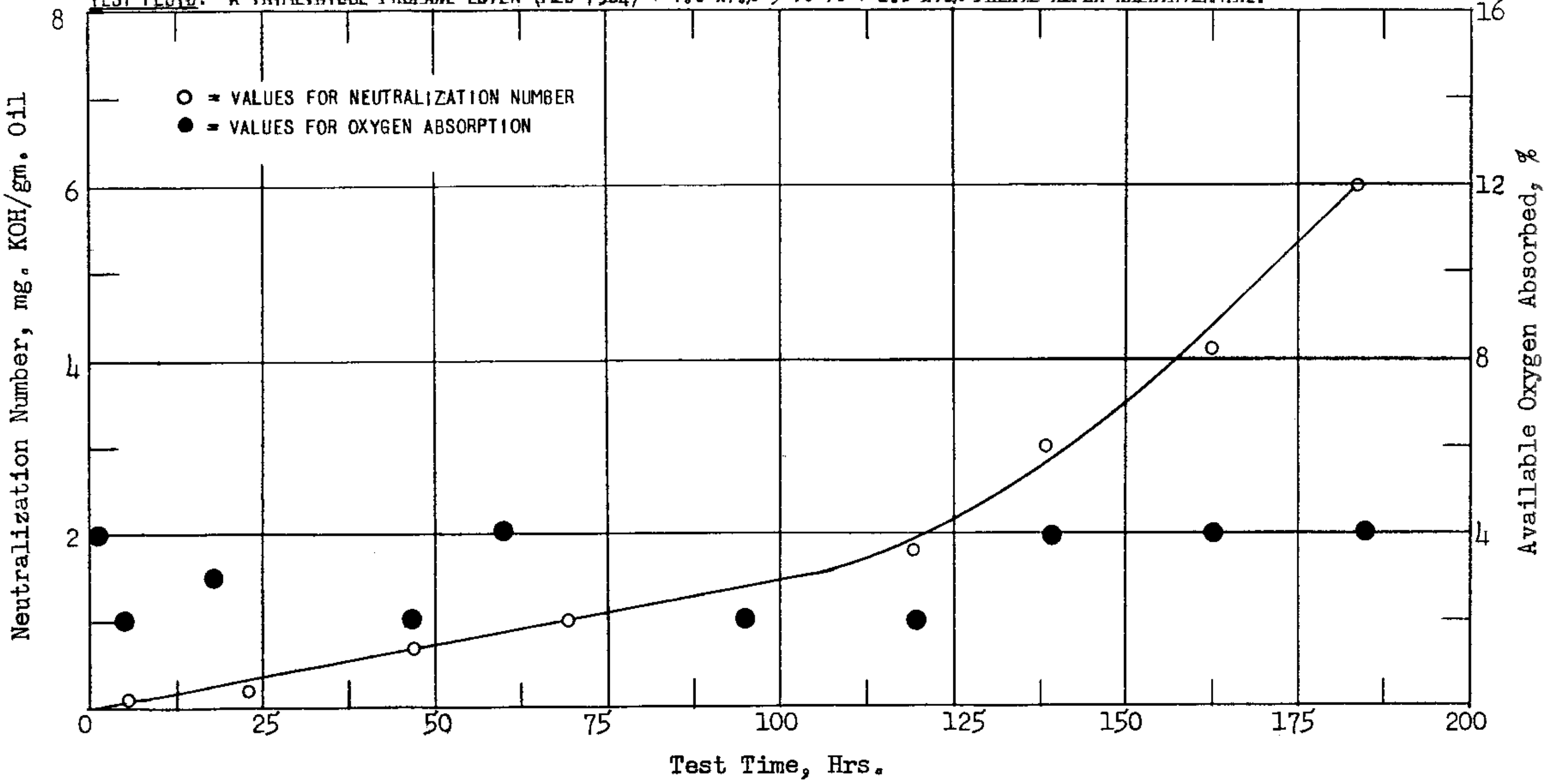


Figure 61. OXIDATION STABILITY AS A FUNCTION OF TEST TIME AT 400°F

Table 72

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF DI-2-ETHYLHEXYL SEBACATE AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; AIR RATE = 5 ± 0.5 L./HR.; TEST TIME = 168 HOURS; TEST FLUID CHARGED = 125 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

ADDITIVE DESIGNATION:
PTZ = PHENOTHIAZINE
5,10,10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	<- - - - - DI-2-ETHYLHEXYL SEBACATE (MLO 7112)- - - - ->					
OXIDATION INHIBITOR, WT. %	<- - - 1.0 PTZ - - ->			<- 1.0 PTZ + 2.0 PAN ->		
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+11	+46	SOLID(2)	+9	+29	+50
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	10.6	20.4	27.3	4.8	15.5	25.9
ASTM UNION COLOR						
ORIGINAL	2	-	-	3-1/2	-	-
FINAL	>8	>8	>8	>8	>8	>8
WT. % OIL INSOLUBLE MATERIAL	-	-	SOLID(2)	-	-	1.4
FINAL CATALYST CONDITION						
APPEARANCE						
COPPER	-	-	DULL	-	-	CORRODED
STEEL	-	-	COATED	-	-	COATED
ALUMINUM	-	-	COATED	-	-	COATED
MAGNESIUM	-	-	CORRODED	-	-	CORRODED
WT. LOSS (MG./SQ. CM.)						
COPPER	-	-	0.14	-	-	0.27
STEEL			+0.16	-	-	+0.20
ALUMINUM			+0.14	-	-	+0.31
MAGNESIUM			35.08	-	-	1.40

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 72 AND AT 120 HOURS.

(2) PRODUCT WAS AN INTIMATE MIXTURE OF OXIDIZED FLUID AND SOLIDS WHICH COULD NOT BE SEPARATED WITHOUT DILUTION.

(TABLE CONCLUDED ON NEXT PAGE)

Table 72 (Concluded)

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF DI-2-ETHYLHEXYL SEBACATE AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; AIR RATE = 5 ± 0.5 L./HR.; TEST TIME = 168 HOURS; TEST FLUID CHARGED = 125 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

ADDITIVE DESIGNATION:
PTZ = PHENOTHIAZINE
5,10,10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	< - - - DI-2-ETHYLHEXYL SEBACATE (MLO 7112) - - - >								
OXIDATION INHIBITOR, WT.%	< - - - 1.0 PTZ + 2.0 PR-81R - - - >						< -1.0 5-10-10 + 2.0 PAN ->		
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+13	+22	+12	+12	+37	+22	+14	+19	+49
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	2.3	5.3	2.4	4.1	9.8	7.6	6.0	7.1	7.8
ASTM UNION COLOR									
ORIGINAL	2	-	-	2	-	-	3-1/2	-	-
FINAL	>8	>8	>8	>8	>8	>8	>8	>8	>8
WT. % OIL INSOLUBLE MATERIAL	1.0	1.0	6.9	1.4	2.5	8.0	-	-	1.2
FINAL CATALYST CONDITION									
APPEARANCE									
COPPER	-	-	DULL	-	-	COATED	-	-	COATED
STEEL	-	-	COATED	-	-	COATED	-	-	COATED
ALUMINUM	-	-	COATED	-	-	COATED	-	-	COATED
MAGNESIUM	-	-	CORRODED	-	-	CORRODED	-	-	CORRODED
WT. LOSS (MG./SQ. CM.)									
COPPER	-	-	0.07	-	-	+0.72	-	-	+0.05
STEEL	-	-	+0.08	-	-	+1.16	-	-	+0.23
ALUMINUM	-	-	+0.50	-	-	+0.77	-	-	+0.09
MAGNESIUM	-	-	24.71	-	-	18.36	-	-	13.40

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 72 AND AT 120 HOURS.
(2) PRODUCT WAS AN INTIMATE MIXTURE OF OXIDIZED FLUID AND SOLIDS WHICH COULD NOT BE SEPARATED WITHOUT DILUTION.

Table 73

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF DI-2-ETHYLHEXYL SEBACATE AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME =168 HOURS; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 125 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

ADDITIVE DESIGNATION: 5-10-10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PTZ = PHENOTHIAZINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	<- - - - - - - - - - - - - - - - -DI-2-ETHYLHEXYL SEBACATE (MLO 7112)- - - - - - - - - - - - - - - - ->								
OXIDATION INHIBITOR, WT.%	<- - - - - 1.0 PTZ - - - - ->			<- - -1.0 PTZ + 2.0 PAN -->			1.0 PTZ + 2.0 PR-81R		
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+19	+31	+33	+8	+11	+17	+12	+14	+40
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	15.1	30.2	43.3	4.9	8.8	10.1	6.3	6.1	21.3
ASTM UNION COLOR									
ORIGINAL	2	-	-	3 1/2	-	-	2	-	-
FINAL	>8	>8	>8	>8	>8	>8	>8	>8	>8
WT.% OIL INSOLUBLE MATERIAL	2.0	3.3	5.7	2.1	2.4	2.6	1.0	0.1	2.5
FINAL CATALYST CONDITION									
APPEARANCE									
COPPER	-	-	CORRODED	-	-	COATED	-	-	COATED
STEEL	-	-	COATED	-	-	COATED	-	-	COATED
ALUMINUM	-	-	COATED	-	-	COATED	-	-	COATED
WT. LOSS (MG./SQ. CM.)									
COPPER	-	-	5.29	-	-	+0.24	-	-	+0.40
STEEL	-	-	+1.27	-	-	+0.44	-	-	+1.44
ALUMINUM	-	-	+0.62	-	-	+0.39	-	-	+0.88

(TABLE CONCLUDED ON NEXT PAGE)

Table 73 (Concluded)

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF DI-2-ETHYLHEXYL SEBACATE AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE : TEST TEMPERATURE = 400 ± 4°F ; TESTTIME = 168 HOURS; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 125 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

ADDITIVE DESIGNATION:

5-10-10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PTZ = PHENOTHIAZINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	<- - - - - - - - - - - - - - - - DI-2-ETHYLHEXYL SEBACATE (MLO 7112)- - - - - - - - - - - - - - - ->					
OXIDATION INHIBITOR, WT.%	<- - - 1.0 5-10-10 + 2.0 PAN - - ->			<- -1.0 5-10-10 + 2.0 PR-81R ->		
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+14	+20	+24	+14	+25	+53
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	5.3	9.7	13.8	4.7	11.4	29.2
ASTM UNION COLOR						
ORIGINAL	3 1/2	-	-	2	-	-
FINAL	>8	>8	>8	>8	>8	>8
WT.% OIL INSOLUBLE MATERIAL	0.6	0.6	1.2	0.1	0.2	1.6
FINAL CATALYST CONDITION						
APPEARANCE						
COPPER	-	-	COATED	-	-	COATED
STEEL	-	-	COATED	-	-	COATED
ALUMINUM	-	-	COATED	-	-	COATED
WT. LOSS (MG./SQ. CM.)						
COPPER	-	-	+0.66	-	-	+0.98
STEEL	-	-	+0.47	-	-	+0.93
ALUMINUM	-	-	+0.21	-	-	+1.37

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 72 HOURS AND AT 120 HOURS TEST TIME.

Table 74

EFFECT OF A DISPERSANT ACRYLOID ON THE OXIDATION AND CORROSION CHARACTERISTICS OF VARIOUS ADDITIVE COMBINATIONS IN DI-2-ETHYLHEXYL SEBACATE AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME = 168 HOURS; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 125 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

ADDITIVE DESIGNATION:
PTZ = PHENOTHIAZINE
5-10-10 = 5-ETHYL-10,10-DIPHENYL PHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE
DAP = DIISOPROPYL ACID PHOSPHITE

TEST FLUID	DI-2-ETHYHEXYL SEBACATE (MLO 7112)											
DISPERSANT, WT. %	5.0 DISPERSANT ACRYLOID SOLUTION (PRL AC333), 30 WT.% ACTIVE											
OXIDATION INHIBITOR, WT. %	1.0 PTZ + 2.0 PAN						1.0 5-10-10 + 2.0 PAN					
LUBRICITY ADDITIVE, WT. %	NONE			0.25 DAP			NONE			0.25 DAP		
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	-19	-19	-16	-22	-23	-25	-22	-20	-20	-18	-21	-24
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	4.6	10.3	16.7	5.6	7.9	11.8	6.2	10.5	15.9	10.6	8.5	11.4
ASTM UNION COLOR												
ORIGINAL	3	-	-	3	-	-	3	-	-	3	-	-
FINAL	>8	>8	>8	>8	>8	>8	>8	>8	>8	>8	>8	>8
WT. % OIL INSOLUBLE MATERIAL	0.1	0.3	0.4	11.5	13.0	12.0	0.3	0.7	1.8	10.6	14.0	7.6
FINAL CATALYST CONDITION												
APPEARANCE												
COPPER	-	-	CORRODED	-	-	COATED	-	-	DULL	-	-	CORRODED
STEEL	-	-	COATED	-	-	COATED	-	-	COATED	-	-	COATED
ALUMINUM	-	-	DULL	-	-	COATED	-	-	COATED	-	-	COATED
WT. LOSS (MG./SQ. CM.)												
COPPER	-	-	0.94	-	-	+0.44	-	-	0.12	-	-	0.18
STEEL	-	-	+0.10	-	-	+0.56	-	-	+0.11	-	-	+0.11
ALUMINUM	-	-	+0.02	-	-	+0.40	-	-	+0.10	-	-	+0.14

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 72 HOURS AND AT 120 HOURS TEST TIME.

(TABLE CONCLUDED ON NEXT PAGE)

Table 74 (Concluded)

EFFECT OF A DISPERSANT ACRYLOID ON THE OXIDATION AND CORROSION CHARACTERISTICS OF VARIOUS ADDITIVE COMBINATIONS IN DI-2-ETHYLHEXYL SEBACATE AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME = 168 HOURS; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 125 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

ADDITIVE DESIGNATION:
PTZ = PHENOTHIAZINE
5-10-10 = 5-ETHYL-10,10-DIPHENYL PHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE
DAP = DIISOPROPYL ACID PHOSPHITE

TEST FLUID	<- DI-2-ETHYHEXYL SEBACATE (MLO 7112) ->											
DISPERSANT, WT. %	<- 5.0 DISPERSANT ACRYLOID SOLUTION (PRL AC333), 30 WT.% ACTIVE ->											
OXIDATION INHIBITOR, WT. %	<- 1.0 PTZ + 2.0 PR-81R ->						<- 1.0 PTZ + 2.0 PR-81R ->					
LUBRICITY ADDITIVE, WT. %	<- NONE ->						<- 0.25 DAP ->					
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	-13	-14	-13	-9	-12	-17	-3	-10	-10	-1	-7	-13
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	5.1	9.3	15.4	5.1	6.9	11.0	12.2	11.8	21.3	7.8	9.6	14.1
ASTM UNION COLOR												
ORIGINAL	2	-	-	2	-	-	2	-	-	2	-	-
FINAL	>8	>8	>8	>8	>8	>8	>8	>8	>8	>8	>8	>8
WT. % OIL INSOLUBLE MATERIAL	0.4	0.2	0.3	-	-	0.1	0.2	0.1	0.6	-	-	0.5
FINAL CATALYST CONDITIONS												
APPEARANCE												
COPPER	-	-	CORRODED	-	-	CORRODED	-	-	CORRODED	-	-	CORRODED
STEEL	-	-	DULL	-	-	DULL	-	-	DULL	-	-	DULL
ALUMINUM	-	-	DULL	-	-	DULL	-	-	DULL	-	-	DULL
WT. LOSS (MG./SQ. CM.)												
COPPER	-	-	1.02	-	-	0.47	-	-	0.60	-	-	12.16
STEEL	-	-	0.00	-	-	+0.04	-	-	0.07	-	-	0.00
ALUMINUM	-	-	0.04	-	-	+0.06	-	-	0.01	-	-	+0.06

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 72 HOURS AND AT 120 HOURS TEST TIME.

Table 75

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF A TRIMETHYLOL PROPANE ESTER AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME = 168 HOURS; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 125 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

ADDITIVE DESIGNATION:
PTZ = PHENOTHIAZINE
5,10,10 = 5-ETHYL-10,10-PHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	< - - - - A TRIMETHYLOL PROPANE ESTER (MLO 7427)- - - - - >					
OXIDATION INHIBITOR, WT. %	< - - - 1.0 PTZ - - - >			< - 1.0 PTZ + 2.0 PAN - >		
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+17	+39	+80	+18	+18	+26
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	3.4	9.1	16.7	1.8	1.1	5.5
ASTM UNION COLOR						
ORIGINAL	1	-	-	3-1/2	-	-
FINAL	>8	>8	>8	>8	>8	>8
WT. % OIL INSOLUBLE MATERIAL	-	-	1.0	-	-	1.6
FINAL CATALYST CONDITION						
APPEARANCE						
COPPER	-	-	CORRODED	-	-	CORRODED
STEEL	-	-	COATED	-	-	COATED
ALUMINUM	-	-	COATED	-	-	COATED
MAGNESIUM	-	-	CORRODED	-	-	COATED
WT. LOSS (MG./SQ. CM.)						
COPPER	-	-	0.67	-	-	0.35
STEEL	-	-	+0.22	-	-	+0.47
ALUMINUM	-	-	+0.23	-	-	0.53
MAGNESIUM	-	-	1.63	-	-	+0.30

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 72 HOURS AND AT 120 HOURS TEST TIME.

(TABLE CONCLUDED ON NEXT PAGE)

Table 75 (Concluded)

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF A TRIMETHYLOL PROPANE ESTER AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME = 168 HOURS; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 125 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

ADDITIVE DESIGNATION:
PTZ = PHENOTHIAZINE
5,10,10 = 5-ETHYL-10,10-PHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	< - - - A TRIMETHYLOL PROPANE ESTER (MLO 7427) - - - >								
OXIDATION INHIBITOR, WT. %	< - - - 1.0 PTZ + 2.0 PR-81R - - - >						< -1.0 5-10-10 + 2.0 PAN ->		
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+14	+42	+239	+14	+42	+178	+14	+15	+23
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	1.6	5.3	9.3	2.3	6.8	9.5	1.4	3.9	4.4
ASTM UNION COLOR									
ORIGINAL	1	–	–	1	–	–	3-1/2	–	–
FINAL	>8	>8	>8	>8	>8	>8	>8	>8	>8
WT. % OIL INSOLUBLE MATERIAL	–	–	2.6	0.4	0.4	3.4	–	–	1.1
FINAL CATALYST CONDITION									
APPEARANCE									
COPPER	–	–	CORRODED	–	–	CORRODED	–	–	DULL
STEEL	–	–	COATED	–	–	COATED	–	–	COATED
ALUMINUM	–	–	COATED	–	–	COATED	–	–	COATED
MAGNESIUM	–	–	CORRODED	–	–	CORRODED	–	–	CORRODED
WT. LOSS (MG./SQ. CM.)									
COPPER	–	–	0.48	–	–	0.95	–	–	0.13
STEEL	–	–	+0.56	–	–	+1.17	–	–	+0.32
ALUMINUM	–	–	+0.20	–	–	+0.57	–	–	+0.28
MAGNESIUM	–	–	15.20	–	–	15.84	–	–	0.29

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 72 HOURS AND AT 120 HOURS TEST TIME.

Table 76

EFFECT OF MAGNESIUM CATALYST ON THE OXIDATION AND CORROSION CHARACTERISTICS OF A TRIMETHYLOL PROPANE ESTER AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME = 168 HOURS; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 125 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, MAGNESIUM.

ADDITIVE DESIGNATION: PTZ = PHENOTHIAZINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	<- - - - - - - A TRIMETHYLOL PROPANE ESTER (MLO 7427) + 1.0 WT.% PTZ + 2.0 WT.% PR-81R- - - - - - ->								
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+14	+42	+239	+14	+42	+178	+18	+23	+79
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	1.6	5.3	9.3	2.3	6.8	9.5	2.6	3.5	14.9
ASTM UNION COLOR									
ORIGINAL	1	–	–	1	–	–	1	–	–
FINAL	>8	>8	>8	>8	>8	>8	>8	>8	>8
WT.% OIL INSOLUBLE MATERIAL	–	–	2.6	0.4	0.4	3.4	0.1	0.2	2.0
FINAL CATALYST CONDITION									
APPEARANCE									
COPPER	–	–	CORRODED	–	–	CORRODED	–	–	COATED
STEEL	–	–	COATED	–	–	COATED	–	–	COATED
ALUMINUM	–	–	COATED	–	–	COATED	–	–	COATED
MAGNESIUM	–	–	CORRODED	–	–	CORRODED	<- - - - NONE - - - - - ->		
WT. LOSS (MG./SQ. GM.)									
COPPER	–	–	0.48	–	–	0.95	–	–	+0.28
STEEL	–	–	+0.56	–	–	+1.17	–	–	+0.58
ALUMINUM	–	–	+0.20	–	–	+0.57	–	–	+1.10
MAGNESIUM	–	–	15.20	–	–	15.84	<- - - - NONE - - - - - ->		

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 72 HOURS AND AT 120 HOURS TEST TIME.

Table 77

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF A TRIMETHYLOL PROPANE ESTER AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME = 168 HOURS; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 125 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

ADDITIVE DESIGNATION:

PTZ = PHENOTHIAZINE
5-10-10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	<- - - - - - - - - - - - - - - - A TRIMETHYLOL PROPANE ESTER (MLO 7427)- - - - - - - - - - - - - - - - ->											
OXIDATION INHIBITOR, WT.%	<- - - 1.0 PTZ - - ->			1.0 PTZ + 2.0 PAN			1.0 5-10-10 + 2.0 PAN			1.0 5-10-10 + PR-81R		
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+11	+36	+89	+15	+16	+21	+12	+14	+36	+10	+12	+10
NEUT. NO. (MG. KOH/GM. OIL)												
ORIGINAL	0.1	–	–	0.1	–	–	0.1	–	–	0.1	–	–
FINAL	1.5	9.6	18.7	1.3	1.9	3.3	1.4	1.9	8.2	2.1	1.6	3.2
ASTM UNION COLOR												
ORIGINAL	1	–	–	3 1/2	–	–	3 1/2	–	–	1	–	–
FINAL	>8	>8	>8	>8	>8	>8	>8	>8	>8	>8	>8	>8
WT.% OIL INSOLUBLE MATERIAL	–	–	0.8	–	–	1.6	–	–	1.6	–	–	0.7
FINAL CATALYST CONDITION												
APPEARANCE												
COPPER	–	–	CORRODED	–	–	COATED	–	–	DULL	–	–	DULL
STEEL	–	–	COATED	–	–	COATED	–	–	COATED	–	–	COATED
ALUMINUM	–	–	COATED	–	–	COATED	–	–	COATED	–	–	COATED
WT. LOSS (MG./SQ. CM.)												
COPPER	–	–	0.38	–	–	+0.12	–	–	0.19	–	–	0.12
STEEL	–	–	+0.23	–	–	+0.57	–	–	+0.29	–	–	+0.33
ALUMINUM	–	–	+0.39	–	–	+0.90	–	–	+0.25	–	–	+0.22

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 72 HOURS AND AT 120 HOURS TEST TIME.

Table 78

EFFECT OF A DISPERSANT ACRYLOID ON THE OXIDATION AND CORROSION CHARACTERISTICS OF VARIOUS ADDITIVE COMBINATIONS IN A TRIMETHYLOL PROPANE ESTER AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME = 168 HOURS; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 125 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

ADDITIVE DESIGNATION:

PTZ = PHENOTHIAZINE
5-10-10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE
DAP = DIISOPROPYL ACID PHOSPHITE

TEST FLUID	A TRIMETHYLOL PROPANE ESTER (MLO 7427)											
DISPERSANT, WT. %	5.0 DISPERSANT ACRYLOID SOLUTION (PRL AC333), 30 WT.% ACTIVE											
OXIDATION INHIBITOR, WT. %	1.0 PTZ + 2.0 PAN						1.0 PTZ + 2.0 PR-81R					
LUBRICITY ADDITIVE, WT. %	NONE			0.25 DAP			NONE			0.25 DAP		
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	-2	-6	+8	-9	-14	-17	-1	0	+15	+7	+32	SOLID (2)
NEUT. NO. INCREASE (MG.KOH/GM. OIL)	1.0	1.4	3.0	1.7	2.2	3.4	4.1	4.2	6.0	3.7	5.0	9.1
ASTM UNION COLOR ORIGINAL FINAL	 3 >8	 - >8	 - >8	 3 >8	 - >8	 - >8	 2 >8	 - >8	 - >8	 2 >8	 - >8	 - >8
WT. % OIL INSOLUBLE MATERIAL	0.1	2.8	1.4	10.5	8.5	11.5	0.1	0.2	0.4	0.2	0.4	7.6
FINAL CATALYST CONDITION APPEARANCE COPPER STEEL ALUMINUM	 - - -	 - - -	 CORRODED DULL BRIGHT	 - - -	 - - -	 CORRODED DULL BRIGHT	 - - -	 - - -	 CORRODED DULL DULL	 - - -	 - - -	 CORRODED DULL DULL
WT. LOSS (MG./SQ. CM.) COPPER STEEL ALUMINUM	 - - -	 - - -	 0.67 0.05 0.04	 - - -	 - - -	 1.57 +0.03 0.04	 - - -	 - - -	 3.02 0.00 0.04	 - - -	 - - -	 15.81 +0.08 +0.07

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 72 HOURS AND AT 120 HOURS TEST TIME.
(2) FINAL PRODUCT WAS ON INTIMATE MIXTURE OF TEST FLUID AND SOLIDS AND COULD NOT BE SEPARATED WITHOUT DILUTION.

(TABLE CONCLUDED ON NEXT PAGE)

Table 78 (Concluded)

EFFECT OF DISPERSANT ACRYLOID ON THE OXIDATION AND CORROSION CHARACTERISTICS OF VARIOUS ADDITIVE COMBINATIONS IN A TRIMETHYLOL PROPANE ESTER AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME = 168 HOURS; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 125 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

ADDITIVE DESIGNATION:
PTZ = PHENOTHIAZINE
5-10-10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE
DAP = DIISOPROPYL ACID PHOSPHITE

TEST FLUID	< - - - A TRIMETHYLOL PROPANE ESTER (MLO 7427) - - - - >					
DISPERSANT, WT. %	< - - 5.0 DISPERSANT ACRYLOID SOLUTION (PRL AC333), - - > 30 WT.% ACTIVE					
OXIDATION INHIBITOR, WT. %	< - - - - - - - - - 1.0 5-10-10 + 2.0 PAN - - - - - - - - - >					
LUBRICITY ADDITIVE, WT. %	< - - - NONE - - - >			< - - 0.25 DAP - - - >		
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	-14	-15	+6	+29		+90
NEUT. NO. INCREASE (MG.KOH/GM OIL)	1.4	1.6	3.1	2.5	2.4	4.7
ASTM UNION COLOR						
ORIGINAL	2	-	-	2	-	-
FINAL	>8	>8	>8	>8	>8	>8
WT. % OIL INSOLUBLE MATERIAL	TRACE	0.1	0.3	2.4	4.8	8.5
FINAL CATALYST CONDITION						
APPEARANCE						
COPPER	-	-	CORRODED	-	-	CORRODED
STEEL	-	-	DULL	-	-	DULL
ALUMINUM	-	-	BRIGHT	-	-	DULL
WT. LOSS (MG./SQ. CM.)						
COPPER	-	-	0.69	-	-	1.60
STEEL	-	-	0.00	-	-	+0.01
ALUMINUM	-	-	0.02	-	-	0.02

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 72 HOURS AND AT 120 HOURS TEST TIME.

(2) FINAL PRODUCT WAS ON INTIMATE MIXTURE OF TEST FLUID AND SOLIDS AND COULD NOT BE SEPARATED WITHOUT DILUTION.

Table 79

THERMAL STABILITY BEHAVIOR OF A DIBASIC ACID ESTER BLEND CONTAINING A DISPERSANT ACRYLOID

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME = 168 HOURS.

TEST WAS CONDUCTED IN GLASS TEST TUBE USING A 125-GRAM CHARGE OF TEST FLUID. THE TUBE IS SEALED WITH A U-TUBE CONTAINING APPROXIMATELY 3 ML. OF TEST FLUID. THE SEAL ALLOWS PASSAGE OF GAS OUT OR AIR IN WITH PRESSURE CHANGES GREATER THAN 4 INCHES OF FLUID; APPROXIMATELY 0.25 LB./SQ. IN. PRIOR TO THE START OF THE TEST, THE VOLUME OF THE SEALED TUBE IS REPLACED APPROXIMATELY 4 TIMES WITH NITROGEN. THE NITROGEN IS INTRODUCED ABOVE THE SURFACE OF THE TEST FLUID BY MEANS OF A SEALED-IN CAPILLARY TUBE.

TEST FLUID			
BASE STOCK	DI-2-ETHYLHEXYL SEBACATE		
OXIDATION INHIBITOR, WT.%	1.0 PHENOTHIAZINE + 2.0 PHENYL-ALPHA-NAPHTHYLAMINE		
DISPERSANT ACRYLOID, WT.%	5.0 DISPERSANT ACRYLOID SOLUTION (PRL Ac333), 30 WT.% ACTIVE		
SAMPLE TIME, HOURS (1)	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	-10	-12	-14
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	0.0	0.1	0.3
WT.% OIL INSOLUBLE MATERIAL	-	-	TRACE
FINAL CATALYST CONDITION			
APPEARANCE			
COPPER	-	-	BRIGHT
STEEL	-	-	DULL
ALUMINUM	-	-	BRIGHT
WT. LOSS (MG./SQ. CM.)			
COPPER	-	-	0.02
STEEL	-	-	0.01
ALUMINUM	-	-	+0.05

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 72 HOURS AND AT 120 HOURS TEST TIME.

Table 80

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF A TRIMETHYLOL PROPANE ESTER AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME = 168 HOURS; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 125 ML.; CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

ADDITIVE DESIGNATION: 5-10-10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PTZ = PHENOTHIAZINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	<---- A TRIMETHYLOL PROPANE ESTER (MLO 7384) ---->					
OXIDATION INHIBITOR, WT.%	<---1.0 PTZ ---->			<– 1.0 PTZ + 2.0 PAN –>		
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+37	+68	+387	+48	+55	+60
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	2.7	6.2	9.9	1.5	1.7	2.9
ASTM UNION COLOR						
ORIGINAL	1	–	–	3 1/2	–	–
FINAL	>8	>8	>8	>8	>8	>8
WT.% OIL INSOLUBLE MATERIAL	–	–	1.2	–	–	0.7
FINAL CATALYST CONDITION						
APPEARANCE						
COPPER	–	–	CORRODED	–	–	CORRODED
STEEL	–	–	DULL	–	–	DULL
ALUMINUM	–	–	DULL	–	–	DULL
MAGNESIUM	–	–	CORRODED	–	–	DULL
WT. LOSS (MG./SQ. CM.)						
COPPER	–	–	6.64	–	–	0.79
STEEL	–	–	0.01	–	–	0.02
ALUMINUM	–	–	0.02	–	–	+0.04
MAGNESIUM	–	–	10.95	–	–	0.08

(TABLE CONCLUDED ON NEXT PAGE)

Table 80 (Concluded)

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF A TRIMETHYLOL PROPANE ESTER AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME = 168 HOURS; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 125 ML.; CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

ADDITIVE DESIGNATION: 5-10-10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PTZ = PHENOTHIAZINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	A TRIMETHYLOL PROPANE ESTER (MLO 7384)								
OXIDATION INHIBITOR, WT.%	1.0 PTZ + 2.0 PR-81R						1.0 5-10-10 + 2.0 PAN		
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+114	+125	+112	+48	+59	+69	+31	+42	+73
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	3.5	3.0	4.1	2.0	2.7	5.2	1.3	1.6	4.9
ASTM UNION COLOR									
ORIGINAL	1	-	-	1	-	-	3 1/2	-	-
FINAL	>8	>8	>8	>8	>8	>8	>8	>8	>8
WT.% OIL INSOLUBLE MATERIAL	-	-	0.9	-	-	0.4	-	-	0.5
FINAL CATALYST CONDITION									
APPEARANCE									
COPPER	-	-	CORRODED	-	-	CORRODED	-	-	CORRODED
STEEL	-	-	DULL	-	-	DULL	-	-	DULL
ALUMINUM	-	-	DULL	-	-	DULL	-	-	BRIGHT
MAGNESIUM	-	-	CORRODED	-	-	DULL	-	-	CORRODED
WT. LOSS (MG./SQ. CM.)									
COPPER	-	-	0.73	-	-	0.69	-	-	0.46
STEEL	-	-	0.01	-	-	0.00	-	-	0.05
ALUMINUM	-	-	0.04	-	-	0.01	-	-	0.02
MAGNESIUM	-	-	11.60	-	-	0.14	-	-	0.49

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 72 AND AT 120 HOURS TEST TIME.

Table 81

EFFECT OF A DISPERSANT ACRYLOID ON THE OXIDATION AND CORROSION CHARACTERISTICS OF ADDITIVE COMBINATIONS IN A TRIMETHYLOL PROPANE ESTER AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME = 168 HOURS; AIR RATE = 5 ±0.5 L./HR.; TEST FLUID CHARGED = 125 ML.; AND CATALYSTS = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

ADDITIVE DESIGNATION: 5-10-10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
DAP = DIISOPROPYL ACID PHOSPHITE

TEST FLUID	<------ A TRIMETHYLOL PROPANE ESTER (MLO 7384) ------>					
DISPERSANT ACRYLOID, WT.%	5.0 DISPERSANT ACRYLOID SOLUTION (PRL Ac 333), 30 WT.% ACTIVE					
OXIDATION INHIBITOR, WT.%	<---------- 1.0 5-10-10 + 2.0 PAN---------->					
LUBRICITY ADDITIVE, WT.%	<---- NONE ---->			<--- 0.25 DAP --->		
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+14	+20	+32	+37	+47	+56
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	1.2	1.8	4.4	3.8	4.9	7.8
ASTM UNION COLOR						
ORIGINAL	3	–	–	3	–	–
FINAL	>8	>8	>8	>8	>8	>8
WT.% OIL INSOLUBLE MATERIAL	TRACE	0.1	0.2	2.0	2.0	2.0
FINAL CATALYST CONDITION						
APPEARANCE						
COPPER	–	–	CORRODED	–	–	CORRODED
STEEL	–	–	DULL	–	–	DULL
ALUMINUM	–	–	BRIGHT	–	–	BRIGHT
WT. LOSS (MG./SQ. CM.)						
COPPER	–	–	0.68	–	–	3.47
STEEL	–	–	0.04	–	–	+0.05
ALUMINUM	–	–	0.05	–	–	0.02

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM TEST TUBE AT 72 AND AT 120 HOURS TEST TIME.

Table 82

EFFECT OF ADDITIVE COMBINATIONS ON THE OXIDATION AND CORROSION CHARACTERISTICS OF A DIPENTAERYTHRITOL ESTER AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F ; TEST TIME = 168 HOURS; AIR RATE = 5 ± 0.5 L./HR.; TEST FLUID CHARGED = 125 ML.; AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

ADDITIVE DESIGNATION:
PTZ = PHENOTHIAZINE
5-10-10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	<- - - - - - - - - - - - - - - - A DIPENTAERYTHRITOL ESTER (MLO 7023)- - - - - - - - - - - - - - - - ->											
OXIDATION INHIBITOR, WT.%	<- - 1.0 PTZ - - ->			1.0 PTZ + 2.0 PAN			1.0 PTZ + 2.0 PR-81R			1.0 5-10-10 + 2.0 PAN		
SAMPLE TIME, HOURS (1)	72	120	168	72	120	168	72	120	168	72	120	168
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+25	+52	+98	+36	+46	+61	+40	+52	+74	+35	+55	+80
NEUT. NO. INCREASE (MG. KOH/GM. OIL)	1.7	4.7	12.2	0.6	1.2	1.9	1.9	1.7	2.9	0.4	1.1	1.3
ASTM UNION COLOR												
ORIGINAL	2	-	-	3 1/2	-	-	2	-	-	3 1/2	-	-
FINAL	>8	>8	>8	>8	>8	>8	>8	>8	>8	>8	>8	>8
WT. % OIL INSOLUBLE MATERIAL	-	-	0.8	-	-	1.3	-	-	0.5	-	-	0.2
FINAL CATALYST CONDITION												
APPEARANCE												
COPPER	-	-	CORRODED	-	-	DULL	-	-	CORRODED	-	-	CORRODED
STEEL	-	-	DULL	-	-	COATED	-	-	DULL	-	-	DULL
ALUMINUM	-	-	DULL	-	-	COATED	-	-	COATED	-	-	BRIGHT
MAGNESIUM	-	-	DULL	-	-	COATED	-	-	COATED	-	-	BRIGHT
WT. LOSS (MG./SQ. CM.)												
COPPER	-	-	0.40	-	-	0.04	-	-	0.51	-	-	0.40
STEEL	-	-	+0.08	-	-	+0.29	-	-	+0.08	-	-	0.00
ALUMINUM	-	-	+0.09	-	-	+0.22	-	-	+0.13	-	-	+0.06
MAGNESIUM	-	-	0.01	-	-	+0.37	-	-	+0.09	-	-	0.06

(1) APPROXIMATELY 25 MILLILITERS OF TEST FLUID WERE WITHDRAWN FROM THE TEST TUBE AT 72 AND AT 120 HOURS TEST TIME.

Table 83

A COMPARISON OF SMALL VOLUME AND STANDARD OXIDATION TEST PROCEDURES AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: STANDARD TEST: TEST TEMPERATURE = 400 ± 4°F ; TEST FLUID CHARGE = 100 ML.; AIR RATE = 5 ± 0.5 L./HR.; TIME = 168 HRS.; AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

SMALL VOLUME TEST: TEST TEMPERATURE = 400 ± 4°F.; TEST FLUID CHARGE = 25 ML.; AIR RATE = 1.25 ± 0.1 L./HR.; TIME = 168 HRS.; AND CATALYST = A 0.5-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

ADDITIVE SYMBOL:
PTZ = PHENOTHIAZINE
5-10-10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	<- - - - - - DI-2-ETHYLHEXYL SEBACATE (MLO 7112)- - - - - - ->				DIPENTAERYTRITOL ESTER (MLO 7023)	
OXIDATION INHIBITOR, WT. %	1.0 5-10-10 + 2.0 PAN				1.0 PTZ + 2.0 PR-81R	
TEST TYPE	STANDARD	SMALL VOLUME	STANDARD	SMALL VOLUME	STANDARD	SMALL VOLUME
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+49	+20	+24	+61	+74	+60
NEUT. NO. (MG. KOH/GM. OIL)						
ORIGINAL	0.0	0.0	0.0	0.0	0.1	0.1
FINAL	7.8	12.6	13.8	33.0	3.0	5.4
ASTM UNION COLOR						
ORIGINAL	3 1/2	3 1/2	3 1/2	3 1/2	2	2
FINAL	>8	>8	>8	>8	>8	>8
WT. % OIL INSOLUBLE MATERIAL	1.2	0.4	1.2	0.9	0.5	0.9
FINAL CATALYST CONDITION						
APPEARANCE						
COPPER	COATED	COATED	COATED	DULL	CORRODED	CORRODED
STEEL	COATED	COATED	COATED	COATED	DULL	DULL
ALUMINUM	COATED	COATED	COATED	COATED	COATED	COATED
MAGNESIUM	CORRODED	CORRODED	-	-	COATED	CORRODED
WT. LOSS (MG./SQ. CM.)						
COPPER	+0.05	+0.50	+0.66	+0.16	0.51	0.28
STEEL	+0.23	+0.28	+0.47	+0.34	+0.08	+0.03
ALUMINUM	+0.09	+0.30	+0.21	+0.30	+0.13	+0.28
MAGNESIUM	13.40	2.16	-	-	+0.09	0.91

(TABLE CONCLUDED ON NEXT PAGE)

Table 83 (Concluded)

A COMPARISON OF SMALL VOLUME AND STANDARD OXIDATION TEST PROCEDURES AT 400°F

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.

TEST CONDITIONS INCLUDE: STANDARD TEST: TEST TEMPERATURE = 400 +4°F ; TEST FLUID CHARGE = 100 ML.; AIR RATE = 5 ±0.5 L./HR.; TIME = 168 HRS.; AND CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

SMALL VOLUME TEST: TEST TEMPERATURE = 400 +4°F ; TEST FLUID CHARGE = 25 ML.; AIR RATE = 1.25+0.1 L./HR.; TIME=168 HRS.; CATALYST = A 0.5-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

ADDITIVE SYMBOL:
PTZ = PHENOTHIAZINE
5-10-10 = 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PR-81R = PRIMENE-81R, A PRIMARY AMINE

TEST FLUID	<---A TRIMETHYLOL PROPANE ESTER (MLO 7427)--->			
OXIDATION INHIBITOR, WT.%	1.0 5-10-10 + 2.0 PR-81R		1.0 5-10-10 + 2.0 PAN	
TEST TYPE	STANDARD	SMALL VOLUME	STANDARD	SMALL VOLUME
% CHANGE IN CENTISTOKE VISCOSITY AT 100°F	+10	+38	+23	+67
NEUT. NO. (MG. KOH/GM. OIL)				
ORIGINAL	0.1	0.1	0.1	0.1
FINAL	3.2	7.3	4.5	12.0
ASTM UNION COLOR				
ORIGINAL	1	1	3 1/2	3 1/2
FINAL	>8	>8	>8	>8
WT.% OIL INSOLUBLE MATERIAL	0.7	0.8	1.1	1.7
FINAL CATALYST CONDITION				
APPEARANCE				
COPPER	DULL	CORRODED	DULL	DULL
STEEL	COATED	DULL	COATED	DULL
ALUMINUM	COATED	COATED	COATED	DULL
MAGNESIUM	-	-	CORRODED	DULL
WT. LOSS (MG./SQ. CM.)				
COPPER	0.12	0.31	0.13	0.22
STEEL	+0.33	+0.09	+0.32	+0.26
ALUMINUM	+0.22	+0.38	+0.28	0.00
MAGNESIUM	-	-	0.29	+0.03

Preliminary quantitative oxidation studies in the controlled atmosphere panel coker suggest a number of trends concerning oxidation rate and oxygen tolerance based on deposits on the metal surface.

(1) Panel deposits at 600°F are not a direct function of the amount of oxygen assimilated by the different fluid types.

(2) For a given fluid type, oxidation rate is increased with increasing fluid volatility.

(3) Under comparable conditions, aromatic hydrocarbons oxidize at a substantially lower rate than do the paraffinic and naphthenic mineral oils.

(4) The oxygen assimilation with all fluids evaluated tends to increase with increasing panel temperature.

(5) Increasing the panel temperature from 600° to 700° or 750°F for a paraffinic mineral oil increases the oxygen assimilated but may actually decrease the total deposit.

(6) The inhibitor in Spec. MIL-L-7808 fluids appears to be effective in limiting oxygen assimilation at 600°F panel temperature but ineffective at 700°F and higher panel temperatures.

Additional studies have been conducted to amplify these preliminary findings.

1. Comparison of Paraffinic and Naphthenic Mineral Oil Formulations in the Controlled Atmosphere (C.A.) Panel Coker. Several naphthenic and paraffinic mineral oil formulations representing different refining techniques and additive packages are shown in Table 84. Formulations MLO 7360, MLO 7295, MLO 7296, and MLO 7341 are prepared with super-refined stocks. The remaining three fluids MLO 7361, MLO 7362, and MLO 7339 have been prepared with conventionally-refined stocks. The formulations including phenyl-alpha-naphthylamine as the antioxidant, silicone antifoam additive, and Acryloid dispersant represent an effective additive package for mineral oils designed for use under severe oxidative conditions. Previous data discussed in WADC TR 55-30 part VII indicate that this additive package in mineral oils appears to be relatively effective in bulk oil oxidation tests.

Coking tendencies of these mineral oil formulations are shown on Table 85 for the Model C coker at 600°F and the controlled atmosphere coker at 700°F. Both neutral formulations (78 to 120 cs. at 100°F) and bright stock formulations (360 and 415 cs. at 100°F) are shown for each of the mineral oil types. For the same viscosity level, the paraffinic formulations exhibit lower coking values than the naphthenic formulations in the C.A. coker. It should be noted that there is no close correlation between the values for the naphthenic formulations between the Model C coker at 600°F and the C.A. coker at 700°F.

In general, the addition of polar additives to a mineral oil formulation tends to increase coke deposit. The relationship between MLO 7273 (naphthenic mineral oil base stock) and the formulation MLO 7360 which is formulated from this base stock illustrates this trend in both cokers. A comparison of MLO 7360 with MLO 7361 or MLO 7341 with MLO 7339 illustrates for the naphthenic and paraffinic series the improved coking values obtained by using super-refined stocks as base stocks.

2. Effect of Fluid Volatility on C.A. COKER VALUES. The volatility of mineral oil fluids has been shown to affect panel coker values. These data have been discussed in WADC TR 55-30 part V. The mineral oils used in these previous studies had boiling ranges of 200°F or greater. As a part of the super-refining program, narrow boiling mineral oil fractions have become available by this Laboratory for further evaluation in the panel coker. These narrow boiling fractions have a boiling range between 10 and 90 per cent distilled of the order of 25°F or less. These fractions tend to optimize viscosity-volatility relationships for the specific mineral oil type.

A number of these narrow boiling fractions from a variety of paraffinic and naphthenic neutrals have been evaluated in the C. A. panel coker at 700°F. as shown in Table 86. The coke deposit is represented graphically as a function of boiling point of the narrow boiling fractions in Figure 62. The oxygen assimilated in these tests has been measured quantitatively. These data show decreased coking tendencies with increasing boiling point.

Extremely large amounts of coke are noted for both paraffinic and naphthenic mineral oils boiling below 725°F. These materials would be expected to provide large amounts of hydrocarbon vapor in the immediate vicinity of the test panel. In every case of high volatility fluids with excessive coking, the oxygen assimilated is substantially lower than with the higher boiling fluids which exhibit low coke values. Prior to oxygen assimilation measurements, vapor phase oxidation at an increased rate was suggested as the reason for excessive coking. These quantitative oxidation data suggest that the presence of large quantities of vapor in the vicinity of the panel actually reduces the oxidation reaction occurring.

Bulk oil oxidation tests show that adequately mixed air and vapor at elevated temperatures react to use larger quantities of oxygen than for a mixture of liquid and air at the same temperature. In the panel coker, the vapors from the hot panel may act to reduce the quantity of air in contact with the hot oil, thereby lowering the total oxygen assimilated. The oxygen tolerance of these volatile mineral oils is drastically reduced as indicated by the coke deposit.

The coke deposit appears to decrease slowly with increasing boiling point from 750° to 925°F. The values for fractions from four paraffinic neutrals all appear to fit on a common curve as shown on Figure 62. The data for the naphthenic mineral oil fractions show the same general relationship to the paraffinic mineral oil fractions as that shown previously for wide boiling range mineral oils.

3. Effect of Cadmium Diamyldithiocarbamate on Coking Tendencies. One of the most effective high temperature oxidation inhibitors in super-refined mineral oils is cadmium diamyldithiocarbamate (PRL 3666). The additive, PRL 3666, is supplied as a 50 weight per cent solution of the active ingredient in a mineral oil solvent. Oxidative and thermal tests of blends containing PRL 3666 show a tendency to form a yellow solid material at temperatures above 500°F. In oxidation tests at 500°F , these solids can effectively be dispersed with Acryloid 917. The effect of PRL 3666 in mineral oil and ester blends has been evaluated in the Model C and C.A. panel cokers at 600° and 700°F. The results of these studies are shown in Table 87.

The addition of the PRL 3666 additive to both the mineral oils and ester results in a substantial increase in coke deposit at all test conditions. There was evidence of a yellow deposit in the coke lay down from all of the blends containing PRL 3666 antioxidant and PRL 2095 silicone antifoam additive. The addition of Acryloid 917 to the additive package in all cases materially reduces the amount of coke deposit. The characteristic yellow deposit from the PRL 3666 was not apparent in the mineral oil blends containing both PRL 3666 and the Acryloid dispersant.

4. Effect of Additives on the Oxygen Assimilated in the C.A. Panel Coker. The effect of polar additives on coke deposit has been adequately demonstrated in previous studies. In general, the presence of additives in the ester and mineral oil base stocks actually increases the coke value under most test conditions. Studies shown in Table 88 and Figures 63 and 64 illustrate the effect of oxidation inhibitors on the amount of oxygen assimilated throughout the coker tests. Data are shown for both esters and mineral oils at temperatures of 600° and 700°F. A comparison of di-2-ethylhexyl sebacate and Hercoflex 600, a pentaerythritol ester, shows almost identical oxygen absorption characteristics over the temperature range studied. The effect of additives on the oxidation rate for these two esters is similar. The amount of coke deposit is consistently lower for the Hercoflex 600 pentaerythritol ester fluid than for the di-2-ethylhexyl sebacate. The advantage of the Hercoflex 600 at 700°F. is considerable. These data emphasize the effects of molecular structure and thermal stability (non-oxidative phenomena) in determining coking.

An interesting comparison between oxidation rate and coking is shown for Hercoflex 600 with oxidation inhibitors at 700°F. The addition of phenothiazine reduces the rate of oxidation over Hercoflex 600 without additives and the use of PRL 3666 oxidation inhibitor decreases still further the rate of oxidation. The coke values follow the inverse order of the oxidation rate. This is indicative of the lack of direct correlation between degree of oxidation and coking under the standard eight-hour tests. The coke in this case may be attributable to the additive itself or to the effect of the additive on the mechanism of oxidation.

A series of tests have been conducted with a conventionally-refined and a super-refined paraffinic neutral to show the effect of additives on oxidation rate and coke formation. The addition of phenyl-alpha-naphthylamine (PAN) or PRL 3666 to the paraffinic neutral effects a reduction in oxidation rate at both 600° and 700°F. The reduction in oxidation rate at 600°F. is not as great for inhibited mineral oils as for inhibited esters. As in the case of the esters, the inhibitors effect less reduction in oxygen assimilation at 700° than at 600°F. panel temperature.

The mineral oil blends differ from the ester blends in the relationship of coke formation at 600° and 700°F. For the mineral oil blends, with the exception of those containing PRL 3666, the coke value at 700°F. is less than the corresponding value at 600°F. In all cases, however, the amount of oxygen assimilated at 700°F is substantially increased over the values obtained at 600°F. These data comprise further evidence suggesting a change in oxidation mechanism with increasing temperature. The net result of this change is improved oxygen tolerance.

The addition of the PRL 3666 to the mineral oils causes an excessive rise in coking value. The addition of a dispersant Acryloid 917 to the blends containing PRL 3666 does not greatly affect oxygen assimilation but does substantially reduce the coke formation noted.

It should be emphasized that the mineral oils and esters show a high absorption of oxygen at 700°F. approaching all of the available oxygen that can be assimilated under these non-ideal mixing conditions. The differences in oxidative deterioration may be obscured by the generally high rate of oxygen absorption noted at 700°F.

5. Successive Panel Coker Tests. Preliminary investigations in the panel coker (WADC TR 55-30 part IV) indicated that the maximum rate of coke formation occurred at the start of the test. In most cases, there was a substantial fall off of the rate of coke formation during the eight-hour test period. These data suggested a decrease in test severity in the viscosity of the test panel due to coke lay down and/or a decrease in coking tendency of the fluid by the depletion of the less stable or coke forming constituents present in the fluid.

A series of successive tests in the panel cokers has been used to explore further the mechanism of coking and the principal variables governing the deposit. In the successive panel coking tests, a standard eight-hour test has been followed by additional eight-hour test increments employing the same fluid used in the preceding test or tests but using a new test panel for each additional test. Exploratory tests of this type were conducted at 600° and 700°F using the Model C and C.A. conditions.

These preliminary data for a naphthenic mineral oil and Hercoflex 600 are shown in Table 89. Two successive runs with the PAN-inhibited mineral oil in the Model C coker at 600°F and in the C.A. coker at 700°F indicate about the same rate of oxidation and degree of coking for the first and second incremental tests.

The mineral oil and the Hercoflex 600 have been evaluated in blends containing PRL 3666 oxidation inhibitor in both the Model C and C.A. panel cokers. In all cases, the first incremental test gives a high coke value followed by substantially lower coke values for the subsequent incremental tests. The oxygen assimilated in all of the incremental tests of the ester and mineral oil blends containing PRL 3666 is about the same value. These data suggest that a substantial amount of the deposit in the first incremental test may be attributed to the additive PRL 3666 itself.

The inclusion of dispersant Acryloid 917 in the mineral oil and ester blends containing PRL 3666 effectively lowers the coke value for the first incremental tests and the values stay at the low level for subsequent incremental tests. These data indicate that the Acryloid 917 may prevent the PRL 3666 additive from decomposing to form coke on the hot surface. Additional testing is required to determine the continued effectiveness, if any, of the PRL 3666 as a bulk oil oxidation inhibitor after a panel coker test in the presence of the Acryloid 917.

After the preliminary Model C and C.A. successive panel coker tests, it was decided to conduct these successive panel coker tests at an air rate of 25 liters per hour in the controlled atmosphere panel coker. The use of 25 versus 5 liters of air per hour allows sufficient oxidative deterioration of the fluid in a limited number of incremental tests to determine the effects of severely oxidized components on coking tendencies.

Additional successive C.A. panel coker tests at 600° and 700°F. for mineral oils and esters are shown in Tables 90, 91, 92, and 93 and Figures 65 through 71. Data for a number of esters with and without phenothiazine are shown on Table 90. Uninhibited esters, di-2-ethylhexyl sebacate, Hercoflex 600, and Synthetics J-7, show a tendency toward increased coke formation with increased test time or additional incremental tests. The rate of oxidation actually decreases with test time or additional incremental tests. These data suggest the formation of deposit precursors with increasing test time.

Data are also shown for the phenothiazine-inhibited versions of these three esters and a polymer, Paraplex AP-52. Oxygen assimilation values decrease with increasing test time as in the case of the uninhibited esters. The overall rates of oxidation for the inhibited fluids are only slightly lower than for the uninhibited fluids. This relationship is shown in Figures 65, 66, and 67. The trend in deposit formation is modified substantially by the inhibitors. Only in the case of inhibited di-2-ethylhexyl sebacate, is there a substantial increase in deposit with increasing test time. The two neopentyl esters and the polyester show about the same or a lower amount of deposits in the incremental tests with increasing test time.

The advantage of neopentyl esters and polyesters over conventional dibasic acid esters is demonstrated in the successive panel coker tests. The effects of inhibitors can also be shown. These studies have, therefore, been extended to include the effect of combinations that have proven to be effective in bulk oil oxidation tests to meet the requirements of Specification MIL-L-9236. Combinations of phenothiazine and phenyl-alpha-naphthylamine have been studied in blends with Hercoflex 600 (Table 91 and Figure 68), and Synthetics J-7 (Table 92 and Figure 69). Studies with both esters have been conducted at 700° and at 600°F. The amount of oxygen assimilated at 700°F by the esters containing the phenothiazine and phenyl-alpha-naphthylamine inhibitor combination is substantially lower than the oxygen assimilated by the phenothiazine-inhibited esters, which is in turn slightly lower than the oxygen assimilated by the uninhibited esters. At 600°F there is a very substantial decrease in rate of oxidation with the addition of phenothiazine to the ester and a slight additional decrease in rate for the combination of phenothiazine and phenyl-alpha-naphthylamine inhibitors. As noted previously, the deposit or coke values do not follow the oxygen absorption values. At 600°F , the highest deposit or coke values are obtained with the inhibitor combination (lowest oxidation rate) and the lowest deposit with the non-additive ester (highest oxidation rate).

A series of additive studies in a super-refined paraffinic mineral oil are shown in Table 93 and Figures 70 and 71. The mineral oil MLO 7301 with successive panel coker tests shows the same general behavior as the uninhibited esters. That is, with increasing time the coke deposit rate increases but the oxidation rate decreases.

Dispersant Acryloid 917 has been included in all of the additive combinations evaluated in this series. Data shown previously on Table 85 suggest that the Acryloid 917 does not adversely affect coke deposit in a mineral oil and additional data presented on Tables 89 and 93 illustrate the beneficial effect of the Acryloid 917 on coke deposit when used in conjunction with a mineral oil blend of PRL 3666. Successive panel coker tests of a blend of MLO 7301 with phenyl-alpha-naphthylamine and Acryloid 917 show a slight increase in overall oxidation rate but a substantial reduction in the total deposit for four incremental tests. The same general trend in oxidation rate and coke deposit is shown for the blends containing phenyl-alpha-naphthylamine, PRL 3666, and Acryloid 917, and phenyl-alpha-naphthylamine and Acryloid 917.

Combinations of phenyl-alpha-naphthylamine and Acryloid 917 with phenothiazine or 5-10-10 inhibitor give a substantial reduction in oxidation rate over the other inhibitors evaluated. In each case, however, the deposit noted is higher than for the other inhibitor combinations evaluated.

J. STUDIES IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG. Studies in the single-pass high temperature lube rig have been continued. This rig measures deposit forming tendencies on a hot metal surface under severe oxidation conditions at 700°F. The effects of molecular weight, fluid type, additives, and variation in test conditions are discussed in WADC TR 55-30 part VI. The application of oxygen absorption techniques to the single-pass rig is described in WADC TR 55-30 part VII. The oxygen absorption measurements allow the application of quantitative comparisons in the study of deposit formation.

Table 84

COMPOSITIONS OF SEVERAL MINERAL OIL FORMULATIONS

BLEND DESIG.	BASE STOCK	ADDITIVE, WT.%	CS. VISCOSITY AT 100°F
MLO 7273	NAPHTHENIC WHITE OIL	NONE	78.7
MLO 7360	NAPHTHENIC WHITE OIL (MLO 7273)	1.0 PHENYL-ALPHA-NAPHTHYLAMINE 5.0 DISPERSANT ACRYLOID 917 0.001 SILICONE ANTIFOAM	114
MLO 7361	NAPHTHENIC NEUTRAL (MLO 7122)	1.0 PHENYL-ALPHA-NAPHTHYLAMINE 5.0 DISPERSANT ACRYLOID 917 0.001 SILICONE ANTIFOAM	78.3
MLO 7362	NAPHTHENIC BRIGHT STOCK (PRL 3460)	1.0 PHEYNL-ALPHA-NAPHTHYLAMINE 5.0 DISPERSANT ACRYLOID 917 0.001 SILICONE ANTIFOAM	415
MLO 7339	PARAFFINIC NEUTRAL (MLO 7325)	1.0 PHENYL-ALPHA-NAPHTHYLAMINE 5.0 DISPERSANT ACRYLOID 917 0.001 SILICONE ANTIFOAM	118
MLO 7341	SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)	1.0 PHENYL-ALPHA-NAPHTHYLAMINE 5.0 DISPERSANT ACRYLOID 917 0.001 SILICONE ANTIFOAM	107
MLO 7296	SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7288)	1.0 PHENYL-ALPHA-NAPHTHYLAMINE 0.001 SILICONE ANTIFOAM	75.2
MLO 7295	SUPER-REFINED PARAFFINIC BRIGHT STOCK (MLO 7287)	1.0 PHENYL-ALPHA-NAPHTHYLAMINE 5.0 DISPERSANT ACRYLOID 917 0.1 DIISOPROPYL ACID PHOSPHITE 0.001 SILICONE ANTIFOAM	360

Table 85

PANEL COKING VALUES FOR SEVERAL MINERAL OIL FORMULATIONS

TEST CONDITIONS INCLUDE: PANEL TEMPERATURE AS INDICATED; TEST TIME = 8 HOURS; AND AIR RATE IN THE CONTROLLED ATMOSPHERE PANEL COKER = 25 LITERS PER HOUR

TEST FLUID COMPOSITION AND VISCOSITY SHOWN ON TABLE 84.

TEST FLUID	COKER	PANEL TEMP., °F	WT. GAIN, MG.	NEUT. NUMBER (MG. KOH/GM. OIL) ORIG.	FINAL	FLUID LOSS ML.	MAXIMUM RESERVOIR TEMP., °F
MLO 7273	MODEL C	600	64	0.0	2.2	140	217
	C.A.*	700	25	0.0	3.4	45	289
MLO 7360	MODEL C	600	81	0.2	0.7	80	209
	C.A.*	700	63	0.2	3.5	80	318
MLO 7361	MODEL C	600	98	0.3	0.7	120	219
	C.A.*	700	136	0.3	4.4	65	314
MLO 7362	MODEL C	600	51	0.1	0.3	45	218
	C.A.*	700	113	0.1	2.1	70	276
MLO 7339	MODEL C	600	100	0.0	0.7	65	320
	C.A.*	700	33	0.0	2.3	90	268
MLO 7341	MODEL C	600	73	0.0	1.1	60	233
	C.A.*	700	25	0.0	3.0	65	257
MLO 7296	MODEL C	600	-	-	-	-	-
	C.A.*	700	12	0.0	2.8	40	300
MLO 7295	MODEL C	600	-	-	-	-	-
	C.A.*	700	44	0.0	2.0	25	283

* CONTROLLED ATMOSPHERE

Table 86

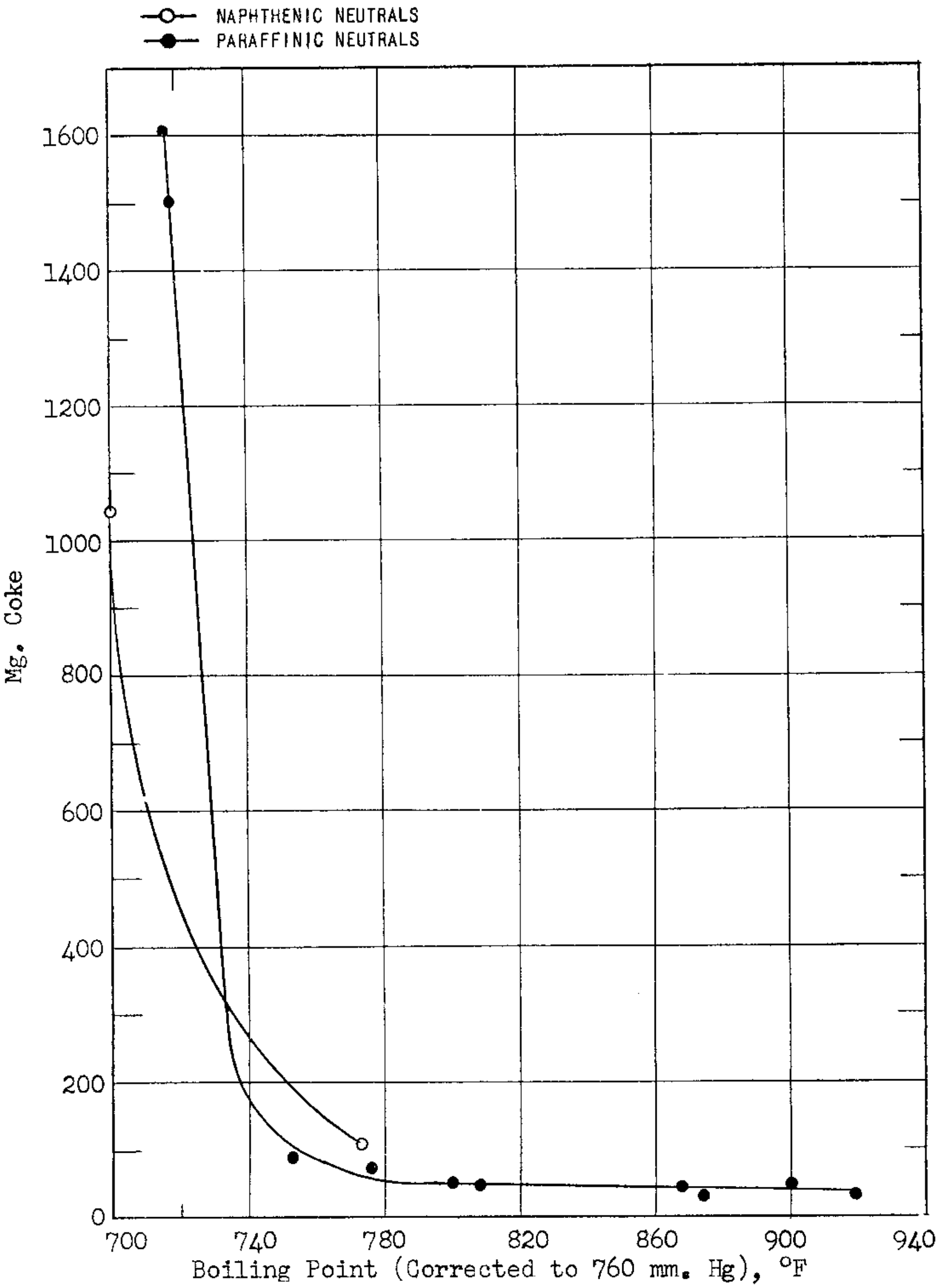
EFFECT OF VOLATILITY ON THE COKING BEHAVIOR OF SEVERAL MINERAL OILS

ALL TEST CONDUCTED IN THE CONTROLLED ATMOSPHERE PANEL COKER

TEST CONDITIONS INCLUDE: TEST TIME = 8 HOURS; PANEL TEMPERATURE = 700°F ; AND AIR RATE = 25 LITERS PER HOUR

FLUID DESIG.	NORMAL BOILING RANGE, °F	CS. VISCOSITY AT 100°F	WT. GAIN, MG.	<------ OXYGEN ABSORPTION(1)	---->	NEUT. NUMBER (MG. KOH/GM. OIL)		FLUID LOSS ML.	MAXIMUM RESERVOIR TEMP., °F
				% OF AVAILABLE O_2	MOLS O_2/426 GM. OIL	ORIG	FINAL		
PARAFFINIC NEUTRAL FRACTIONS									
MLO 7374-1	690 - 715	11.9	1610	34	0.88	0.0	3.0	50	362
MLO 7374-11	740 - 765	16.9	89	65	1.91	0.0	4.8	10	366
MLO 7374-16	775 - 800	22.0	69	63	1.63	0.1	1.8	55	332
MLO 7375-7	785 - 810	28.4	54	61	1.63	0.0	4.0	40	342
MLO 7375-15	875 - 900	62.3	30	63	1.59	0.1	3.6	60	303
MLO 7376-3	860 - 885	41.7	38	65	1.67	0.0	4.6	55	323
MLO 7376-9	915 - 940	61.8	30	67	1.64	0.1	3.8	75	292
MLO 7358-2	710 - 735	12.3	1501	41	1.06	0.1	2.9	55	368
MLO 7358-10	795 - 820	26.9	43	66	1.83	0.0	5.3	25	349
MLO 7358-18	895 - 920	62.9	58	71	1.76	0.0	2.7	65	302
NAPHTHENIC NEUTRAL FRACTIONS									
MLO 7343-2	610 - 635	6.3	1215	44	1.04	0.0	3.7	85	335
MLO 7343-7	685 - 710	11.7	1048	40	1.12	0.0	4.0	25	332
MLO 7343-16	775 - 800	29.4	111	70	1.73	0.0	4.1	65	332

(1) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2. THE MOLS OF O_2 FOR 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSROBED.



ALL TESTS CONDUCTED IN THE CONTROLLED ATMOSPHERE PANEL COKER

TEST CONDITIONS INCLUDE: TEST TIME = 8 HOURS; PANEL TEMPERATURE = 700°F ; AIR RATE = 25 LITERS PER HOUR.

Figure 62. EFFECT OF VOLATILITY ON DEPOSITION IN THE PANEL COKER

Table 87

EFFECT OF A DITHIOCARBAMATE ADDITIVE ON THE COKING BEHAVIOR OF SEVERAL FLUIDS

TEST CONDITIONS INCLUDE: TEST TIME = 8 HOURS; PANEL TEMPERATURE AS INDICATED; AND AIR RATE IN THE CONTROLLED ATMOSPHERE COKER = 25 LITERS PER HOUR.

ADDITIVE DESIGNATION: PRL 3666 = A DITHIOCARBAMATE ADDITIVE (50 WT.% IN A MINERAL OIL)
PRL AC337 = DISPERSANT ACRYLOID 917 SOLUTION (30 WT.% IN A MINERAL OIL)

TEST FLUID (CONCENTRATIONS IN WT.%)	COKER	< - - - - - PANEL TEMPERATURE = 600°F. - - - >					< - - PANEL TEMPERATURE = 700°F. - - - >				
		WT. GAIN, MG.	NEUT. NUMBER (MG. KOH/GM. OIL)		FLUID LOSS, ML.	MAXIMUM RESERVOIR TEMP., °F	WT. GAIN, MG.	NEUT. NUMBER (MG. KOH/GM. OIL)		FLUID LOSS, ML.	MAXIMUM RESERVOIR TEMP., °F
			ORIG.	FINAL				ORIG.	FINAL		
A PARAFFINIC NEUTRAL (MLO 7186)	MODEL C	77	0.0	2.1	25	255	43	0.0	3.3	60	282
	C.A.*	28	0.0	2.9	5	250	70	0.0	2.5	60	303
+ 2.0 PRL 3666 + 0.001 ANTIFOAM	MODEL C	242	0.1	1.1	35	217	-	-	-	-	-
	C.A.*	159	0.1	1.0	25	241	191	0.1	2.4	40	298
+ 2.0 PRL 3666 + 0.001 ANTIFOAM + 5.0 PRL AC337	MODEL C	69	0.1	1.9	25	223	-	-	-	-	-
	C.A.*	58	0.1	2.0	25	233	84	0.1	3.3	75	275
A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7209)	MODEL C	23	0.0	3.6	35	285	-	-	-	-	-
	C.A.*	12	0.0	3.6	10	248	19	0.0	3.7	65	295
+ 2.0 PRL 3666 + 0.001 ANTIFOAM	MODEL C	297	0.1	1.2	30	214	-	-	-	-	-
	C.A.*	-	-	-	-	-	175	0.1	3.0	80	297
+ 2.0 PRL 3666 + 0.001 ANTIFOAM + 5.0 PRL AC337	MODEL C	57	0.1	0.6	40	217	-	-	-	-	-
	C.A.*	-	-	-	-	-	82	0.1	2.7	85	297
A PENTAERYTHRITOL-TYPE ESTER (MLO 7064)	MODEL C	0.0	0.1	3.5	90	215	37	0.1	18.3	200	302
	C.A.*	-	-	-	-	-	-	-	-	-	-
+ 2.0 PRL 3666 + 0.001 ANTIFOAM	MODEL C	332	0.0	0.5	40	230	-	-	-	-	-
	C.A.*	-	-	-	-	-	308	0.0	8.1	75	295
+ 2.0 PRL 3666 + 0.001 ANTIFOAM + 5.0 PRL AC337	MODEL C	27	0.0	0.2	40	208	-	-	-	-	-
	C.A.*	-	-	-	-	-	221	0.0	8.6	60	293

* CONTROLLED ATMOSPHERE

Table 88

EFFECT OF ADDITIVES ON THE OXYGEN ABSORPTION FOR SEVERAL FLUIDS IN THE PANEL COKER

ALL TESTS CONDUCTED IN THE CONTROLLED ATMOSPHERE PANEL COKER

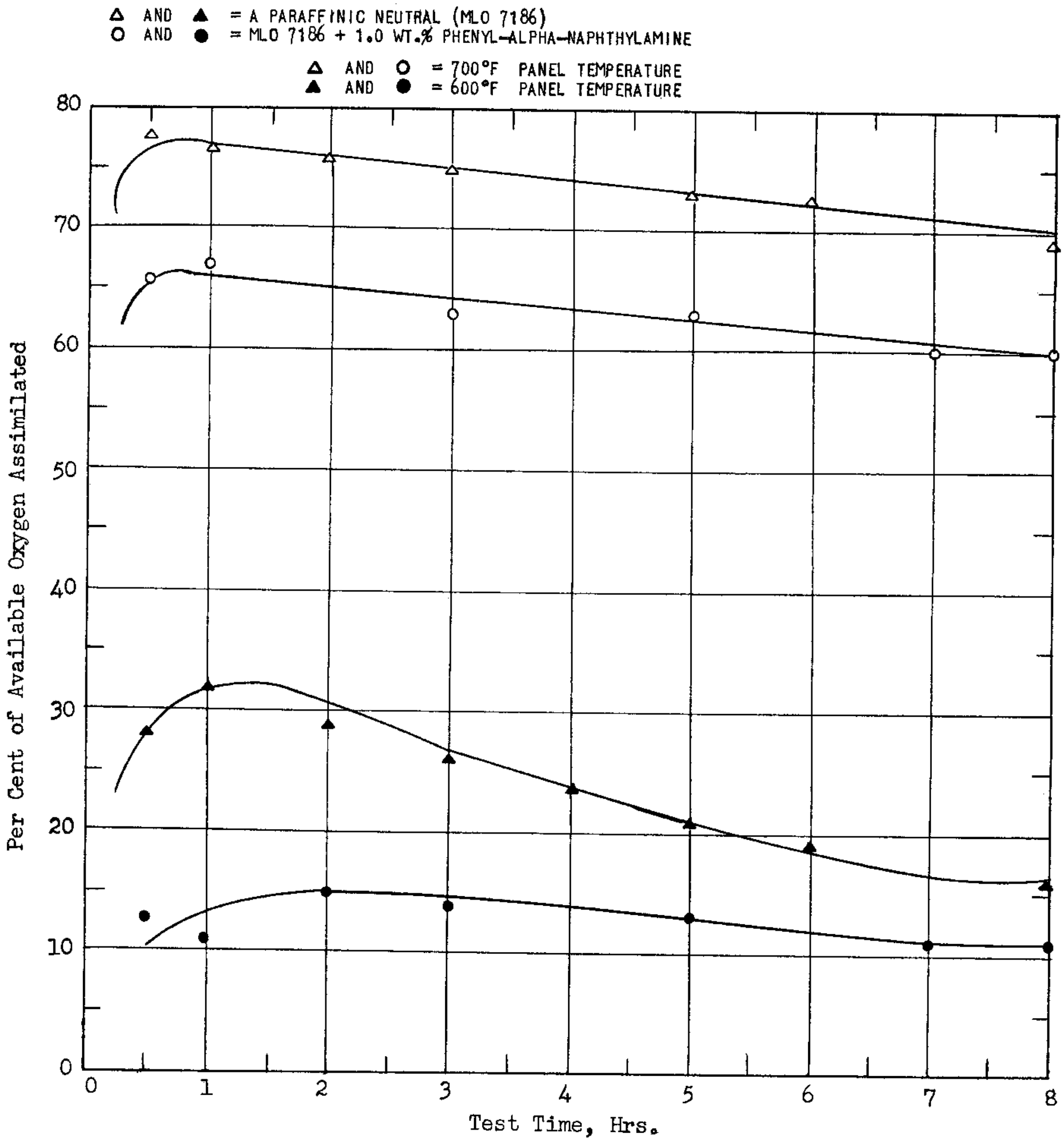
TEST CONDITIONS INCLUDE: TEST TIME = 8 HOURS; PANEL TEMPERATURE AS INDICATED; AND AIR RATE = 25 LITERS PER HOUR

ADDITIVE DESIGNATIONS: PRL 3666 = A DITHIOCARBAMATE ADDITIVE (50 WT.% IN A MINERAL OIL)
PRL AC337 = A DISPERSANT ACRYLOID SOLUTION (30 WT.% IN A MINERAL OIL)

TEST FLUID (CONCENTRATION IN WT.%)	PANEL TEMP., °F	PER CENT AVAILABLE OXYGEN ABSORBED(1) AT INDICATED TEST TIME									TOTAL O2 ABSORBED, MOLS O2/(2) 426 GM. OIL	WT. GAIN, MG.	NEUT. NO. INCREASE (MG. KOH/GM. OIL)
		0.5 HR.	1 HR.	2 HR.	3 HR.	4 HR.	5 HR.	6 HR.	7 HR.	8 HR.			
A PARAFFINIC NEUTRAL (MLO 7186)	600	28	32	29	26	23	21	19	-	16	0.73	89	1.4
	700	78	77	76	75	-	73	73	-	69	2.03	70	2.5
+ 1.0 PHENYL-ALPHA-NAPHTHYLAMINE	600	13	11	15	14	-	13	-	11	11	0.38	62	0.9
	700	66	67	-	63	-	63	-	60	60	1.58	28	2.6
+ 2.0 PRL 3666	600	12	11	14	-	15	16	-	16	-	0.40	159	1.0
	700	67	69	-	71	-	70	-	65	66	1.88	191	2.4
+ 2.0 PRL 3666 + 5.0 PRL AC337 + 0.001 ANTIFOAM	600	12	-	12	-	14	-	-	12	-	0.37	58	2.0
	700	63	65	-	64	-	-	64	-	62	1.61	84	3.3
A SUPER-REFINED PAR. NEUT. (MLO 7301)	-	-	-	-	-	-	-	-	-	-	-	-	-
+ 1.0 PHENYL-ALPHA-NAPHTHYLAMINE	600	15	14	15	-	15	-	17	-	14	0.43	66	0.8
+ 2.0 PRL 3666	700	65	68	68	-	-	66	65	65	64	1.61	175	3.0
+ 2.0 PRL 3666 + 5.0 PRL AC337 + 0.001 ANTIFOAM	700	65	68	-	-	71	68	-	64	63	1.63	82	2.7
DI-2-ETHYLHEXYL SEBACATE (MLO 7112)	600	30	37	38	40	-	38	38	-	38	0.93	2.0	20.5
	700	81	77	75	-	65	-	54	-	49	1.49	347	18.5
+ 0.5 PHENOTHIAZINE	600	4.8	3.8	2.8	-	4.8	-	3.3	-	3.8	0.11	13	0.3
	700	69	63	72	69	-	68	-	61	62	1.55	67	16.4
A PENTAERYTHRITOL ESTER (MLO 7064)	600	28	24	-	34	35	-	36	-	36	0.80	0.0	10.3
	700	67	70	-	67	-	64	-	63	63	1.41	4.4	12.5
+ 0.5 PHENOTHIAZINE	600	3.8	3.3	3.8	-	3.3	-	3.3	-	3.3	0.08	2.3	0.0
	700	35	38	49	52	48	47	-	46	44	1.22	27	9.8
+ 2.0 PRL 3666	700	-	36	-	38	-	37	-	-	33	0.76	308	8.1

(1) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER).
AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

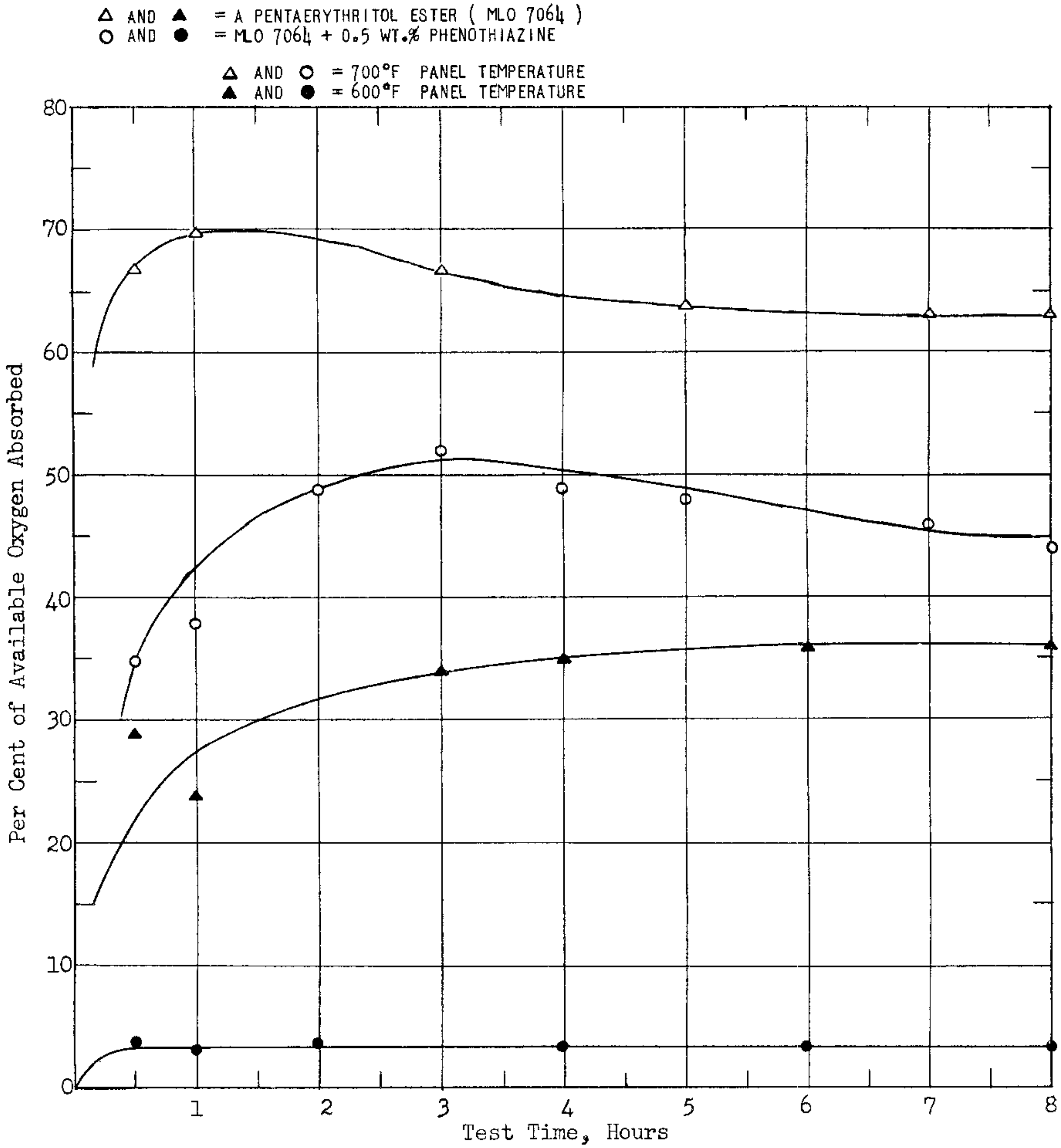
(2) THE MOLS OF OXYGEN FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.



ALL TESTS CONDUCTED IN THE CONTROLLED ATMOSPHERE PANEL COKER

TEST CONDITIONS INCLUDE: TEST TIME = 8 HOURS; PANEL TEMPERATURE AS INDICATED; AND AIR RATE = 25 LITERS PER HOUR

Figure 63. OXYGEN ASSIMILATION FOR A PARAFFINIC NEUTRAL IN THE PANEL COKER



ALL TESTS CONDUCTED IN THE CONTROLLED ATMOSPHERE PANEL COKER

TEST CONDITIONS INCLUDE: TEST TIME = 8 HOURS; PANEL TEMPERATURE AS INDICATED; AND AIR RATE = 25 LITERS PER HOUR.

Figure 64. OXYGEN ASSIMILATION FOR A PENTAERYTHRITOL ESTER IN THE PANEL COKER

Table 89

SUCCESSIVE PANEL COKER TESTS WITH SEVERAL FLUIDS

TEST CONDITIONS INCLUDE: TEST TIME = 8-HOUR INCREMENTS; PANEL TEMPERATURE AND AIR RATE IN THE CONTROLLED ATMOSPHERE COKER AS INDICATED.

NOTE: TESTS ARE RUN IN SUCCESSIVE 8-HOUR INCREMENTS. A NEW TEST PANEL IS USED FOR EACH 8-HOUR INCREMENT. THE SAME TEST FLUID IS USED FOR THE TOTAL TEST TIME.

ADDITIVE DESIGNATIONS: PRL 3666 = A DITHIOCARBAMATE ADDITIVE (50 WT.% IN A MINERAL OIL)
PRL AC337 = A DISPERSANT ACRYLOID 917 SOLUTION (30 WT.% IN A MINERAL OIL)

TEST FLUID (CONC. IN WT.%)	TIME INCREMENT, HOURS	PANEL TEMP., °F	COKER	AIR RATE, L./HR.	MOLES OXYGEN(1) ABSORBED/426 GM. OIL	WT. GAIN, MG.	NEUT. NUMBER (MG. KOH/GM. OIL)		FLUID LOSS, ML.	MAXIMUM RESERVOIR TEMP., °F
							ORIG.	FINAL		
A NAPHTHENIC WHITE OIL (MLO 7273)	0–8	700	C.A.*	5	0.31	6.0	0.0	1.4	20	289
	0–8	700	C.A.*	25	1.31	25	0.0	3.4	45	289
+ 1.0 PHENYL-ALPHA-NAPHTHYLAMINE + 0.001 ANTIFOAM	0–8	600	MODEL C	–	–	68	0.0	1.2	85	217
	8–16	600	MODEL C	–	–	50	1.2	1.7	95	205
	0–8	700	C.A.*	5	0.36	13	0.0	1.8	0	327
	8–16	700	C.A.*	5	0.29	29	1.8	2.8	25	322
+ 2.0 PRL 3666	0–8	600	MODEL C	–	–	302	0.0	1.2	70	213
	8–16	600	MODEL C	–	–	88	1.2	2.3	75	208
	0–8	700	C.A.*	5	0.32	263	0.0	1.7	0	310
	8–16	700	C.A.*	5	0.30	33	1.7	3.1	10	296
	16–24	700	C.A.*	5	0.34	31	3.1	4.6	0	312
+ 2.0 PRL 3666 + 5.0 AC337 + 0.001 ANTIFOAM	0–8	600	MODEL C	–	–	43	0.0	2.5	80	207
	8–16	600	MODEL C	–	–	67	2.5	3.7	50	220
	16–24	600	MODEL C	–	–	58	3.7	5.0	65	246
A PENTAERYTHRITOL ESTER (MLO 7064)	–	–	–	–	–	–	–	–	–	–
+ 2.0 PRL 3666	0–8	600	MODEL C	–	–	332	0.0	0.5	40	230
	8–16	600	MODEL C	–	–	122	0.5	3.3	50	231
	16–24	600	MODEL C	–	–	93	3.3	5.6	60	230
	0–8	700	C.A.*	5	0.31	373	0.0	7.0	0	312
	8–16	700	C.A.*	5	0.34	34	7.0	11.1	10	313
	16–24	700	C.A.*	5	0.33	46	11.1	14.4	10	317
+ 2.0 PRL 3666 + 5.0 AC917 + 0.001 ANTIFOAM	0–8	600	MODEL C	–	–	27	0.0	0.2	40	208
	8–16	600	MODEL C	–	–	34	0.2	0.4	45	202
	16–24	600	MODEL C	–	–	41	0.4	0.7	25	226
	24–32	600	MODEL C	–	–	44	0.7	1.4	35	208
	0–8	700	C.A.*	5	0.32	185	0.0	8.1	15	308
	8–16	700	C.A.*	5	0.33	72	8.1	10.7	0	310

* CONTROLLED ATMOSPHERE

(1) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2. THE MOLS OF OXYGEN FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

Table 90

SUCCESSIVE PANEL COKER TESTS WITH SEVERAL ESTERS

ALL TESTS CONDUCTED IN THE CONTROLLED ATMOSPHERE COKER

TEST CONDITIONS INCLUDE: TEST TIME = 8-HOUR INCREMENTS; PANEL TEMPERATURE = 700°F ; AND AIR RATE = 25 LITERS PER HOUR

NOTE: TESTS ARE RUN IN SUCCESSIVE 8-HOUR INCREMENTS. A NEW TEST PANEL IS USED FOR EACH 8-HOUR INCREMENT. THE SAME TEST FLUID IS USED FOR THE TOTAL TEST TIME.

TEST FLUID (CONCENTRATIONS IN WT.%)	TIME INCREMENT, HOURS	MOLES OXYGEN(1) ABSORBED/426 GM. OIL	WT. GAIN, MG.	NEUT. NUMBER (MG. KOH/GM. OIL)		FLUID LOSS, ML.	MAXIMUM RESERVOIR TEMP., °F
				ORIG.	FINAL		
DI-2-ETHYLHEXYL SEBACATE (MLO 7112)	0-8	1.41	347	0.0	14.5	75	330
	8-16	1.23	332	14.5	27.0	85	337
	16-24	1.03	1670	27.0	39.7	80	328
+ 0.5 PHENOTHIAZINE	0-8	1.30	79	0.0	16.4	80	308
	8-16	1.36	96	16.4	20.0	75	307
	16-24	1.15	196	20.0	24.8	65	285
A PENTAERYTHRITOL ESTER (MLO 7064)	0-8	1.41	4.4	0.0	12.5	70	297
	8-16	1.13	49	12.5	17.8	85	303
	16-24	0.97	77	17.8	18.6	65	276
	24-32	0.96	192	18.6	19.4	50	324
+ 0.5 PEHNOTHIAZINE	0-8	1.27	79	0.0	9.1	35	290
	8-16	1.09	41	9.1	10.4	45	280
	16-24	1.13	25	10.4	11.8	50	303
	24-32	0.90	36	11.8	11.4	50	302
A DIPENTAERYTHRITOL ESTER (MLO 7023)	0-8	1.15	8.5	0.0	9.0	140	285
	8-16	1.15	23	9.0	14.5	65	292
	16-24	1.04	44	14.5	15.2	65	295
	24-32	0.96	39	15.2	12.4	65	297
+ 0.5 PHENOTHIAZINE	0-8	0.98	66	0.1	7.2	85	276
	8-16	0.97	90	7.2	10.5	70	276
	16-24	0.95	84	10.5	10.0	30	262
	24-32	0.93	61	10.0	10.0	45	313
A POLYESTER (PRL 3075)	-	-	-	-	-	-	-
+ 0.5 PHENOTHIAZINE	0-8	1.06	37	3.7	23.5	130	269
	8-16	1.08	16	23.5	31.7	105	284
	16-24	0.94	22	31.7	32.7	105	272

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2. THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

Table 91

EFFECT OF ADDITIVES ON COKING BEHAVIOR IN SUCCESSIVE TESTS WITH A PENTAERYTHRITOL ESTER

ALL TESTS CONDUCTED IN THE CONTROLLED ATMOSPHERE COKER.

TEST CONDITIONS INCLUDE: TEST TIME = 8-HOUR INCREMENTS; PANEL TEMPERATURE AS INDICATED; AND AIR RATE = 25 LITERS PER HOUR.

NOTE: TESTS ARE RUN IN SUCCESSIVE 8-HOUR INCREMENTS. A NEW TEST PANEL IS USED FOR EACH 8-HOUR INCREMENT. THE SAME TEST FLUID IS USED FOR THE TOTAL TEST TIME.

TEST FLUID (CONCENTRATIONS IN WT.%)	TIME INCREMENT, HOURS	MOLES OXYGEN(1) ABSORBED PER 426 GM. OIL	WT. GAIN, MG.	NEUT. NUMBER (MG. KOH/GM. OIL)		FLUID LOSS, ML.	MAXIMUM RESERVOIR TEMP., °F
				ORIG.	FINAL		
PANEL TEMPERATURE = 700°F.							
A PENTAERYTHRITOL ESTER (MLO 7064)	0-8	1.41	4.4	0.0	12.5	70	297
	8-16	1.13	49	12.5	17.8	85	303
	16-24	0.97	77	17.8	18.6	65	276
	24-32	0.96	192	18.6	19.4	50	324
+ 0.5 PHENOTHIAZINE	0-8	1.27	79	0.0	9.1	35	290
	8-16	1.09	41	9.1	10.4	45	280
	16-24	1.13	25	10.4	11.8	50	303
	24-32	0.90	36	11.8	11.4	50	302
+ 1.0 PHENOTHIAZINE + 2.0 PHENYL-ALPHA-NAPHTHYLAMINE	0-8	0.58	51	0.0	3.6	65	287
	8-16	0.70	78	3.6	4.3	45	285
	16-24	0.42	61	4.3	4.5	45	285
	24-32	0.29	33	4.5	4.5	65	276
PANEL TEMPERATURE = 600°F.							
A PENTAERYTHRITOL ESTER (MLO 7064)	0-8	0.80	0.0	0.0	10.3	45	265
+ 0.5 PHENOTHIAZINE	0-8	0.08	2.3	0.0	0.0	15	265
+ 1.0 PHENOTHIAZINE + 2.0 PHENYL-ALPHA-NAPHTHYLAMINE	0-8	0.05	12	0.0	0.2	30	227
	8-16	0.04	28	0.2	0.2	5	222
	16-24	0.07	31	0.2	0.3	25	232
	24-32	0.06	21	0.3	0.4	25	225

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2. THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

Table 92

EFFECT OF ADDITIVES ON COKING BEHAVIOR IN SUCCESSIVE TESTS WITH A DIPENTAERYTHRITOL ESTER

ALL TESTS CONDUCTED IN THE CONTROLLED ATMOSPHERE COKER.

TEST CONDITIONS INCLUDE: TEST TIME = 8-HOUR INCREMENTS; PANEL TEMPERATURE AS INDICATED; AND AIR RATE = 25 LITERS PER HOUR.

NOTE: TESTS ARE RUN IN SUCCESSIVE 8-HOUR INCREMENTS. A NEW TEST PANEL IS USED FOR EACH 8-HOUR INCREMENT. THE SAME TEST FLUID IS USED FOR THE TOTAL TEST TIME.

TEST FLUID (CONCENTRATIONS IN WT.%)	TIME INCREMENT, HOURS	MOLES OXYGEN (1) ABSORBED PER 426 GM. OIL	WT. GAIN, MG.	NEUT. NUMBER (MG. KOH/GM. OIL) ORIG.	NEUT. NUMBER (MG. KOH/GM. OIL) FINAL	FLUID LOSS, ML.	MAXIMUM RESERVOIR TEMP., °F
PANEL TEMPERATURE = 700°F.							
A DIPENTAERYTHRITOL ESTER (MLO 7023)	0-8	1.15	8.5	0.0	9.0	140	285
	8-16	1.15	23	9.0	14.5	65	292
	16-24	1.04	44	14.5	15.2	65	295
	24-32	0.94	39	15.2	12.4	65	297
+ 0.5 PHENOTHIAZINE	0-8	0.98	66	0.1	7.2	85	276
	8-16	0.97	90	7.2	10.5	70	276
	16-24	0.95	84	10.5	11.8	30	262
	24-32	0.93	61	11.8	11.4	45	313
+ 1.0 PHENOTHIAZINE + 2.0 PHENYL-ALPHA-NAPHTHYLAMINE	0-8	0.61	41	0.1	3.4	50	307
	8-16	0.78	15	3.4	5.6	40	302
	16-24	0.68	17	5.6	6.7	55	287
	24-32	0.65	35	6.7	6.2	45	283
PANEL TEMPERATURE = 600°F.							
A DIPENTAERYTHRITOL ESTER (MLO 7023)	-	-	-	-	-	-	-
+ 1.0 PHENOTHIAZINE + 2.0 PHENYL-ALPHA-NAPHTHYLAMINE	0-8	0.07	34	0.0	0.4	0	255
	8-16	0.09	26	0.4	0.5	0	247
	16-24	0.07	17	0.5	0.4	0	232
	24-32	0.06	5.1	0.4	0.2	0	248

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2. THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

Table 93

EFFECT OF ADDITIVE COMBINATIONS ON THE COKING BEHAVIOR OF A SUPER-REFINED PARAFFINIC NEUTRAL

ALL TESTS CONDUCTED IN THE CONTROLLED ATMOSPHERE COKER

TEST CONDITIONS INCLUDE: TEST TIME = 8-HOUR INCREMENTS; PANEL TEMPERATURE = 700°F ; AND AIR RATE = 25 LITERS PER HOUR

NOTE: TESTS ARE RUN IN SUCCESSIVE 8-HOUR INCREMENTS. A NEW TEST PANEL IS USED FOR EACH 8-HOUR INCREMENT. THE SAME TEST FLUID IS USED FOR THE TOTAL TEST TIME.

ADDITIVE DESIGNATION: PRL 3666 = A DITHIOCARBAMATE ADDITIVE (50 WT.% IN A MINERAL OIL)
PRL AC337 = A DISPERSANT ACRYLOID SOLUTION (30 WT.% IN A MINERAL OIL)
5-10-10 = 5-ETHYL-10, 10-DIPHENYLPHENAZASILINE

TEST FLUID (CONCENTRATIONS IN WT.%)	TIME INCREMENT, HOURS	MOLES OXYGEN(1) ABSORBED/426 GM. OIL	WT. GAIN, MG.	NEUT. NUMBER (MG. KOH/GM. OIL)		FLUID LOSS, ML.	MAXIMUM RESERVOIR TEMP., °F
				ORIG.	FINAL		
A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)	0-8	1.46	37	0.0	4.3	45	290
	8-16	1.33	124	4.3	6.4	75	255
	16-24	1.18	464	6.4	6.8	70	252
	24-32	1.06	548	6.8	4.7	60	250
+ 2.0 PHENYL-ALPHA-NAPHTHYLAMINE	0-8	0.99	139	0.0	2.3	95	300
	8-16	1.00	577	2.3	3.3	80	335
	16-24	0.43	1258	3.3	3.7	65	392
	24-32	0.21	744	3.7	4.0	55	350
+ 2.0 PHENYL-ALPHA-NAPHTHYLAMINE + 5.0 PRL AC337 + 0.001 ANTIFOAM	0-8	1.59	59	0.0	2.6	95	258
	8-16	1.45	98	2.6	3.9	85	287
	16-24	1.59	121	3.9	5.1	80	307
	24-32	1.45	70	5.1	6.2	80	328
+ 2.0 PRL 3666 + 0.001 ANITFOAM	0-8	1.61	175	0.1	1.2	80	297
+ 2.0 PRL 3666 + 5.0 PRL AC337 + 0.001 ANTIFOAM	0-8	1.62	82	0.1	2.7	85	297
+ 2.0 PHENYL-ALPHA-NAPHTHYLAMINE + 2.0 PRL 3666 + 5.0 PRL AC337	0-8	1.54	134	0.0	3.2	95	303
	8-16	1.43	75	3.2	4.6	85	288
	16-24	1.40	95	4.6	4.6	80	320
	24-32	1.32	202	4.6	3.2	80	318
+ 2.0 PHENYL-ALPHA-NAPHTHYLAMINE + 1.0 5-10-10 + 5.0 PRL AC337	0-3	0.48	29	0.0	1.0	30	273
	3-11	1.32	85	1.0	4.0	85	317
	11-19	0.94	285	4.0	5.0	85	312
	19-25	0.78	120	5.0	5.4	50	307

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2. THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

ALL TESTS CONDUCTED IN THE CONTROLLED ATMOSPHERE PANEL COKER

TEST CONDITIONS INCLUDE: TEST TIME = 8-HOUR INCREMENTS; PANEL TEMPERATURE = 700°F ; AND AIR RATE = 25 LITERS PER HOUR.

NOTE: TESTS ARE RUN IN SUCCESSIVE 8-HOUR INCREMENTS. A NEW TEST PANEL IS USED FOR EACH 8-HOUR INCREMENT. THE SAME TEST FLUID IS USED FOR THE TOTAL TEST TIME.

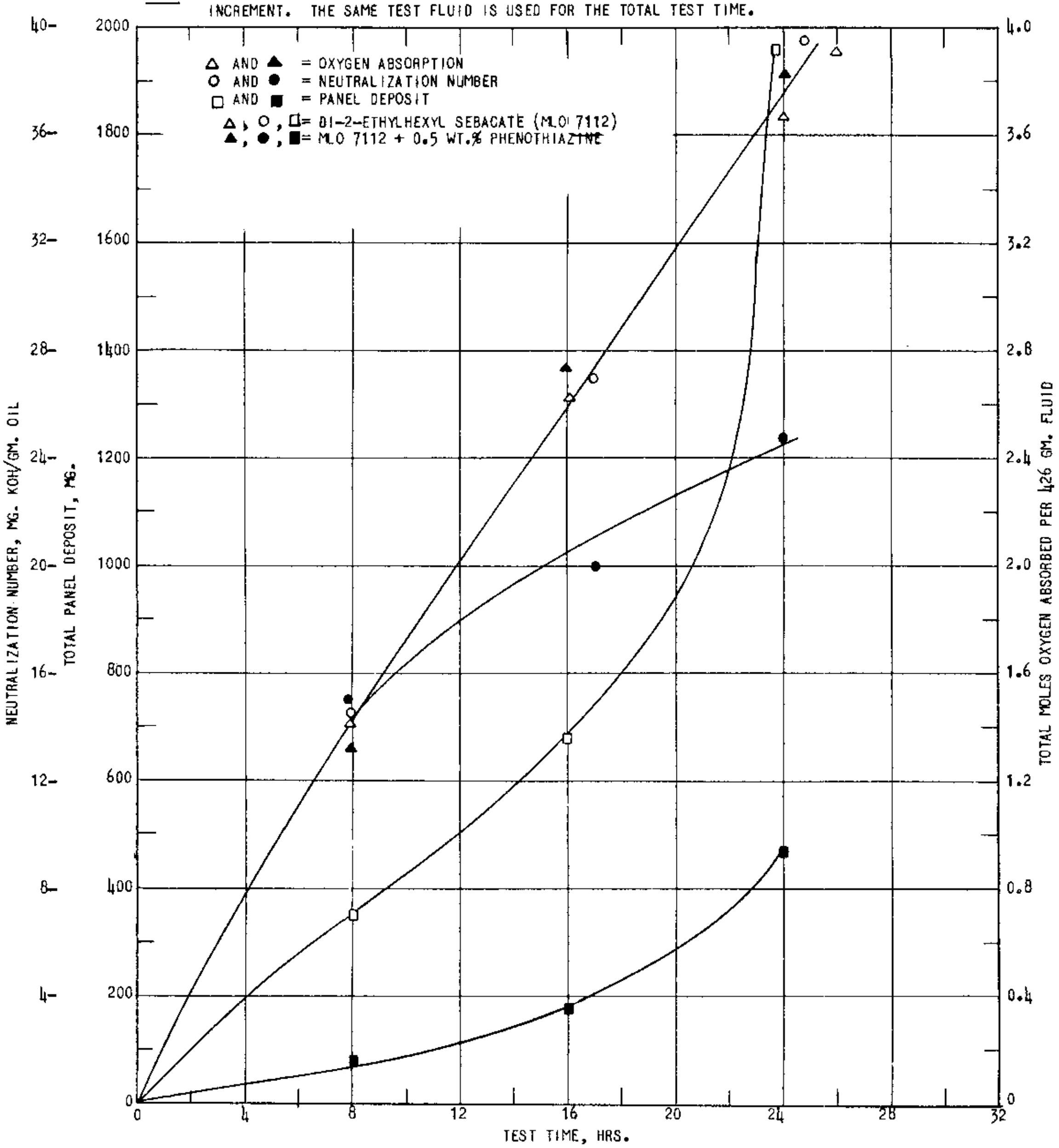


Figure 65. SUCCESSIVE PANEL COKER TESTS WITH DI-2-ETHYLHEXYL SEBACATE AT 700°F

ALL TESTS CONDUCTED IN THE CONTROLLED ATMOSPHERE PANEL COKER

TEST CONDITIONS INCLUDE: TEST TIME = 8-HOUR INCREMENTS; PANEL TEMPERATURE = 700°F ; AND AIR RATE = 25 LITERS PER HOUR.

NOTE: TESTS ARE RUN IN SUCCESSIVE 8-HOUR INCREMENTS. A NEW TEST PANEL IS USED FOR EACH 8-HOUR INCREMENT. THE SAME TEST FLUID IS USED FOR THE TOTAL TEST TIME.

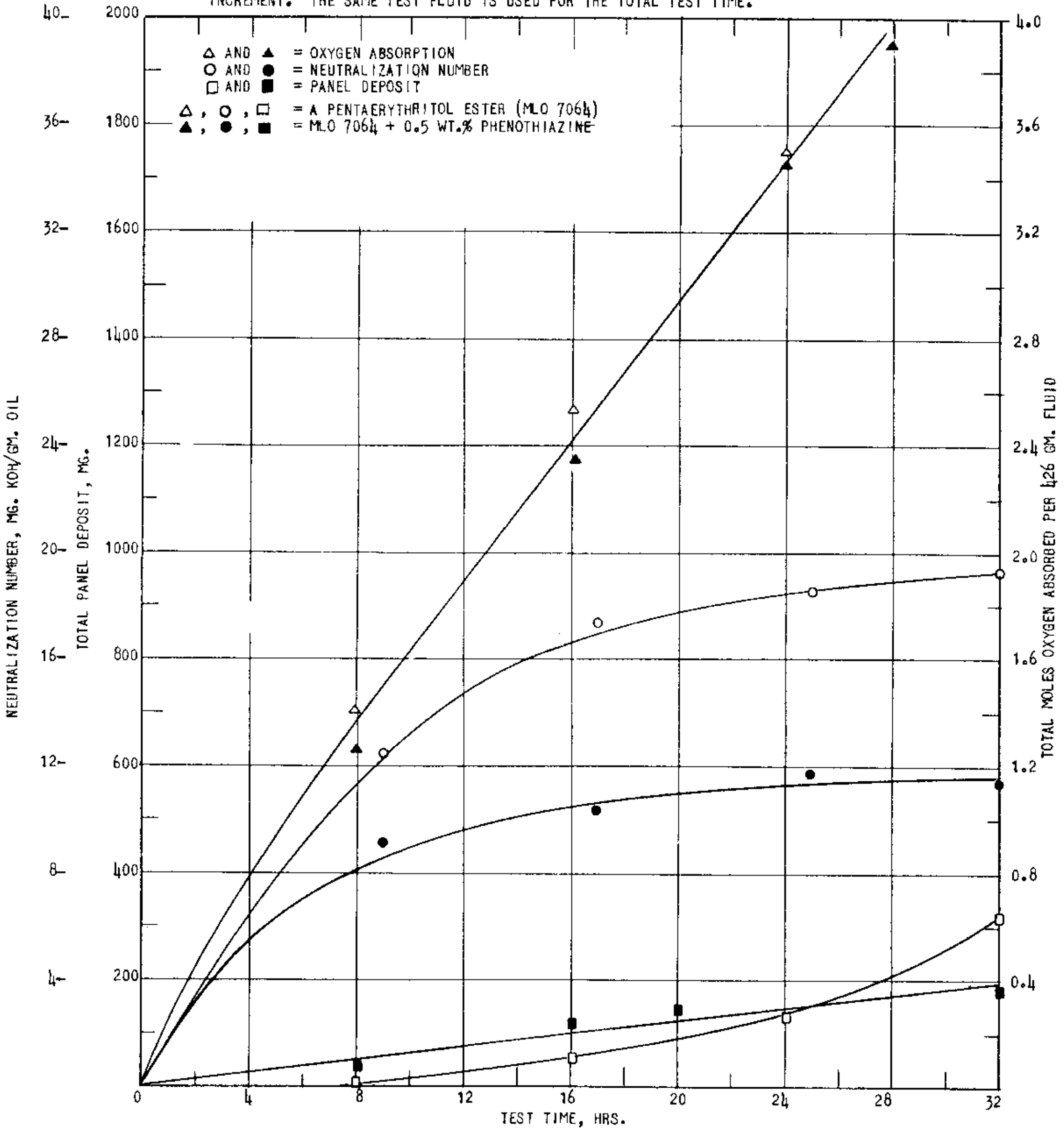


Figure 66. SUCCESSIVE PANEL COKER TESTS WITH A PENTAERYTHRITOL ESTER AT 700°F

ALL TESTS CONDUCTED IN THE CONTROLLED ATMOSPHERE PANEL COKER

TEST CONDITIONS INCLUDE: TEST TIME = 8-HOUR INCREMENTS; PANEL TEMPERATURE = 700°F.; AND AIR RATE = 25 LITERS PER HOUR.

NOTE: TESTS ARE RUN IN SUCCESSIVE 8-HOUR INCREMENTS. A NEW TEST PANEL IS USED FOR EACH 8-HOUR INCREMENT. THE SAME TEST FLUID IS USED FOR THE TOTAL TEST TIME.

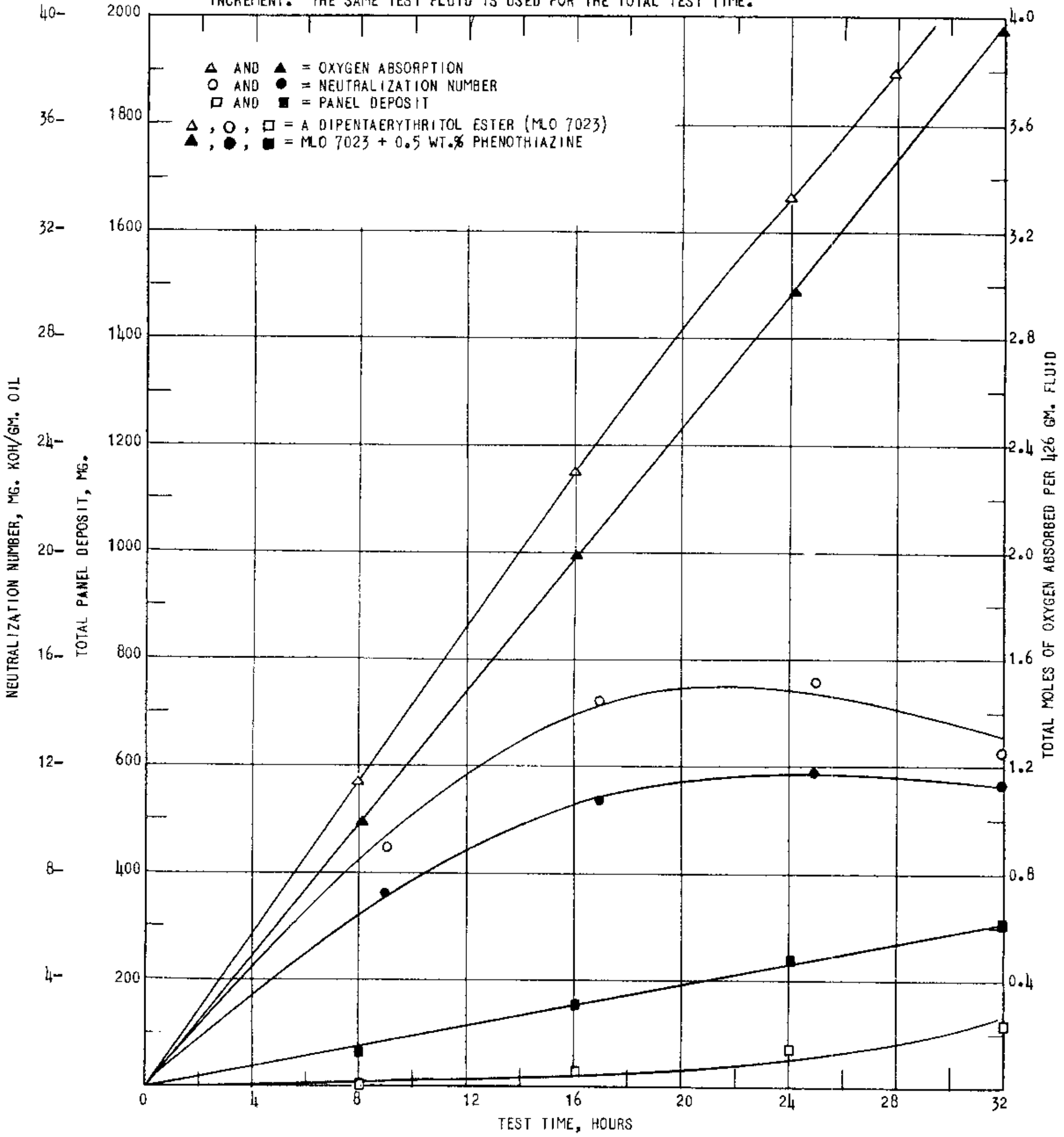


Figure 67. SUCCESSIVE PANEL COKER TESTS WITH A DIPENTAERYTHRITOL ESTER AT 700°F

ALL TESTS CONDUCTED IN THE CONTROLLED ATMOSPHERE PANEL COKER

TEST CONDITIONS INCLUDE: TEST TIME = 8-HOUR INCREMENTS; PANEL TEMPERATURE = 700°F ; AND AIR RATE = 25 LITERS PER HOUR.

NOTE: TESTS ARE RUN IN SUCCESSIVE 8-HOUR INCREMENTS. A NEW TEST PANEL IS USED FOR EACH 8-HOUR INCREMENT. THE SAME TEST FLUID IS USED FOR THE TOTAL TEST TIME.

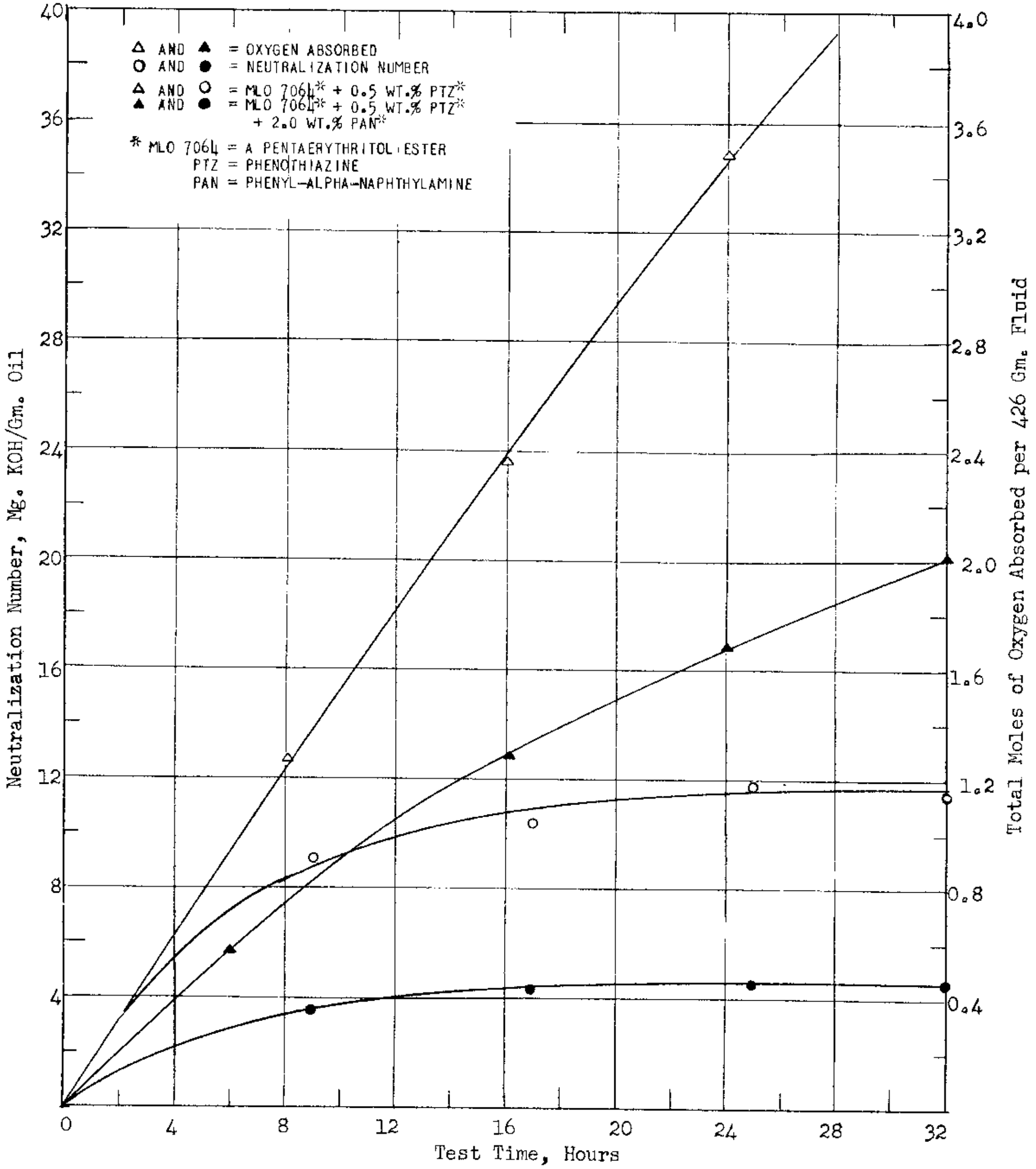
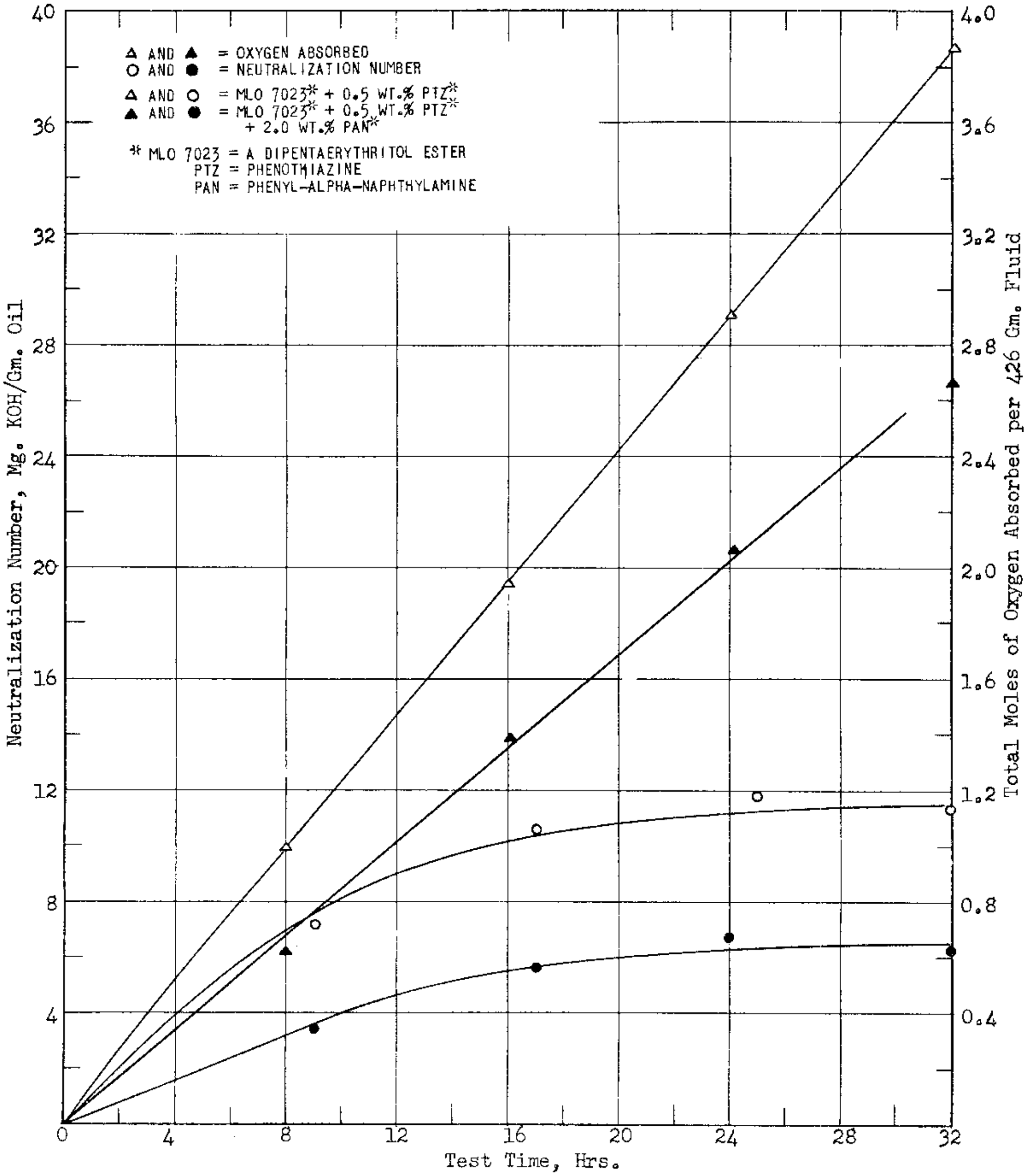


Figure 68. SUCCESSIVE PANEL COKER TESTS WITH PENTAERYTHRITOL ESTER BLENDS AT 700°F



ALL TESTS CONDUCTED IN THE CONTROLLED ATMOSPHERE PANEL COKER.

TEST CONDITIONS INCLUDE: TEST TIME = 8-HOUR INCREMENTS; PANEL TEMPERATURE = 700°F ; AND AIR RATE = 25 LITERS PER HOUR.

NOTE: TESTS ARE RUN IN SUCCESSIVE 8-HOUR INCREMENTS. A NEW TEST PANEL IS USED FOR EACH 8-HOUR INCREMENT. THE SAME TEST FLUID IS USED FOR THE TOTAL TEST TIME.

Figure 69. SUCCESSIVE PANEL COKER TESTS WITH DIPENTAERYTHRITOL ESTER BLENDS AT 700°F

ALL TESTS CONDUCTED IN THE CONTROLLED ATMOSPHERE PANEL COKER.

TEST CONDITIONS INCLUDE: TEST TIME = 8-HOUR INCREMENTS; PANEL TEMPERATURES 700°F ; AND AIR RATE = 25 LITERS PER HOUR.

NOTE: TESTS ARE RUN IN SUCCESSIVE 8-HOUR INCREMENTS. A NEW TEST PANEL IS USED FOR EACH 8-HOUR INCREMENT. THE SAME TEST FLUID IS USED FOR THE TOTAL TEST TIME.

TEST FLUID: A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)

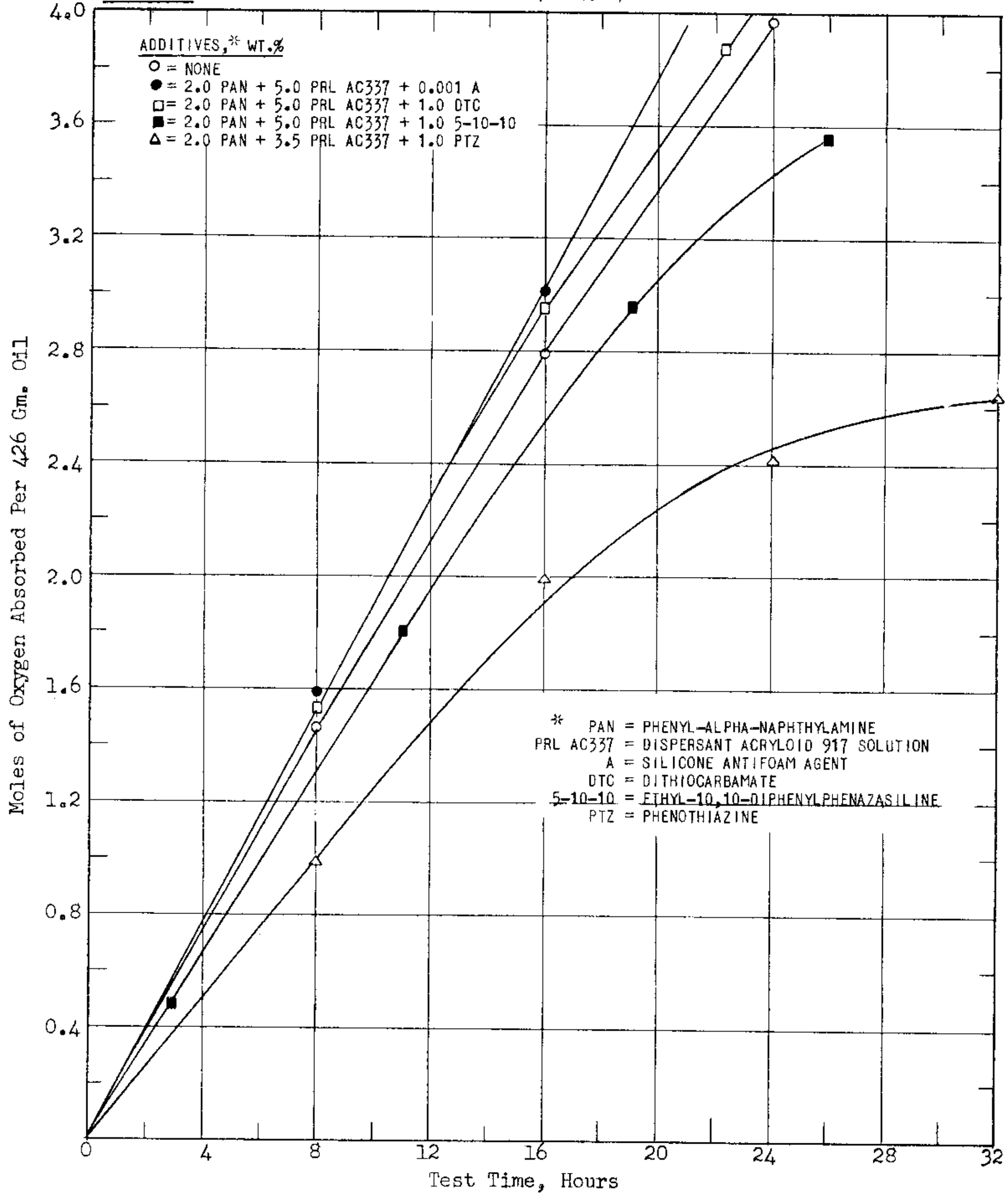


Figure 70. EFFECT OF ADDITIVE COMBINATIONS ON OXYGEN ASSIMILATION IN SUCCESSIVE PANEL COKER TESTS

ALL TESTS CONDUCTED IN THE CONTROLLED ATMOSPHERE PANEL COKER

TEST CONDITIONS INCLUDE: TEST TIME = 8-HOUR INCREMENTS; PANEL TEMPERATURE = 700°F ; AND AIR RATE = 25 LITERS PER HOUR.

NOTE: TESTS ARE RUN IN SUCCESSIVE 8-HOUR INCREMENTS. A NEW TEST PANEL IS USED FOR EACH 8-HOUR INCREMENT. THE SAME TEST FLUID IS USED FOR THE TOTAL TEST TIME.

TEST FLUID: A SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7301)

ADDITIVES,* WT.%

○ = NONE
● = 2.0 PAN + 5.0 PRL AC337 + 0.001 ANTIFOAM
□ = 2.0 PAN + 5.0 PRL AC337 + 1.0 DITHIOCARBAMATE
■ = 2.0 PAN + 5.0 PRL AC337 + 1.0 5-ETHYL-10,10-DIPHENYLPHENAZASILINE
△ = 2.0 PAN + 3.5 PRL AC337 + 1.0 PEHNOTHIAZINE

* PAN = PHENYL-ALPHA-NAPHTHYLAMINE
PRL AC337 = A DISPERSANT ACRYLOID 917 SOLUTION (30 WT.% IN MINERAL OIL)

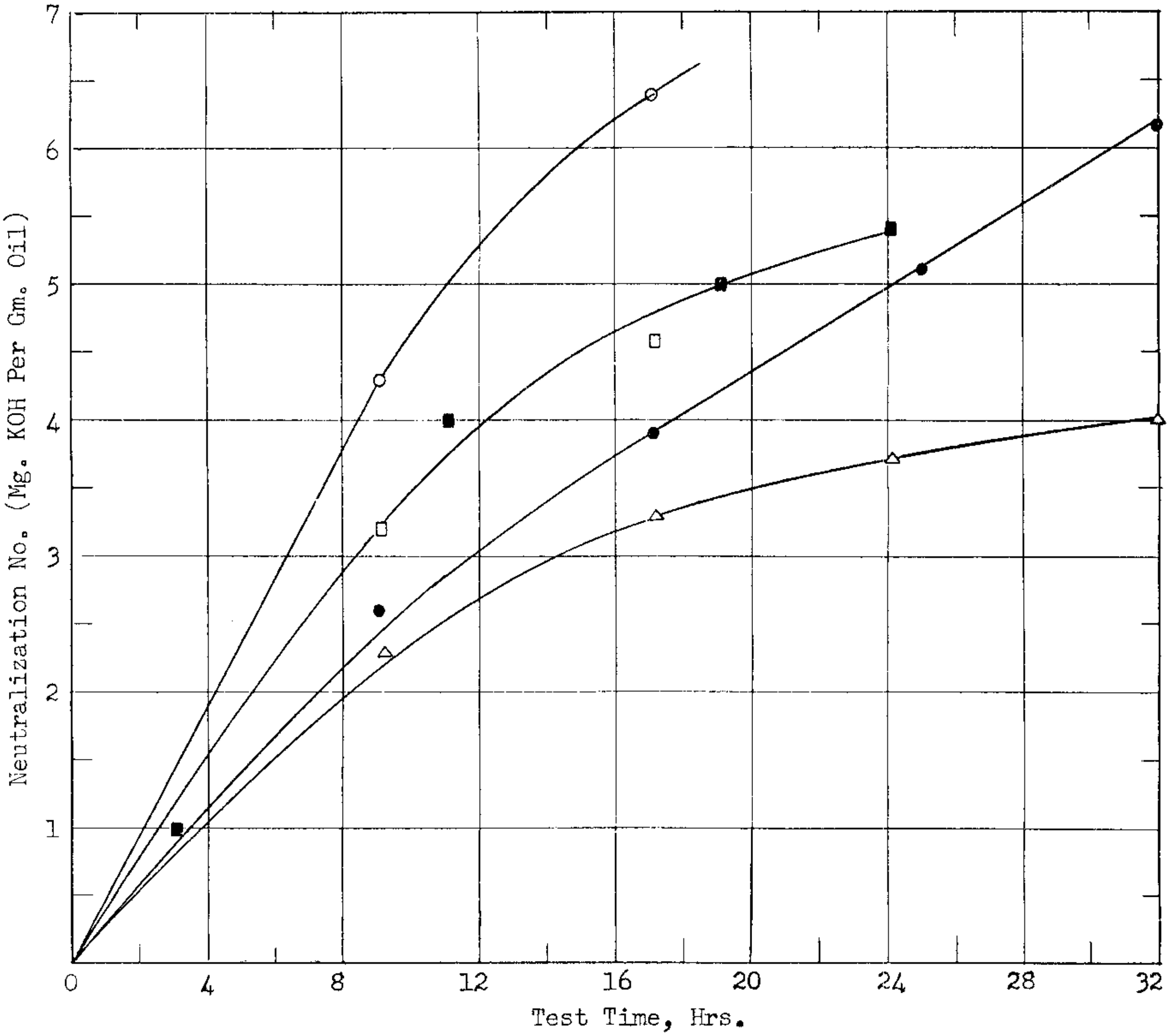


Figure 71. EFFECT OF ADDITIVE COMBINATIONS ON NEUTRALIZATION NUMBER IN SUCCESSIVE PANEL COKER TESTS

One of the problems noted with the single-pass rig was an apparent scatter of results with the same or essentially the same test fluid. Considerable work has been done to determine the cause of this apparent scatter of data. It was determined from a review of the data that the deposit values for given fluid types did show a scatter but generally did not vary excessively from an average value for the specific fluid type. While fluid properties for the used fluid are measured, the primary measurement discussed in this report is the deposit on the metal tube.

1. Effect of Storage Time on Deposition. Test values in the single-pass rig are available over a three-year period for several fluid types. A number of these fluids show higher values of deposition in recent tests than was obtained in earlier tests under the same conditions. This general drift in values was noted particularly in the cases of a polyolefin MLO 7123 and a heavy paraffinic neutral MLO 7120. These two fluids have been evaluated over the three-year test program in the rig. All of the fluids showing the progressive increase in deposit values are uninhibited stocks which are prone to oxidize under storage conditions. The data for MLO 7120 in the single-pass rig as a function of storage time of the sample is shown on Table 94 and Figure 72. Similar rig values for MLO 7123 over a several-year storage span are shown in Table 95. Both fluids indicate the consistent increase with storage time of the test fluids. It should be emphasized that the deposit values for these fluids range from original values of the order of 0.02 weight per cent to 0.1 weight per cent after three years of storage. These data suggest progressive oxidative deterioration of the uninhibited hydrocarbons with increased storage time with a resultant increase in deposition values. The small total amounts of deposit involved and the small changes in fluid properties noted on storage makes additional corroborative evidence difficult to obtain.

2. Effect of Acid Phosphite Additives on Deposition. In the critical examination of the scatter of deposition values for fluids of established behavior, it was noted that unusually low values for a fluid followed a test in which an alkyl acid phosphite was used as an additive in the test fluid. When this alkyl acid phosphite additive is used in 0.5 weight per cent concentration in either a mineral oil or ester, there is a general increase in sludging and deposit formation for the fluid under bulk oil or thin film oxidation tests. These trends have been noted in 500°F bulk oil and successive oxidation tests, thin film oxidation tests at 347° and 500°F, the panel cokers, and in the single-pass tests at 27 liters of air per hour. Further studies in the single-pass rig have shown, however, that lower concentrations of dialkyl acid phosphite additive do, in fact, reduce the deposit.

A series of tests with a super-refined paraffinic neutral is shown in Table 96. These data are shown to illustrate the sensitivity of the deposition to small concentrations of the dialkyl acid phosphite. Test 288 contained 0.5 weight per cent dialkyl acid phosphite. The subsequent Test 289 was conducted with a fluid containing no dialkyl acid phosphite. However, the deposit value for Test 289 was much lower than anticipated from the fluid composition being evaluated. Between tests the single-pass rig is thoroughly cleaned and flushed with solvent and fresh test fluid. It is estimated that the maximum concentration of original test fluid that could remain in the test system after a cleaning operation is of the order of one to two per cent of the fluid charge.

Tests 291 and 292 show higher deposition typical of the base fluid without the dialkyl acid phosphite. Tests 293 through 296 were conducted with decreasing quantities of dialkyl acid phosphite. Concentrations of 0.1 to 0.0001 weight per cent dialkyl acid phosphite all show a reduced deposit value. Test 297 contained no dialkyl acid phosphite and followed a test containing only 0.0001 weight per cent dialkyl acid phosphite. The results show a high deposition value suggesting less than an effective concentration of dialkyl acid phosphite.

In the test sequence from 293 to 297, the concentration of dialkyl acid phosphite was decreased. The test sequence 298, 299, 333, and 334 shows the effect of increasing dialkyl acid phosphite concentration. Concentrations of 0.001 to 0.1 weight per cent dialkyl acid phosphite appears to be equally effective in reducing deposit values. The test (No. 298) following evaluation of a non-additive fluid shows a high value for 0.0001 weight per cent dialkyl acid phosphite. Tests 335 and 336 show high deposit values typical of the base stock. It is interesting to note that throughout this sequence of tests the total insolubles in the liquid show excellent correlation with the deposit values on the tube. The amount of oxygen assimilated for every test shown on Table 96 is the same within the limits of error of the determination.

These experiments show that the dialkyl acid phosphite is effective in lowering deposit build-up on hot metal surfaces when used in small concentrations. Data shown on Table 97 illustrate several cases of reduced deposits in tests with fluids of known deposition tendencies that appear to be due to contamination from a previous test on a fluid containing dialkyl acid phosphite. The effect of additives on deposit formation in the single-pass rig needs further study to determine the extent of these effects and effective cleaning techniques to prevent the carry over of these effects to subsequent tests.

3. Effect of Fluid Volatility on Deposit Formation. Fluid volatility has been shown to be a critical factor in the coke deposit in the panel cokers. These data are discussed in Section I-2 of this report. Volatility also appears to be a factor in the single-pass rig tests. A number of paraffinic neutrals of increasing viscosity level and boiling range have been evaluated in the single-pass rig and the results shown in Table 98. Results for a similar series of naphthenic mineral oils are shown in Table 99. Deposit values for several narrow boiling fractions of paraffinic neutrals obtained by vacuum fractionation are shown in Table 100. The viscosity properties and approximate boiling ranges of the paraffins and naphthenes discussed here are shown in Table 101. In general, the boiling range of the commercial neutrals evaluated is of the order of 200°F. The narrow boiling fractions derived from these neutrals have a boiling range of the order of 25°F.

The highest boiling of the paraffinic neutrals (MLO 7376) is the only one of the paraffinic and naphthenic neutrals to exhibit a low deposit value. The highest naphthenic mineral oil (MLO 7273) has essentially the same boiling range as paraffinic neutral MLO 7375. Both of these materials show a high deposit value.

There is some indication of the importance of boiling range in the fractions of the paraffinic neutrals. The residues of the distillations of MLO 7374 and MLO 7375, representing about 10 per cent of the overall fluid, show a reduced deposit level. The fraction of MLO 7376 boiling between 925° and 950°F and the 40 per cent residue boiling above 950°F. show low deposit values while a fraction boiling between 900° and 925°F. shows a high deposit value. These data indicate that volatility or boiling range of the fraction does influence deposit values. The volatility of the fluid does not affect the amount of oxygen assimilated in this series of tests.

A number of tests have been conducted to determine the amount of non-volatile residue that must be added to a volatile neutral fraction to lower substantially the deposit value. The non-volatile or low volatility component in the blends is a paraffinic resin (MLO 7308) which shows a very low deposit value when tested neat. The effect of increasing concentration of MLO 7308 in a paraffinic neutral MLO 7375 is shown on Table 102. These data indicate a lowering of deposit with increasing MLO 7308 concentration from 10 to 25 weight per cent.

A group of neutrals increasing in boiling ranges have been evaluated with 20 weight per cent MLO 7308 as shown on Table 103. For a constant paraffinic resin concentration, the deposit value decreases with decreasing volatility of the paraffinic neutral fraction. Data are presented in Table 104 to show a similar trend with naphthenic neutrals.

4. <u>Rate of Deposit Formation as a Function of Test Time</u>. Thus far, quantitative oxidation data indicate about the same rate of oxidation for all of the neutrals tested. The amount of deposit for the 5-hour test period varies greatly depending on the properties and type of test fluid. Additional studies have been conducted to determine the effect of test time on deposit formation and oxidation rate. Tests of 1, 2, 3, 4, and 5 hours duration have been conducted with each of five neutrals. The results of these tests are shown on Tables 105 and 106 and Figures 73 and 74.

The two naphthenic and two paraffinic neutrals that show a high deposit value after five hours, exhibit an initially low rate of deposit formation followed by a substantial increase in the rate of deposit formation. In all four cases, a constant rate of deposit formation is established for the final two to three hours of the five-hour test period. In the case of MLO 7120 which produces a low total deposit, the rate of deposit formation appears to be constant throughout the five-hour test period.

It should be emphasized that the behavior in the single-pass rig differs considerably from that in the panel coker. The highest rate of deposit formation in the panel coker occurs at the beginning of the test and, in most cases, decreases with increasing test time. The oxidation rate may also decrease with increasing test time. In the single-pass rig, the rate of oxygen assimilation remains constant throughout the test period. In the case of fluids exhibiting a high deposit value, the deposit value appears to increase sharply following an induction period during which deposit formation is low.

5. Effect of Metal Type on Deposit. All of the discussions, thus far, are for rig tests using an aluminum heat exchanger surface. Extensive bulk oil oxidation tests with metal catalysts have shown that aluminum is inert under these conditions for a wide variety of test fluids and temperatures up to 700°F. That is, no corrosion has been noted for the aluminum and no catalytic activity has been shown for the aluminum on the oxidation rate. Under bulk oil oxidation conditions at elevated temperatures, steel has shown, in many cases, a substantial catalytic effect on the oxidation reaction and copper is corroded by many of the oxidized test fluids.

Steel and copper surfaces have, therefore, been used in place of the aluminum to determine the effect of the metal surface on deposit formation and oxidation. Four mineral oils showing deposit values with the aluminum surfaces ranging from 10 to 2000 milligrams have been chosen for this study. The results of the study are shown on Table 107. The test conditions in the rig are the same for all these tests with the exception of the hot metal surface used. The inner surface of the heat exchanger for these tests was changed by using half-inch steel or copper tubing to replace the aluminum tubing.

The method for determining the deposit value was changed somewhat for the steel and copper. Both of these materials gained weight upon heating the tube surface with a Meeker burner because of the oxide formation. The flame treatment for removing the deposit was not used with these metals. Instead, a more vigorous solvent and brushing treatment was used to remove the deposit. The steel and copper can be more vigorously cleaned by solvents and brushing without loss in the metal from abrasion than in the case of aluminum.

The results of these tests comparing the effects of copper, steel, and aluminum are shown in Table 107. The four fluids are rated in the same order of deposit forming tendencies by each of the three metals. A comparison of oxygen assimilation and fluid insolubles plus the tube deposit indicate the same order of reaction rate and fluid deterioration for the three metals. The somewhat higher values for the deposits on the copper in the case of the resin and bright stock may be attributable to actual reaction of oxidized products with the copper and the accumulation of these corrosion products on the copper surface. The cleaned copper surface following these tests appeared to be pitted.

6. Effect of Fluid Formulation and Blending of Base Stocks on Deposit Formation. Several formulations and blends have been prepared with polyolefin and ester base stocks for evaluation in the single-pass rig. Data for blends prepared with polyolefin MLO 7123 are shown in Table 108. The unsaturated polyolefin, as indicated previously, has shown a trend toward higher values of deposit with storage time. This trend is again illustrated by the three values shown for MLO 7123 without additives. The blends were all evaluated at about the same storage time as the highest of the three values shown for MLO 7123. The polyolefin has been percolated through super-filtrol and then evaluated in the rig. The super-filtrol treatment did not lower the deposit value. The addition of silicone antifoam additive or phenyl-alpha-naphthylamine antioxidant did not significantly alter the deposit values. The use of 0.2 weight per cent dialkyl acid phosphite did increase the deposit value. The presence of the dialkyl acid phosphite in this concentration range generally lowers deposit values in the rig tests with conventional mineral oils. The mixture of MLO 7123 with substantial quantities of conventional mineral oils tends to increase the deposit formation far beyond that obtained from either component.

By comparison with the conventional mineral oils in the rig tests, two other factors should be noted. The oxygen assimilated by the polyolefin is only about half as much as that assimilated by the conventional mineral oils under the same conditions. Secondly, the oil insolubles and the water formed in the oxidation reaction are very low compared with the deposit on the metal surface. The data for the 50:50 blend of MLO 7123 and a paraffinic neutral show an oxygen assimilation, total insolubles, and water formation values approaching those of the conventional mineral oils.

The effect of hydrogenating the polyolefin is shown in Table 109. In bulk oil oxidation tests at 347°F, hydrogenation greatly improves the stable life of inhibited polyolefins. In fact, inhibitors in the unsaturated polyolefins provide essentially no stable life or induction period in the 347°F oxidation tests. The unsaturated polyolefin, on the other hand, provides somewhat better oxygen tolerance in bulk oil oxidation tests at 500°F The saturated polyolefin MLO 7124 exhibits relatively low deposit values when evaluated without additives. The addition of oxidation inhibitors and/or dialkyl acid phosphite increases substantially the deposit forming tendencies. Blending MLO 7124 with a paraffinic neutral again causes a deposit value considerably higher than either component evaluated alone. The oxygen assimilation for the MLO 7124 fluid is about midway between the values obtained for the unsaturated polyolefin MLO 7123 and the conventional mineral oils.

Deposit values for two esters and a blend of these esters are shown on Table 110. The conventional di-2-ethylhexyl sebacate gives a high deposit value while the MLO 7333 polyester gives a low deposit value. A 50:50 blend of these two ester materials provides an intermediate deposit value. This behavior parallels that of a naphthenic neutral, a paraffinic resin, and blends of these two mineral oils. These data show that molecular size appears to be important in both the ester and mineral oil series.

The evaluation of a silicone 81406 fluid containing 3.0 weight per cent tinsil (MLO 7265) is discussed in report WADC TR 55-30 part VI. Properties such as lubricity, thermal stability, and oxidation and corrosion behavior at 347°, 500°, and 700°F. are included in that report.

The data obtained for silicone 81406 fluids with and without the tin additive in the single-pass high temperature lube rig are shown on Table 111. The tube deposit in both cases is low. On standing at room temperature, the exit fluid gelled and it was not possible to determine a viscosity change for the fluid.

K. CONCLUSIONS. The studies presented in this report emphasize the need for a continued evaluation of materials proposed for use as base stocks for fluids and lubricants and to determine the effect of additive packages on these fluids under comparable test conditions. Studies of the effect of structure and refining on the behavior of such materials should be continued.

The poor lubricity characteristics with steel-on-steel surfaces shown by silicon-containing fluids have been attributed to several of the unique properties of these fluids. These properties include the stability of the silicone structure to deterioration by thermal and oxidizing environments, the non-wetting characteristics of these fluids on metal surfaces, and the high compressibility and viscosity-pressure coefficients of the silicones.

A survey of experimentally determined lubricity data obtained by this Laboratory over a period of years points up an additional potential explanation for lubrication difficulties encountered with these silicone-containing fluids in ferrous bearing systems. Lubricity tests in a gear pump, a vane pump, and in the Shell four-ball wear tester point out consistently evidence of the formation of a relatively soft but inert compound or alloy involving iron and silicon. The mechanism of the antiwear action of materials such as tricresyl phosphate has been shown to comprise the formation at the bearing surface of an iron-phosphorus alloy of relatively low melting point and good ductility.

The silicates and silicones show antiwear characteristics under low bearing loads in boundary conditions coupled with consistently poor antiseize and antiweld properties under more severe boundary conditions. This behavior of the silicones and silicates can be consistently demonstrated to be a function of chemical reactivity with the bearing surface when these materials are tested neat or as an additive in mineral oils and esters. The data indicate that the antiwear behavior of these silicon-containing materials parallels closely the mechanism of the phosphorous type antiwear additives. This parallel suggests that the reaction of the iron and silicon forms a lower melting ductile surface film that is more inert toward further chemical reaction than the original steel surface.

Data obtained on the charging stock, the dewaxed oil, and the wax fraction for a number of experimental dewaxings with mineral oils and hydrocarbons show that, in all cases, sufficiently severe dewaxings produce an oil phase that exhibits an extrapolated viscosity value of 200,000 to 500,000

Table 94

EFFECT OF STORAGE TIME ON THE DEPOSITION BEHAVIOR OF A PARAFFINIC NEUTRAL

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG.

TEST CONDITIONS INCLUDE: TEST TIME = 5 HOURS; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1 ML. PER MINUTE; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

TEST FLUID	A PARAFFINIC HEAVY NEUTRAL (MLO 7120)					
APPROX. STORAGE TIME, MONTHS	0	3	6	12	15	20
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	38	38	38	38	38	38
APPROX. AMOUNT O_2 USED, GMS. (1)	–	35	35	34	34	35
MOLS O_2 USED/426 GMS. FLUID (2)	–	1.9	1.9	1.8	1.9	2.0
TEST FLUID CHARGED, GMS.	251	241	240	248	240	241
TUBE DEPOSIT						
TOTAL DEPOSIT, MGS.	40	79	102	125	181	234
WT.% OF FLUID CHARGED	0.016	0.033	0.043	0.051	0.075	0.097
FLUID PROPERTIES						
INSOLUBLES IN EXIT FLUID						
MG./100 GM. FLUID CHARGED						
SOLIDS	310	1160	1020	762	1970	3360
WATER	2860	4000	2960	3000	3300	3520
WT.% OF FLUID CHARGED						
SOLIDS	0.3	1.2	1.0	0.8	2.0	3.4
WATER	2.9	4.0	3.0	3.0	3.3	3.5
OVERALL LIQUID LOSS, WT.%	20	12	14	10	7	7
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	+18	–	–36	–15	–16	–26
NEUT. NO. (MG. KOH/GM. FLUID)						
ORIGINAL	0.1	0.1	0.0	0.0	0.0	0.0
FINAL	4.3	3.5	4.6	5.4	5.3	5.4

(1) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF OXYGEN FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG

TEST CONDITIONS INCLUDE: TEST TIME = 5 HOURS; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1 ML. PER MINUTE; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

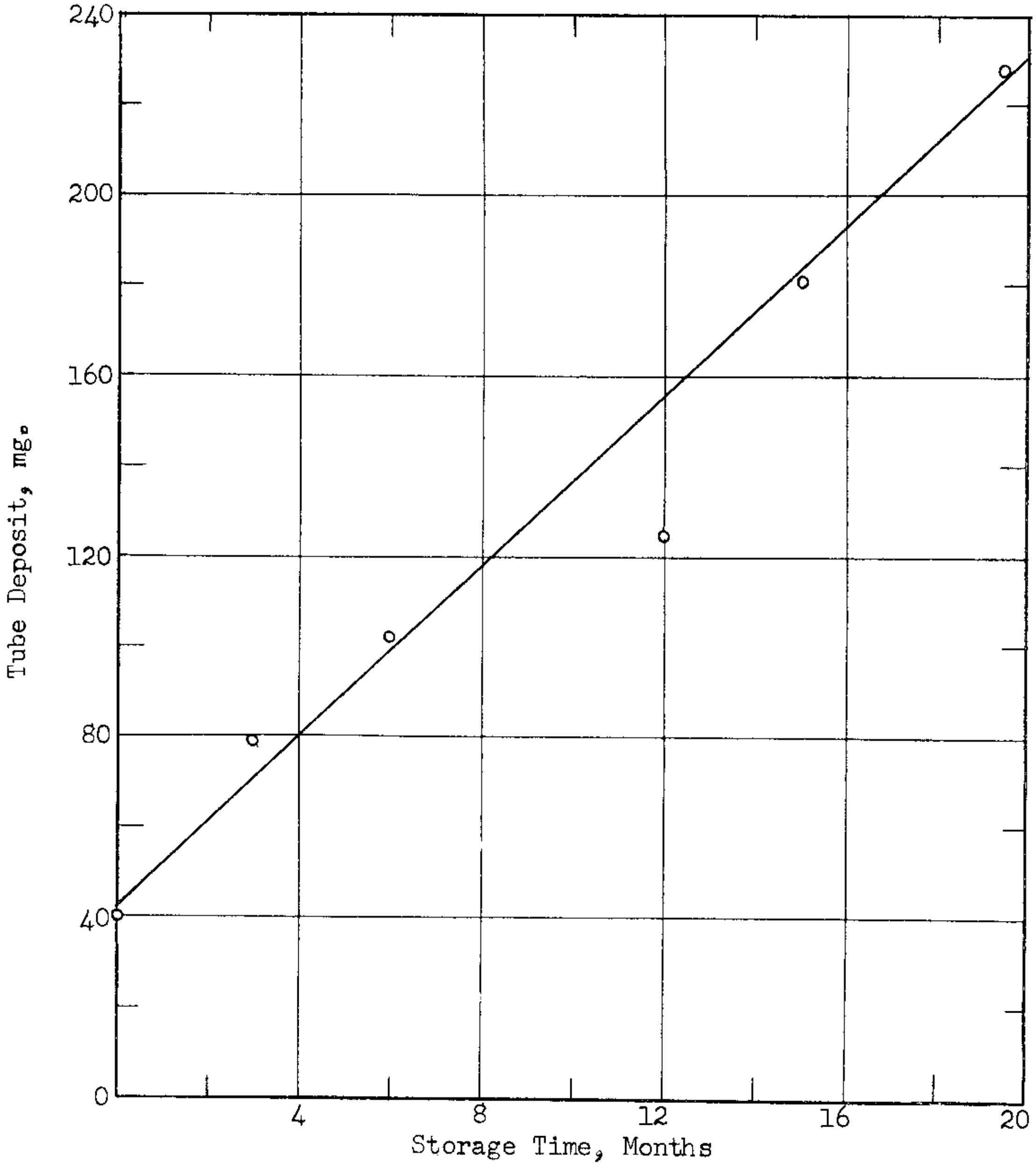


Figure 72. EFFECT OF STORAGE TIME ON THE DEPOSITION BEHAVIOR OF A PARAFFINIC NEUTRAL

Table 95

EFFECT OF STORAGE TIME ON THE DEPOSITION BEHAVIOR OF A POLYOLEFIN

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG

TEST CONDITIONS INCLUDE: TEST TIME = 5 HOURS; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 10 LITERS PER HOUR; FLUID RATE = 1 MILLILITER PER MINUTE; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 8 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

TEST FLUID	A POLYOLEFIN HYDROCARBON (MLO 7123)			
APPROX. STORAGE TIME, MONTHS	0	3	29	29
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	14	14	14	14
APPROX. AMOUNT O_2 USED, GMS. (1)	13	-	11	11
MOLS O_2 USED/426 GMS. FLUID (2)	0.7	-	0.7	0.6
TEST FLUID CHARGED, GMS.	231	231	229	232
TUBE DEPOSIT				
TOTAL DEPOSIT, MGS.	48	46	229	268
WT.% OF FLUID CHARGED	0.021	0.020	0.10	0.12
FLUID PROPERTIES				
INSOLUBLES IN EXIT FLUID				
MG./100 GM. FLUID CHARGED				
SOLIDS	91	104	100	91
WATER	1200	430	1790	1860
WT.% OF FLUID CHARGED				
SOLIDS	0.1	0.1	0.1	0.1
WATER	1.2	0.4	1.8	1.9
OVERALL LIQUID LOSS, WT.%	-	9	5	4
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	-	-	-86	-86
NEUT. NO. (MG. KOH/GM. FLUID)				
ORIGINAL	0.1	0.1	0.1	0.1
FINAL	1.1	0.5	1.2	1.2

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 96

EFFECT OF A DIALKYL ACID PHOSPHITE ON THE DEPOSITION BEHAVIOR OF A HYDROGENATED PARAFFINIC NEUTRAL

TEST CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG.

TEST CONDITIONS INCLUDE: TEST TIME = 5 HOURS; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1 ML. PER MINUTE; AND RESIDENCE TIME IN HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

TEST FLUID	A HYDROGENATED PARAFFINIC NEUTRAL (MLO 7212)													
ACRYLOID 917, WT.%	<-- NONE -->			<--- 5.0 --->			5.0	0.5	0.05	0.005	0.005	0.05	0.05	0.5
DIISOPROPYL ACID PHOSPHITE, WT.%	<-- NONE -->			<--- NONE --->			0.1	0.01	0.001	0.0001	0.0001	0.001	0.001	0.1
TEST NUMBER	289*	292	297	291	335	336	293	294	295	296	298	299	333	334
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	38	38	38	38	38	38	38	38	38	38	38	38	38	38
APPROX. AMOUNT O_2 USED, GMS. (1)	37	37	36	37	37	37	36	37	37	37	37	37	37	36
MOLS O_2 USED/426 GMS. FLUID (2)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.1	2.1	2.0	2.0	2.0	2.0	2.0
TEST FLUID CHARGED, GMS.	247	241	241	241	247	240	239	237	237	241	243	245	244	243
TUBE DEPOSIT														
TOTAL DEPOSIT, MGS.	10	63	160	101	108	221	27	34	35	22	107	39	43	5
WT.% OF FLUID CHARGED	0.00	0.03	0.06	0.04	0.04	0.09	0.01	0.01	0.01	0.01	0.04	0.02	0.02	0.00
FLUID PROPERTIES														
INSOLUBLES IN EXIT FLUID (3)														
MG./100 GM. FLUID CHARGED														
SOLIDS	778	996	2340	1480	1420	2870	841	862	741	917	1740	1180	949	750
WATER	3850	3330	4220	4160	4460	3860	5230	5250	3860	4430	4780	3520	4890	6110
WT.% OF FLUID CHARGED														
SOLIDS	0.8	1.0	2.3	1.5	1.4	2.9	0.8	0.9	0.7	0.9	1.7	1.2	0.9	0.7
WATER	3.8	3.3	4.2	4.2	4.5	3.9	5.2	5.2	3.9	4.4	4.8	3.5	4.9	6.1
OVERALL LIQUID LOSS, WT.%	14	19	13	15	9	9	17	17	16	9	10	2	8	11
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	-27	-34	-28	-56	-52	-49	-44	-35	-32	-23	-33	-34	-26	-45
NEUT. NO. (MG. KOH/GM. FLUID)														
ORIGINAL	0.1	0.1	0.1	0.1	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
FINAL	6.1	5.1	5.1	5.8	6.3	5.5	6.4	6.5	5.8	6.2	5.2	4.6	5.6	6.5

* THE TEST FLUID FOR TEST 288 CONTAINED 0.5 WEIGHT PER CENT DIISOPROPYL ACID PHOSPHITE.

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYLHEXYL SEBACATE IS 426.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 97

RESIDUAL EFFECT OF A DIALKYL ACID PHOSPHITE

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG.

TEST CONDITIONS INCLUDE: TEST TIME AS INDICATED; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1 MILLILITER PER MINUTE; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

TEST DESIGNATION: A = A TYPICAL TEST WITH THE FLUID DESIGNATED.
B = A TEST WITH THE SAME FLUID WHICH WAS CONDUCTED IMMEDIATELY FOLLOWING A TEST WITH A FLUID CONTAINING A DIALKYL ACID PHOSPHITE.

TEST FLUID	A NAPHTHENIC NEUTRAL (PRL 3467)		SUPER-REFINED PARAFFINIC NEUTRAL (MLO 7296)		PARAFFINIC NEUTRAL (MLO 7120)		PARAFFINIC NEUTRAL (MLO 7212)	
TEST DESIGNATION	A	B	A	B	A	B	A	B
TEST TIME	3.5(A)	5	5	5	5	5	5	5
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	28	38	38	38	38	38	38	38
APPROX. AMOUNT O_2 USED, GMS. (1)	19	-	37	-	34	36	36	37
MOLS O_2 USED/426 GMS. FLUID (2)	1.4	-	2.0	-	1.8	2.0	2.0	2.0
TEST FLUID CHARGED, GMS.	168	244	242	246	248	246	241	247
TUBE DEPOSIT								
TOTAL DEPOSIT, MGS.	2512	42	58	8	125	46	160	10
WT.% OF FLUID CHARGED	1.50	0.02	0.02	0.00	0.05	0.02	0.07	0.00
FLUID PROPERTIES								
INSOLUBLES IN EXIT FLUID								
MG./100 GM. FLUID CHARGED								
SOLIDS	1170	474	830	447	762	585	2340	778
WATER	3210	2050	4110	2280	3300	3410	4220	3850
WT.% OF FLUID CHARGED								
SOLIDS	1.2	0.5	0.8	0.4	0.8	0.6	2.3	0.8
WATER	3.2	2.0	4.1	2.3	3.3	3.4	4.2	3.8
OVERALL LIQUID LOSS, WT.%	9	13	9	18	10	7	13	14
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	-	-9	-34	-7	-15	-20	-28	-27
NEUT. NO. (MG. KOH/GM. FLUID)								
ORIGINAL	0.0	0.0	0.1	0.1	0.0	0.0	0.1	0.1
FINAL	2.3	4.8	4.3	3.7	5.4	5.9	5.1	6.1

(A) TEST WAS TERMINATED BECAUSE ANNULUS OF HEAT EXCHANGER WAS PLUGGED.

(1) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2

(2) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 98

EFFECT OF FLUID VOLATILITY ON THE DEPOSITION BEHAVIOR OF A SERIES OF PARAFFINIC NEUTRALS

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG
TEST CONDITIONS INCLUDE: TEST TIME AS INDICATED; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1.0 ML./MIN.; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

FOR VISCOSITY AND VOLATILITY PROPERTIES, SEE TABLE 101.

TEST FLUID	MLO 7372		MLO 7373	MLO 7374	MLO 7375		MLO 7376
TEST TIME, HOURS	5	5	5	2.6 (A)	5	2.8 (A)	5
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	38	38	38	20	38	21	38
APPROX. AMOUNT O_2 USED, GMS. (1)	37	38	37	19	29	19	34
MOLS O_2 USED/426 GMS. FLUID (2)	2.1	2.1	2.1	2.0	1.5	1.8	1.8
TEST FLUID CHARGED, GMS.	242	242	238	118	251	133	247
TUBE DEPOSIT							
TOTAL DEPOSIT, MG.	1441	1967	2673	2978	3878	3792	51
WT.% OF FLUID CHARGED	0.60	0.81	1.12	2.53	1.54	2.85	0.02
FLUID PROPERTIES							
INSOLUBLES IN EXIT FLUID							
MG./100 GM. FLUID CHARGED							
SOLIDS	584	497	495	421	2690	806	754
WATER	5340	5290	5290	5640	2070	5310	3410
WT.% OF FLUID CHARGED							
SOLIDS	0.6	0.5	0.5	0.4	2.7	0.8	0.8
WATER	5.3	5.3	5.3	5.6	2.1	5.3	3.4
OVERALL LIQUID LOSS, WT.%	7	1	7	11	15	7	7
% CHANGE IN CENTISTOKE VISCOSITY AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	-7	-5	-10	-28	-16	-45	-11
NEUT. NO. (MG. KOH/GM. FLUID)							
ORIGINAL	0.0	0.0	0.0	0.0	0.0	0.0	0.1
FINAL	5.9	5.7	6.0	6.0	4.1	3.9	4.7

(A) TEST WAS TERMINATED BECAUSE ANNULUS OF HEAT EXCHANGER WAS PLUGGED.

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BAIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 99

EFFECT OF FLUID VOLATILITY ON THE DEPOSITION BEHAVIOR OF A SERIES OF NAPHTHENIC NEUTRALS

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG

TEST CONDITIONS INCLUDE: TEST TIME AS INDICATED; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1.0 ML./MIN.; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

FOR VISCOSITY AND VOLATILITY PROPERTIES OF TEST FLUIDS, SEE TABLE 101.

TEST FLUID	MLO 7342		MLO 7343	MLO 7345	MLO 7273
TEST TIME, HOURS	5	5	5	3.5(A)	3.2 (A)
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	38	38	38	27	26
APPROX. AMOUNT O_2 USED, GMS. (1)	37	38	38	24	25
MOLS O_2 USED/426 GMS. FLUID (2)	2.0	2.0	2.1	1.9	1.9
TEST FLUID CHARGED, GMS.	244	245	241	167	154
TUBE DEPOSIT					
TOTAL DEPOSIT, MG.	610	1377	1528	4091	2626
WT.% OF FLUID CHARGED	0.25	0.56	0.63	2.45	1.72
FLUID PROPERTIES					
INSOLUBLES IN EXIT FLUID					
MG./100 GM. FLUID CHARGED					
SOLIDS	501	538	613	462	543
WATER	4620	4550	6550	5170	7630
WT.% OF FLUID CHARGED					
SOLIDS	0.5	0.5	0.6	0.5	0.5
WATER	4.6	4.6	6.6	5.2	7.6
OVERALL LIQUID LOSS, WT.%	4	8	9	4	7
% CHANGE IN CENTISTOKE VISCOSITY AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	-25	-19	-17	-41	-51
NEUT. NO. (MG. KOH/GM. FLUID)					
ORIGINAL	0.0	0.0	0.0	0.0	0.0
FINAL	4.7	5.0	6.3	5.7	5.4

(A) TEST WAS TERMINATED BECAUSE ANNULUS OF HEAT EXCHANGER WAS PLUGGED.

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 100

EFFECT OF FLUID VOLATILITY ON THE DEPOSITION BEHAVIOR OF A SERIES OF NARROW BOILING FRACTIONS OF PARAFFINIC NEUTRALS

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG

TEST CONDITIONS INCLUDE: TEST TIME AS INDICATED; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1.0 ML./MIN.; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM

FOR VISCOSITY AND VOLATILITY PROPERTIES OF TEST FLUIDS, SEE TABLE 101.

					FRACTIONATION OF MLO 7375				FRACTIONATION OF MLO 7376		
TEST FLUID	MLO 7374	MLO 7374-R RESIDUE FROM FRACTIONATION	MLO 7375		MLO 7375-5 FRAC.5	MLO 7375-16 FRAC. 16	MLO 7375-R RESIDUE	MLO 7376	MLO 7376-5 FRAC.5	MLO 7376-12 FRAC. 12	MLO 7376-R RESIDUE
TEST TIME	2.6(A)	5	5	2.8(A)	2.1(A)	5	5	5	4.8(A)	5	5
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	20	38	38	21	16	38	38	38	36	38	38
APPROX. AMOUNT O_2 USED, GMS. (1)	19	35	29	19	16	34	34	34	32	35	34
MOLS O_2 USED/426 GMS. FLUID (2)	2.0	1.9	1.5	1.8	2.0	1.8	1.8	1.8	1.9	1.9	1.8
TEST FLUID CHARGED, GMS.	118	250	251	133	98	248	254	247	238	252	253
TUBE DEPOSIT											
TOTAL DEPOSIT, MGS.	2978	239	3878	3792	1831	1240	140	51	5071	244	69
WT.% OF FLUID CHARGED	2.53	0.10	1.54	2.85	1.87	0.50	0.06	0.02	2.13	0.10	0.03
FLUID PROPERTIES											
INSOLUBLES IN EXIT FLUID											
MG./100 GM. FLUID CHARGED											
SOLIDS	421	4180	2690	806	387	3790	1270	754	2340	2600	1290
WATER	5640	3630	2070	5310	5330	3040	3260	3410	3800	3120	3230
WT.% OF FLUID CHARGED											
SOLIDS	0.4	4.2	2.7	0.8	0.4	3.8	1.2	0.8	2.3	2.6	1.3
WATER	5.6	3.6	2.1	5.4	5.3	3.0	3.3	3.4	3.8	3.1	3.2
OVERALL LIQUID LOSS, WT.%	11	14	15	7	3	12	2	7	13	7	12
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	-28	-37	-16	-45	-28	-39	-8	-11	-43	-15	+2
NEUT. NO. (MG. KOH/GM. FLUID)											
ORIGINAL	0.0	0.1	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.1	0.0
FINAL	6.0	4.6	4.1	3.9	4.8	3.9	4.1	4.7	5.8	5.1	4.8

(A) TEST WAS TERMINATED BECAUSE ANNULUS OF HEAT EXCHANGER WAS PLUGGED.

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 101

VISCOSITY AND VOLATILITY PROPERTIES OF SOME MINERAL OILS

Fluid Designation	Centistoke Viscosity at 210°F	Centistoke Viscosity at 100°F	Approx. Boiling Range, °F
Paraffinic Neutrals			
MLO 7372	2.51	9.89	675-725
MLO 7373	2.84	12.1	680-760
MLO 7374	3.64	17.9	700-850
MLO 7375	5.92	39.1	750-950
MLO 7376	11.5	113	800-1000
Naphthenic Neutrals			
MLO 7342	3.45	17.5	610-880
MLO 7343	3.49	17.8	600-850
MLO 7345	6.07	45.1	625-950
MLO 7273	8.41	78.7	800-1000
Fractions from Paraffinic Neutrals			
MLO 7374-Residue	-	-	>800
MLO 7375-Frac. 5	-	23.9	775-800
MLO 7375-Frac. 16	-	70.7	890-915
MLO 7375-Residue	-	-	>925
MLO 7376-Frac. 5	-	56.4	900-925
MLO 7376-Frac. 12	-	53.7	925-950
MLO 7376-Residue	-	-	>950

Table 102

EFFECT OF VARIOUS CONCENTRATIONS OF A LOW VOLATILITY COMPONENT ON THE DEPOSITION BEHAVIOR OF A PARAFFINIC NEUTRAL

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG

TEST CONDITIONS INCLUDE: TEST TIME = 5 HOURS; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1 MILLILITER PER MINUTE; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

NOTE: MLO 7308 = A PARAFFINIC RESIN (5400 CS. AT 100°F)

TEST FLUID	<---- A PARAFFINIC NEUTRAL (MLO 7375) ---->				
CONC. OF MLO 7308, WT.%	NONE	10	15	20	25
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	38	38	38	38	38
APPROX. AMOUNT O_2 USED, GMS. (1)	29	33	35	34	35
MOLS O_2 USED/426 GMS. FLUID (2)	1.5	1.8	1.8	1.8	1.8
TEST FLUID CHARGED, GMS.	251	251	249	248	251
TUBE DEPOSIT					
TOTAL DEPOSIT, MGS.	3878	357	178	118	32
WT.% OF FLUID CHARGED	1.54	0.14	0.07	0.05	0.01
FLUID PROPERTIES					
INSOLUBLES IN EXIT FLUID					
MG./100 GM. FLUID CHARGED					
SOLIDS	2690	2200	1250	812	370
WATER	2070	3230	3960	3520	3120
WT.% OF FLUID CHARGED					
SOLIDS	2.7	2.2	1.2	0.8	0.4
WATER	2.1	3.2	4.0	3.5	3.1
OVERALL LIQUID LOSS, WT.%	15	19	12	12	14
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	-16	-45	-42	-39	-24
NEUT. NO.(MG. KOH/GM. FLUID)					
ORIGINAL	0.0	0.0	0.1	0.1	0.1
FINAL	4.1	4.1	5.3	5.1	4.3

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 103

EFFECT OF A LOW VOLATILITY COMPONENT ON THE DEPOSITION BEHAVIOR OF A SERIES OF PARAFFINIC NEUTRALS

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG.

TEST CONDITIONS INCLUDE: TEST TIME AS INDICATED; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1.0 ML./MIN.; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGE SURFACE = ALUMINUM.

FOR VISCOSITY AND VOLATILITY PROPERTIES OF TEST FLUIDS, SEE TABLE 101.

<u>NOTE</u>: MLO 7308 = A PARAFFINIC RESIN (5400 CS. AT 100°F)

TEST FLUID	MLO 7372		MLO 7373		MLO 7374		MLO 7375	
CONC. OF MLO 7308, WT.%	NONE	20	NONE	20	NONE	20	NONE	20
TEST TIME, HOURS	5	5	5	5	2.6(A)	5	5	5
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	38	38	38	38	20	38	38	38
APPROX. AMOUNT O_2 USED, GMS. (1)	38	35	37	34	19	34	29	35
MOLS O_2 USED/426 GMS. FLUID (2)	2.1	1.9	2.1	1.8	2.0	1.9	1.5	1.9
TEST FLUID CHARGED, GMS.	242	244	238	248	118	246	251	247
TUBE DEPOSIT								
TOTAL DEPOSIT, MGS.	1967	431	2673	219	2973	155	3878	68
WT.% OF FLUID CHARGED	0.81	0.18	1.12	0.09	2.53	0.06	1.54	0.03
FLUID PROPERTIES								
INSOLUBLES IN EXIT FLUID								
MG./100 GM. FLUID CHARGED								
SOLIDS	497	911	495	1630	421	1150	2690	1200
WATER	5290	4440	5290	3800	5640	3890	2070	3740
WT.% OF FLUID CHARGED								
SOLIDS	0.5	0.9	0.5	1.6	0.4	1.2	2.7	1.2
WATER	5.3	4.4	5.3	3.8	5.6	3.9	2.1	3.7
OVERALL LIQUID LOSS, WT.%	1	25	7	27	11	18	15	10
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	-5	-21	-10	-19	-28	-29	-16	-39
NEUT. NO.(MG. KOH/GM. FLUID)								
ORIGINAL	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.1
FINAL	5.7	4.5	6.0	4.1	6.0	4.4	4.1	4.5

(A) TEST WAS TERMINATED BECAUSE ANNULUS OF HEAT EXCHANGER WAS PLUGGED.

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUEST SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 104

EFFECT OF A LOW VOLATILITY COMPONENT ON THE DEPOSITION BEHAVIOR OF TWO NAPHTHENIC NEUTRALS

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG

TEST CONDITIONS INCLUDE: TEST TIME AS INDICATED: HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1 MILLILITER PER MINUTE; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

NOTE: MLO 7150 = A PARAFFINIC RESIN (5900 CS. AT 100°F)

TEST FLUID	NAPHTHENIC WHITE OIL (MLO 7144)		NAPHTHENIC NEUTRAL (PRL 3467)	
CONC. OF MLO 7150 WT.%	NONE	25	NONE	25
TEST TIME, HRS.	3.2 (A)	5	3.5 (A)	5
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	26	38	28	38
APPROX. AMOUNT O_2 USED, GMS. (1)	25	-	19	-
MOLS O_2 USED/426 GMS. FLUID (2)	1.9	-	1.4	-
TEST FLUID CHARGED, GMS.	154	251	168	252
TUBE DEPOSIT				
TOTAL DEPOSIT, MGS.	2626	33	2512	23
WT.% OF FLUID CHARGED	1.72	0.01	1.50	0.01
FLUID PROPERTIES				
INSOLUBLES IN EXIT FLUID				
MG./100 GM. FLUID CHARGED				
SOLIDS	543	186	1170	277
WATER	7630	3620	3210	2700
WT.% OF FLUID CHARGED				
SOLIDS	0.5	0.2	1.2	0.3
WATER	7.6	3.6	3.2	2.7
OVERALL LIQUID LOSS, WT.%	7	8	9	21
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	-51	-	-	-
NEUT. NO.(MG. KOH/GM. FLUID)				
ORIGINAL	0.0	0.0	0.0	0.0
FINAL	5.4	4.0	2.3	4.2

(A) TEST WAS TERMINATED BECAUSE ANNULUS OF HEAT EXCHANGER WAS PLUGGED.

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 105

RATE OF DEPOSIT FORMATION FOR SOME PARAFFINIC NEUTRALS

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG.

TEST CONDITIONS INCLUDE: TEST TIME AS INDICATED; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1.0 ML./MIN.; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

TEST FLUID	PARAFFINIC NEUTRAL, MLO 7120 (100 CS. AT 100°F)					PARAFFINIC NEUTRAL, MLO 7372 (10 CS. AT 100°F)					PARAFFINIC NEUTRAL, MLO 7373 (12 CS. AT 100°F)				
TEST TIME, HOURS	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	8	15	23	30	38	8	15	23	30	38	8	15	23	30	38
APPROX. AMOUNT O_2 USED, GMS. (1)	8	14	21	27	35	8	14	23	29	38	8	15	22	29	37
MOLS O_2 USED/426 GMS. FLUID (2)	2.0	2.0	1.9	1.9	2.0	2.0	2.0	2.0	2.1	2.1	2.0	2.0	2.0	2.0	2.1
TEST FLUID CHARGED, GMS.	39	88	143	192	241	41	90	142	186	242	39	93	143	197	238
TUBE DEPOSIT															
TOTAL DEPOSIT, MG.	45	141	142	210	234	14	82	318	1154	1967	33	587	1119	2009	2673
WT.% OF FLUID CHARGED	0.12	0.16	0.10	0.11	0.10	0.03	0.09	0.22	0.62	0.81	0.08	0.64	0.78	1.02	1.12
FLUID PROPERTIES															
INSOLUBLES IN EXIT FLUID															
MG./100 GM. FLUID CHARGED															
SOLIDS	854	949	1290	952	3360	468	426	545	540	497	465	387	423	578	495
WATER	4860	3680	3670	3330	3520	1590	4580	5500	5230	5290	4850	4490	4670	4940	5290
WT.% OF FLUID CHARGED															
SOLIDS	0.9	0.9	1.3	1.0	3.4	0.5	0.4	0.5	0.5	0.5	0.5	0.4	0.4	0.6	0.5
WATER	4.9	3.7	3.7	3.3	3.5	4.6	4.6	5.5	5.2	5.3	4.8	4.5	4.7	4.9	5.3
OVERALL LIQUID LOSS, WT.%	2	8	3	7	6	5	6	10	9	1	5	7	3	4	7
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	-48	-26	-28	-18	-26	-12	-12	-12	-10	-5	-15	-13	-12	-7	-10
NEUT. NO. (MG. KOH/GM. FLUID)															
ORIGINAL	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
FINAL	4.5	4.8	4.3	5.5	5.4	3.9	4.5	4.9	5.5	5.7	4.1	4.3	4.5	5.4	6.0

(1) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF OXYGEN FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 106

RATE OF DEPOSIT FORMATION FOR SOME NAPHTHENIC NEUTRALS

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG

TEST CONDITIONS INCLUDE: TEST TIME AS INDICATED; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1.0 ML./MIN.; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

TEST FLUID	NAPHTHENIC NEUT., MLO 7342 (18 CS. AT 100°F)				NAPHTHENIC NEUT., MLO 7417 (80 CS. AT 100°F)				
TEST TIME, HOURS	3	4	< - - - 5 - - - >		1	2	3	4	5
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1) APPROX. AMOUNT O_2 USED, GMS. (1)	23 23	30 30	38 37	38 38	8 8	15 15	23 21	30 28	38 32
MOLS O_2 USED/426 GMS. FLUID (2)	2.1	2.1	2.0	2.0	2.0	2.0	1.9	1.9	1.7
TEST FLUID CHARGED, GMS.	140	190	244	245	38	90	139	191	244
TUBE DEPOSIT									
TOTAL DEPOSIT, MG. WT.% OF FLUID CHARGED	338 0.24	729 0.38	610 0.25	1377 0.56	95 0.25	1523 1.69	2211 1.59	3536 1.85	4702 1.93
FLUID PROPERTIES									
INSOLUBLES IN EXIT FLUID									
MG./100 GM. FLUID CHARGED SOLIDS WATER	445 4710	541 4770	501 4620	538 4550	424 6470	484 5380	907 4830	657 4940	543 4440
WT.% OF FLUID CHARGED SOLIDS WATER	0.4 4.7	0.5 4.8	0.5 4.6	0.5 4.6	0.4 6.5	0.5 5.4	0.9 4.8	0.7 4.9	0.5 4.4
OVERALL LIQUID LOSS, WT.%	11	4	4	8	2	5	3	10	8
% CHANGE IN CENTISTOKE VISCOSITY AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	-20	-18	-25	-19	-60	-54	-53	-51	-55
NEUT. NO. (MG. KOH/GM. FLUID) ORIGINAL FINAL	0.0 4.1	0.0 5.2	0.0 4.7	0.0 5.0	0.0 3.7	0.0 3.7	0.0 3.6	0.0 5.4	0.0 4.2

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG.

TEST CONDITIONS INCLUDE: TEST TIME AS INDICATED: HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1 ML. PER MINUTE; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

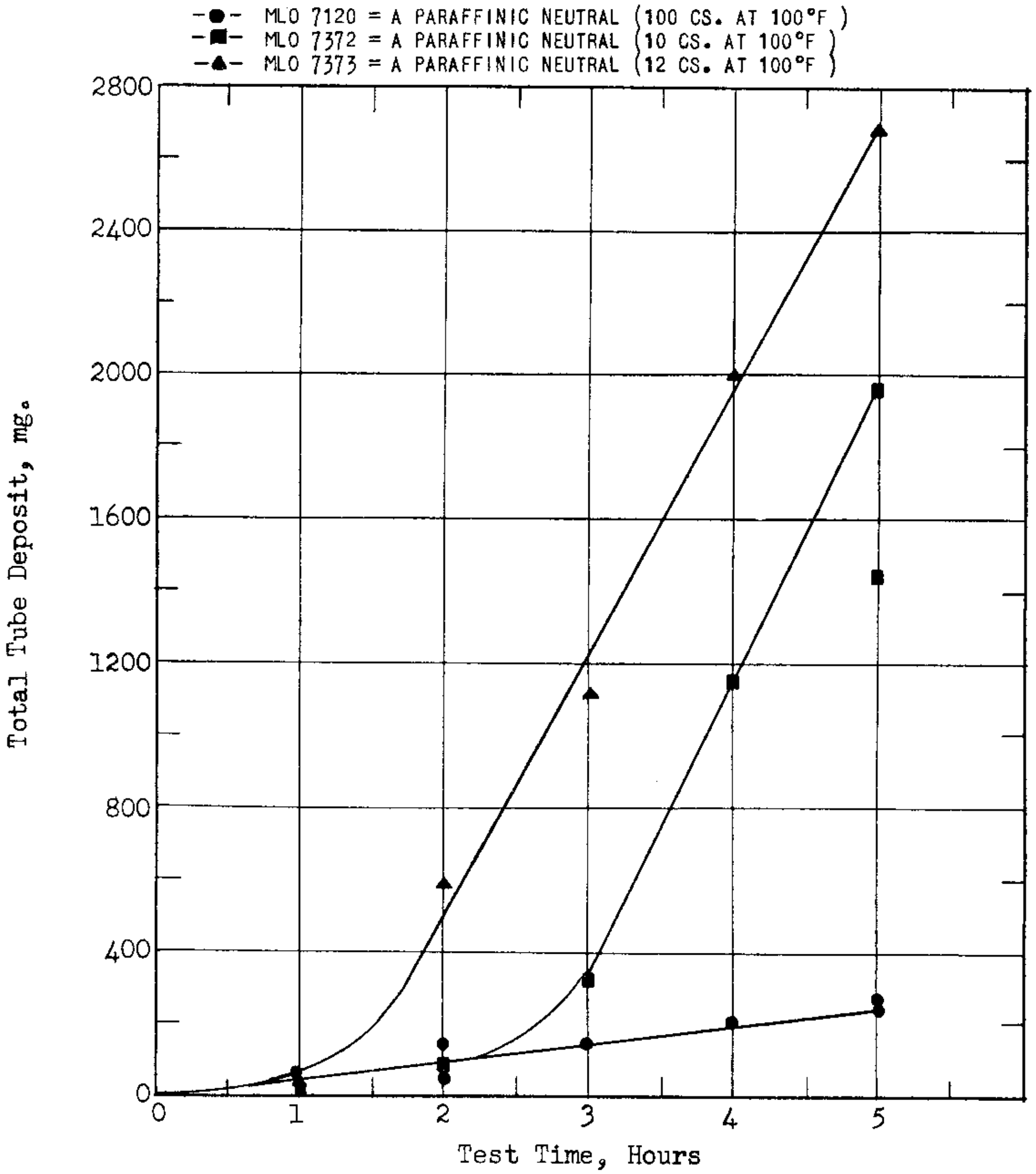


Figure 73. RATE OF DEPOSIT FORMATION FOR SOME PARAFFINIC NEUTRALS.

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG.

TEST CONDITIONS INCLUDE: TEST TIME AS INDICATED; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE ≐ 27 LITERS PER HOUR; FLUID RATE = 1 ML. PER MINUTE; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

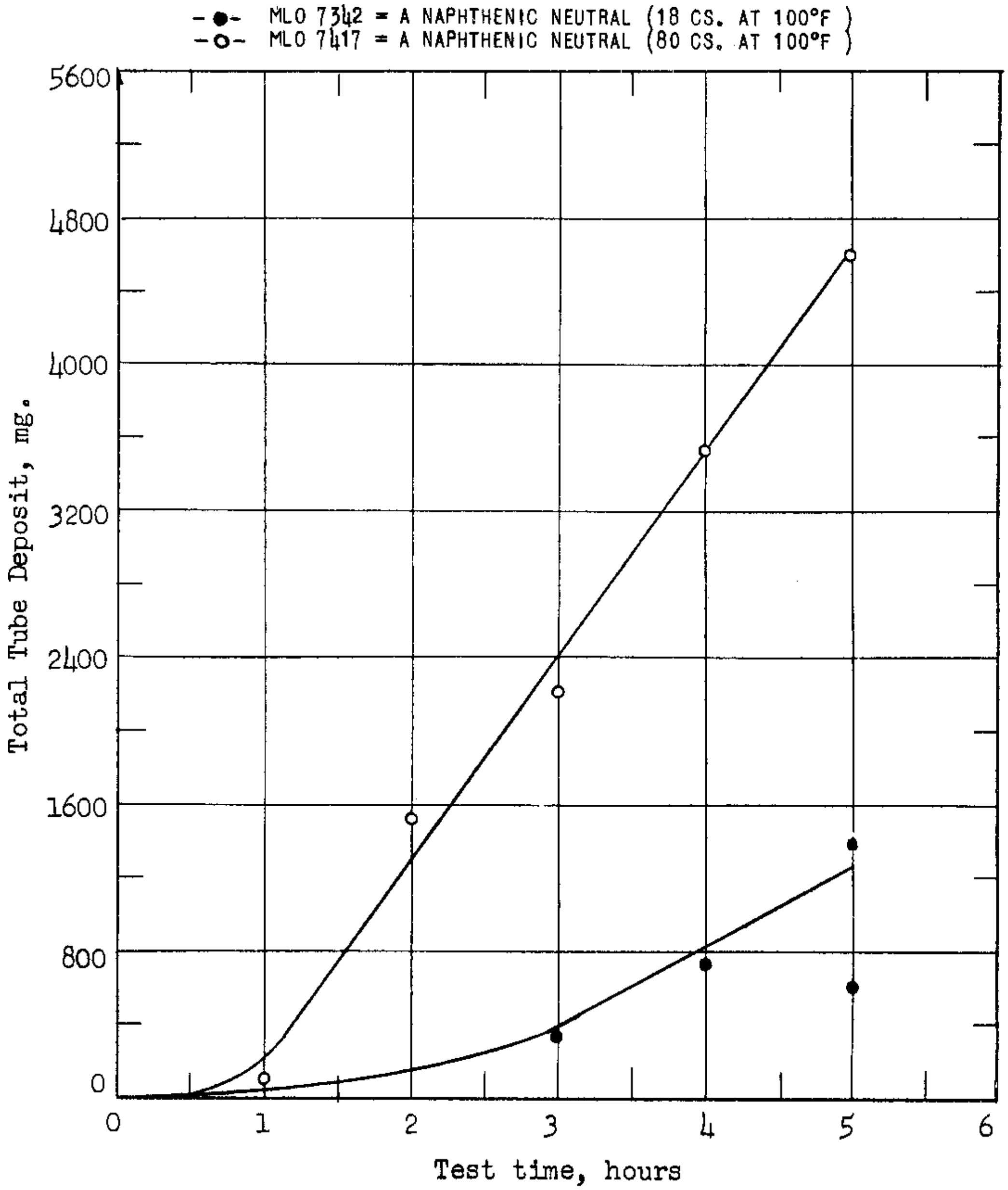


Figure 74. RATE OF DEPOSIT FORMATION FOR SOME NAPHTHENIC NEUTRALS

Table 107

EFFECT OF METAL TYPE ON THE DEPOSITION BEHAVIOR OF SEVERAL MINERAL OILS

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG

TEST CONDITIONS INCLUDE: TEST TIME AS INDICATED; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1.0 ML./MIN.; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE AS INDICATED.

TEST FLUID	PARAFFINIC LIGHT RESIN (MLO 7308)			PARAFFINIC BRIGHT STOCK (MLO 7094)			PARAFFINIC NEUTRAL (MLO 7120)				NAPHTHENIC WHITE OIL (MLO 7273)		
HEAT EXCHANGER SURFACE	ALUMINUM	STEEL	COPPER	ALUMINUM	STEEL	COPPER	ALUMINUM	STEEL		COPPER	ALUMINUM	STEEL	COPPER
TEST TIME, HOURS	5	5	5	5	5	5	5	5		5	5	3.2(A)	5
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	38	38	38	38	38	38	38	38	38	38	38	24	38
APPROX. AMOUNT O_2 USED, GMS. (1)	-	11	13	32	27	27	34	34	32	34	34	22	34
MOLS O_2 USED/426 GMS. FLUID (2)	-	0.6	0.7	1.8	1.4	1.5	1.9	1.8	1.8	1.9	1.9	1.9	1.9
TEST FLUID CHARGED, GMS.	239	246	246	243	245	244	240	246	244	241	242	155	241
TUBE DEPOSIT													
TOTAL DEPOSIT, MG.	13	10	59	12	40	158	181	274	397	235	1925	3007	1072
WT.% OF FLUID CHARGED	0.01	0.00	0.02	0.00	0.02	0.06	0.08	0.11	0.16	0.10	0.80	1.94	0.44
FLUID PROPERTIES													
INSOLUBLES IN EXIT FLUID													
MG./100 GM. FLUID CHARGED													
SOLIDS	55	123	118	657	678	496	1737	2110	2350	1550	934	348	2480
WATER	1710	500	667	4110	3150	3150	3300	2890	3040	3410	4440	4920	3180
WT.% OF FLUID CHARGED													
SOLIDS	0.1	0.1	0.1	0.7	0.7	0.5	1.7	2.1	2.4	1.6	0.9	0.3	2.5
WATER	1.7	0.5	0.7	4.1	3.2	3.2	3.3	2.9	3.0	3.4	4.4	4.9	3.2
OVERALL LIQUID LOSS, WT.%	8	6	3	5	8	8	7	8	6	6	9	6	11
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	+21	+16	+19	-2	+16	+9	-16	-15	-14	-19	-52	-55	-43
NEUT. NO. (MG. KOH/GM. FLUID)													
ORIGINAL	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
FINAL	2.3	1.7	2.2	4.0	2.9	3.0	5.3	4.3	4.1	4.3	3.1	3.3	4.4

(A) TEST WAS TERMINATED BECAUSE ANNULUS OF HEAT EXCHANGER WAS PLUGGED.

(1) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF OXYGEN FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING NAPHTHA AND DRIED BEFORE WEIGHING.

Table 108

EFFECT OF ADDITIVES ON THE DEPOSITION BEHAVIOR OF A POLYOLEFIN HYDROCARBON

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG.
TEST CONDITIONS INCLUDE: TEST TIME AS INDICATED; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1.0 ML./MIN.; AND RESIDENCE TIME IN HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

ADDITIVE DESIGNATION:
PAN = PHENYL-ALPHA-NAPHTHYLAMINE
DAP = DIISOPROPYL ACID PHOSPHITE
DTC = A DITHIOCARBAMATE
MLO 7120 = A PARAFFINIC NEUTRAL (100 CS. AT 100°F)

TEST FLUID	<- - - - - - - - - - -	- - - -	- - - - - - - -	A POLYOLEFIN HYDROCARBON (MLO 7123)	- - - - - - - -	- - - - - -	- - - - - - - -	- - - - - - - - ->
ADDITIVE, WT.%	<- - - NONE	- - -	- - ->	PRETREATED WITH SUPER-FILTROL	0.001 ANTIFOAM	1.0 PAN	1.0 PAN + 0.2 DAP	1.0 DTC	50 MLO 7120
TEST TIME, HOURS	5	5	5	5	5	5	5	5	3.7(A)
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	38	38	38	38	38	38	38	38	28
APPROX. AMOUNT O_2 USED, GMS. (1)	17	19	16	17	18	15	13	16	24
MOLS O_2 USED/426 FLUID (2)	1.0	1.1	1.0	1.0	1.0	0.9	0.7	0.9	1.8
TEST FLUID CHARGED, GMS.	229	234	227	230	230	224	232	228	175
TUBE DEPOSIT									
TOTAL DEPOSIT, MGS.	2[illegible]5	401	573	527	559	508	1362	782	2419
WT.% OF FLUID CHARGED	0.09	0.19	0.25	0.23	0.24	0.23	0.59	0.34	1.38
FLUID PROPERTIES									
INSOLUBLES IN EXIT FLUID									
MG./100 GM. FLUID CHARGED									
SOLIDS	89	144	101	130	86	99	65	137	425
WATER	940	1030	857	1320	1000	482	176	920	3330
WT.% OF FLUID CHARGED									
SOLIDS	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.4
WATER	0.9	1.0	0.8	1.3	1.0	0.5	0.2	0.9	3.3
OVERALL LIQUID LOSS, WT.%	9	8	7	9	10	11	19	32	15
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	-80	-82	-81	-83	-83	-79	-79	-82	-66
NEUT. NO. (MG. KOH/GM. FLUID)									
ORIGINAL	0.1	0.1	0.1	0.2	0.1	0.0	0.1	0.1	0.1
FINAL	2.2	2.9	2.7	2.6	2.5	2.0	1.8	2.3	4.7

(A) -TEST WAS TERMINATED BECAUSE ANNULUS OF HEAT EXCHANGER WAS PLUGGED.

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 109

EFFECT OF ADDITIVES ON THE DEPOSITION BEHAVIOR OF A HYDROGENATED POLYOLEFIN

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG

TEST CONDITIONS INCLUDE: TEST TIME = 5 HOURS; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1 ML. PER MINUTE; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

ADDITIVE DESIGNATIONS: PAN = PHENYL-ALPHA-NAPHTHYLAMINE
DAP = DIISOPROPYL ACID PHOSPHITE
DTC = A DITHIOCARBAMATE
MLO 7120 = A PARAFFINIC NEUTRAL (100 CS. AT 100°F)

TEST FLUID	< - - - A HYDROGENATED POLYOLEFIN HYDROCARBON (MLO 7124) - - - >							
ADDITIVE, WT.%	NONE		0.001 ANTIFOAM	0.01 DAP	1.0 PAN	1.0 PAN + 0.1 DAP	1.0 DTC	50 MLO 7120
APPROX. AMOUNT O_2 SUPPLIED, GMS. (1)	38	38	38	38	38	38	38	38
APPROX. AMOUNT O_2 USED, GMS. (1)	27	28	28	25	24	14	21	34
MOLS O_2 USED/426 GMS. FLUID (2)	1.6	1.6	1.6	1.4	1.4	1.1	1.2	1.9
TEST FLUID CHARGED, GMS.	227	235	232	234	238	229	232	237
TUBE DEPOSIT								
TOTAL DEPOSIT, MGS.	48	68	43	398	182	574	435	1219
WT.% OF FLUID CHARGED	0.02	0.03	0.02	0.17	0.08	0.25	0.19	0.51
FLUID PROPERTIES								
INSOLUBLES IN EXIT FLUID								
MG./100 GM. FLUID CHARGED								
SOLIDS	298	284	268	220	384	272	431	1650
WATER	3570	3450	2990	3100	3100	1410	1920	3180
WT.% OF FLUID-CHARGED								
SOLIDS	0.3	0.3	0.3	0.2	0.4	0.3	0.4	1.6
WATER	3.6	3.4	3.0	3.1	3.1	1.4	1.9	3.2
OVERALL LIQUID LOSS, WT.%	10	11	7	13	7	8	36	17
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	-85	-85	-85	-84	-83	-82	-83	-65
NEUT. NO. (MG. KOH/GM. FLUID)								
ORIGINAL	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1
FINAL	3.8	3.4	3.8	3.7	3.4	2.8	2.5	5.4

(1) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF OXYGEN FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 110

DEPOSITION BEHAVIOR OF SOME ESTERS

ALL TESTS CONDUCTED IN THE SINGLE-PASS HIGH TEMPERATURE LUBE RIG

TEST CONDITIONS INCLUDE: TEST TIME = 5 HOURS; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1 ML. PER MIN.; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM

TEST FLUID (CONC. IN WT.%)	DI-2-ETHYLHEXYL SEBACATE (MLO 7112) + 0.5 PHENOTHIAZINE	A POLYESTER (MLO 7333) + 0.5 PHENOTHIAZINE	50:50 BY WT. MLO 7112:MLO 7333 + 0.5 PHENOTHIAZINE
APPROX. AMOUNT OF O_2 SUPPLIED, GMS. (1)	38	38	38
APPROX. AMOUNT OF O_2 USED, GMS. (1)	37	31	19
MOLS O_2 USED/426 GMS. FLUID (2)	1.8	1.5	0.9
TEST FLUID CHARGED, GMS.	259	287	269
TUBE DEPOSIT			
TOTAL DEPOSIT, MG.	1920	28	358
WT.% OF FLUID CHARGED	0.74	0.01	0.13
FLUID PROPERTIES			
INSOLUBLES IN EXIT FLUID (3)			
MG./100 GM. FLUID CHARGED			
SOLIDS	290	166	961
WATER	4250	887	600
WT.% OF FLUID CHARGED			
SOLIDS	0.3	0.2	1.0
WATER	4.3	0.9	0.6
OVERALL LIQUID LOSS, WT.%	12	26	16
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLES, (3) AT 100°F	-27	-46	-17
NEUT. NO. (MG. KOH/GM. FLUID)			
ORIGINAL	0.1	0.0	0.1
FINAL	23.0	31.5	15.5

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./HR. AT S.T.P.) X TIME (HR.) X O_2 CONTENT (FRACTION) X 1.43 (GM./LITER). AMOUNT OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR O_2.

(2) THE MOLS OF O_2 FOR 426 GRAMS OF FLUID HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE O_2 ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYLHEXYL SEBACTE IS 426.

(3) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLE MATERIAL IS WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

Table 111

SINGLE-PASS HIGH TEMPERATURE LUBE RIG TESTS WITH SOME SILICONE OILS

TEST CONDITIONS INCLUDE: TEST TIME = 5 HOURS; HEAT EXCHANGER TEMPERATURE = 707°F ; AIR RATE = 27 LITERS PER HOUR; FLUID RATE = 1.0 ML./MIN.; AND RESIDENCE TIME IN THE HEAT EXCHANGER = APPROX. 5 MINUTES. HEAT EXCHANGER SURFACE = ALUMINUM.

TEST FLUID	MLO 7017 SILICONE 81406	MLO 7265 SILICONE 81406 + 3.0 WT.% TINSIL
TEST FLUID CHARGED, GMS.	277	280
TUBE DEPOSIT		
TOTAL DEPOSIT, MGS.	41	19
WT.% OF FLUID CHARGED	0.01	0.01
FLUID PROPERTIES		
INSOLUBLES IN EXIT FLUID		
MG./100 GM. FLUID CHARGED		
SOLIDS	214	458
WATER	0	0
WT.% OF FLUID CHARGED		
SOLIDS	0.2	0.5
WATER	0.0	0.0
OVERALL LIQUID LOSS, WT.%	13	14
% CHANGE IN CENTISTOKE VISCOSITY, AFTER REMOVAL OF OIL INSOLUBLES, (1) AT 100°F	-(2)	-(2)
NEUT. NO. (MG. KOH/GM. FLUID)		
ORIGINAL	0.0	0.0
FINAL	1.0	3.0

(1) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

(2) EXIT OIL GELLED ON STANDING AT ROOM TEMPERATURE.

centistokes at the ASTM pour point temperature. The wax fraction from these dewaxings includes an appreciable amount of occluded oil. A second dewaxing of the wax fraction in accordance with the same procedure used in the original dewaxing results in an additional oil fraction exhibiting similar properties to those of the oil fraction from the initial dewaxing. This two-stage dewaxing indicates that simple dewaxing techniques may be used to obtain a wax-oil separation approaching the theoretical yields of each component.

In general, the wax fractions from dewaxings with paraffinic and naphthenic mineral oils and aromatic hydrocarbons exhibit a lower viscosity level and a higher viscosity index than the charging stock. The oil fractions show a higher viscosity level and a lower viscosity index. However, using a measured low temperature viscosity value, the oil fractions show an improvement in viscosity index based on the viscosity-temperature characteristics over the temperature range of 210° to -40° or -65°F. The improvement in low temperature fluidity for the oil fractions is of the order of 35° to 85°F. lowering in pour point. In all cases, the cloud point of the oil fraction is below the pour point. The wax fractions exhibit an increase in pour point of the order of 10° to 25°F.

The amount of oil occluded in the wax fraction is significantly lowered in blends containing a pour depressant type Acryloid polymer. However, filtration time is increased by a factor of 2 to 3 for the Acryloid-containing blends. Essentially all of the pour depressant is found in the wax fraction. Another interesting development arising from these dewaxing studies is concerned with the thickening effect produced by dispersant Acryloid polymers on the dewaxed paraffinic fractions. There is no visual evidence of insolubility at -40°F for the polymer-containing blends. In all cases, the polymer causes less thickening, percentage-wise, at -40°F. that it causes at 210°F. This is in contrast to the behavior of conventional military hydraulic fluids such as Spec. MIL-H-5606 which contain viscosity-index improver type Acryloid polymer.

The solvent to oil ratio required in these low temperature dewaxings is dictated by the relatively high wax concentration and the increased viscosity of the liquid phase at the low temperature. The use of solvent to oil ratios in the range of 6:1 to 8:1 minimizes these oils with a pour point 5° to 15°F higher than the dewaxing temperature. When methylethyl ketone is used as the solvent, a pour point below the dewaxing temperature is obtained. However, the solubility of the paraffinic neutrals in methylethyl ketone at temperatures of -40°F and lower is limited and yields of the oil fraction are affected adversely. A 3:1 blend of methylisobutyl ketone and methylethyl ketone appears to give a good yield as well as a desirable relationship between pour point and dewaxing temperature.

Cooling rates in the range of one to five degrees Fahrenheit per minute do not materially alter the yield or the resultant pour point of the oil fraction. Cooling to -110°F and warming to -75°F for filtration appears to improve the pour point of the oil fraction without any adverse effect on the yield.

A comparison of lubricant properties indicates that a deep dewaxed paraffinic mineral oil can be used to formulate a fluid having about the same volatility level as a Spec. MIL-L-7808 oil and have viscosity, and low temperature properties about the same as a turbo-prop engine oil.

Three types of mineral oil-base high temperature hydraulic fluids have been formulated and evaluated in both laboratory and mock-up studies. The first of these, an aromatic hydrocarbon-base fluid, has been tested to a limited extent in airless systems and for radiation resistence. Current availability of a fluid of this type is quite limited although potential commercial availability of the fluid is good. This fluid appears to have some advantages over paraffinic or naphthenic mineral oil formulations for applications at 700°F and above, or where radiation is encountered.

A naphthenic mineral oil-base formulation (MLO 7243 or MLO 7277) has been quite widely tested by different organizations. About 22 samples have been supplied to 15 different organizations for evaluation. Data and comments from these organizations indicate excellent agreement with the laboratory studies conducted during the development of this fluid.

Work is continuing on the development of a paraffinic mineral oil-base fluid designed for use over the temperature range of -65° to +700°F. A prototype of this fluid, MLO 7460, has been furnished to four different organizations for evaluation. MLO 7460 is identical with the fluid being developed except that it has not been dewaxed and, therefore, does not have the desired low temperature properties. This prototype fluid has been evaluated in a 550°F. hydraulic pump system by Vickers, Incorporated. Examination of the used fluid samples indicates little change in physical properties of the fluid after 50 hours test time. A flocculent precipitate appearing in the used fluid from a 32-hour test has been isolated and examined. Results of this examination indicate that the insoluble material did not come from fluid deterioration, but probably was a result of contamination of the test system from a prior test.

A number of fluid samples which have been stored by this Laboratory for periods ranging from 2 to 17 years have been removed from storage and are being evaluated for property changes and for changes in the effectiveness of additives. This study is part of an overall program to define better the capabilities of various types of fluids and fluid formulations. Previous studies have indicated that fluid behavior under mild conditions of temperature and oxidation does not, in some cases, follow the pattern predicted for it by extrapolation of data from more severe accelerated tests.

Mineral oils of the type used to prepare Spec. MIL-H-5606 hydraulic fluids show no change in physical properties after storage for 17 years. Several samples of synthetic polyolefins show changes in viscosity and neutralization number typical of oxidation and polymerization reactions encountered with olefinic hydrocarbons. Samples of hydrogenated polyolefins (branched chain paraffins) show no changes in these properties as a result of storage. Ester samples which have been stored for periods of 10 to 16 years show no excessive changes due to storage. It is indicated that dibasic acid esters show adequate storage stability for relatively long periods of time providing initial ester quality is high.

A series of mineral oil-base formulations of the Spec. MIL-H-5606, Spec. MIL-F-17111, and Spec. O.S.1113E types show excellent storage stability for extended periods. Preliminary wear tests indicate no change in wear behavior after storage. Some ester-base formulations of the Spec. MIL-L-7808, Spec. MIL-L-6387, and Spec. MIL-L-7499 types have been evaluated. Traces of insoluble material have been found in some of these samples. Based on the appearance of these blends and of the ester base stocks after storage, it appears that the formation of the insolubles is triggered by the additive package. The effect of tricresyl phosphate on storage stability is pointed out through a comparison of a Spec. MIL-L-6387 fluid (1.0 wt.%) and a Spec. MIL-L-7808 fluid (5.0 wt.%). The increased concentration causes some formation of insolubles and an increase in neutralization number with storage. Wear studies with these formulations indicate very little change over the wear behavior noted for the original fluids.

One formulation based on a polyester shows changes in viscosity and neutralization number. This polyester is prepared from a dibasic acid and a glycol containing a secondary alcohol group. Previous data have been shown that materials containing this secondary grouping tend to be unstable on storage.

A series of thermal stability tests have been conducted using the stainless steel pressure cylinder. Test fluids used include paraffinic and naphthenic mineral oils and aromatic and polyolefin hydrocarbons. The rate of gas formation for all of the fluids except the polyolefin is constant with test time for any particular test. For the polyolefin, the rate appears to decrease somewhat with test time. However, the rate of gas formation is not a simple function of overall test conditions but rather a function of the amount of heated gas space available. An increase in the heated gas space (decrease in fluid charge) results in an increase in the rate of gas formation (moles of gas/mole of oil/hour). The rate of gas formation in this test appears to be essentially a zero order reaction. Several tests were conducted in an Aminco Rocking Autoclave of relatively large volume. The data obtained in the autoclave tests are in excellent agreement with those obtained in the smaller pressure cylinder.

The gaseous products which are non-condensable at room temperature have been analyzed by gas chromatography. For the paraffinic and naphthenic oils, about 50 per cent of the material which is a gas at 700°F remains in the gaseous state at 70°F. The gas analyzed contains hydrogen and hydrocarbons up to and including C_5. It is estimated that the gaseous material which is condensed in cooling from 700° to 70°F is composed of C_5 to C_{18} hydrocarbons. In several cases, small amounts of carbon dioxide and carbon monoxide have been detected. The presence of these materials is attributed to dissolved air and oxygen-containing impurities. Somewhat different distributions of gaseous products are noted for the aromatic and polyolefin hydrocarbons. The gas formed in thermal degradation of the polyolefin shows substantial amounts of the monomer from which the polymer was made. This product is indicative of depolymerization or unzippering of the polymer molecule.

The gaseous product from the partially hydrogenated aromatic hydrocarbons shows a significantly larger concentration of hydrogen in the gas. These data emphasize the relative stability of the aromatic ring.

The composition of the gaseous products from thermal tests over the range of 650° to 750°F is essentially independent of the thermal test temperature. Reaction rates, based on pressure build-up have been used to determine the temperature interval for rate doubling. Two consecutive 50°F temperature intervals have been used in these studies. The trend is toward less temperature effect with increasing temperature over the range studied. The aromatic hydrocarbon shows the lowest rate of increase in thermal degradation while the paraffinic mineral oil shows the highest rate of increase in thermal cracking. With the paraffinic mineral oils, the rate of decomposition increases with increasing molecular weight.

A more critical evaluation of the liquid products from the thermal tests has been made. To do this, a small scale vacuum distillation has been conducted to characterize the volatility of these liquid products. These distillations show that these degradation products contain a fraction boiling below the charging stock, a fraction boiling in the same range as the charging stock, and a fraction boiling above the original test fluid. These boiling point curves illustrate the problem encountered in using viscosity change as a measure of thermal degradation. Small amounts of low boiling material in the degradation product can cause a relatively large decrease in the viscosity of the product. On the other hand, this relationship can be altered by a small amount of material in the degradation product having a boiling point above the original fluid. Based on these boiling point curves, the same reaction products are present after 6 or 20 hours under a given set of test conditions. That is, the degradation products appear to approach a constant composition asymptotically with increasing test time.

Data obtained support the theory that an equilibrium exists between reaction products and reactants as opposed to the theory that the unstable molecules have been degraded and that the remaining material in the boiling range of the original fluid is stable under the test conditions.

Examination of the liquid product from thermal tests with the aromatic hydrocarbon indicates a better stability at 700°F than that of the paraffinic and naphthenic mineral oils at 650°F. Distillation curves for the products from 850° and 900°F thermal tests with a polyphenyl ether indicate that more of the degradation product boils above than below the original fluid. The viscosity of the liquid product from these tests is higher than that of the original fluid.

The analysis of the degradation products from thermal tests with a polybutene oil indicates the presence of monomer as the predominant gaseous product and of low boiling liquid products. This suggests a depolymerization of the oil to give the monomer.

Studies of this nature will be continued in an attempt to understand better the basic trends in thermal behavior of fluids. As a result of a better understanding of the thermal reactions occurring, it may be possible to develop more standardized thermal stability tests and thereby improve intra- as well as inter-laboratory reproducibility.

Preliminary tests indicate that the combination of 5-ethyl-10,10-diphenylphenazasiline (5-10-10) or phenothiazine with phenyl-alpha-naphthylamine (PAN) or Primene-81R (an aliphatic primary amine) appears to extend the oxidation stable life at 347°F of the dibasic acid ester or the neopentyl type esters evaluated. That is, it appears that the use of a basic (amine type) material in conjunction with phenothiazine or 5-10-10 extends the stable life and lowers the neutralization number build-up within the stable life of the ester fluids evaluated. Additional studies at 400°F are necessary to show more clearly the effects of the inhibitor combinations on the stable life of the esters in a reasonable test period.

These preliminary tests indicate that, at 500°F in the presence of metal catalysts, the combination of additives reduces somewhat the rate of oxidation and lowers the acidity for neopentyl esters compared with phenothiazine alone. However, the oxygen tolerance at 500°F also appears to be lowered when the inhibitor combinations are used. That is, viscosity change and sludge formation are higher per unit oxygen assimilated when the additive combinations are used than when phenothiazine alone is used as the antioxidant.

In order to evaluate more thoroughly the oxidative behavior of fluids available in limited supply, a small volume oxidation test has been designed. A comparison of data obtained with the small volume equipment and with the standard 100-milliliter test at 347° and at 500°F indicates the equivalence of the two tests. A comparison of some of the dimensions for the two tests are shown below.

	Standard Test	Small Volume Test
Test Tube Diam., mm. o.d.	38	22
Fluid Charge, ml.	100	25
Fluid Height, mm.	120	120
Catalyst Area, sq. cm.	12.9	3.23
Air Rate, liters per hr.		
347°F Test	5.0	1.25
500°F Test	5.0	0.7

The same general test procedures and techniques are applicable to both test procedures.

A series of thirteen (13) neopentyl type esters has been evaluated for oxidative stable life at 347°F and for oxidation rate and oxygen tolerance at 500°F. Five of these esters show a relatively short stable life (less than 72 hours) at 347°F. Properties of these five esters indicate that insufficient refining and purification probably contribute to the relatively short stable life. The remaining esters exhibit stable life values in the range shown by high quality neopentyl esters evaluated previously. Tests at 500°F indicate also that the majority of these materials show oxidation behavior comparing favorably with other high quality neopentyl esters. Low temperature properties of several of these esters are promising. These data, along with previous data, indicate that it is possible to make -65°F esters of the neopentyl type from mono-, di-, and tri-functional alcohols.

A series of esters has been evaluated for oxidation behavior at 400°F using the quantitative procedure previously used for 500°F. oxidation tests. Oxygen assimilation data show that oxygen is abosrbed during the so-called stable life period. In di-2-ethylhexyl sebacate, a combination of inhibitors (5-10-10 and PAN) results in a lower oxygen assimilation rate than that noted for phenothiazine alone. In spite of the lower oxidation rate shown by the combination inhibitor, a relatively large amount of insolubles is formed indicating a reduced oxygen tolerance. A comparison of the effectiveness of the inhibitor combination in three neopentyl type esters shows only minor differences due to the specific ester structure. Oxidation appears to occur at about the same rate with or without metal catalysts. However, property changes in the resultant fluid may be affected by the presence of metal catalysts.

By using an extended 168-hour test with samples at 72 and 120 hours test time, data can be obtained which are indicative of the extent of oxidation over the entire test period. In both di-2-ethylhexyl sebacate and a trimethylol propane ester, combinations of phenothiazine-PAN and 5-10-10-PAN are about equally effective as antioxidants. Both combinations are more effective than phenothiazine alone. Magnesium corrosion is a consistent problem in these tests. This problem is noted in most oxidation tests conducted at temperatures above 347°F. Generally, the use of a dialkyl acid phosphite in a fluid formulation causes some increase in oxidative deterioration (dirtiness) in ester fluids. In some cases, the use of a dispersant Acryloid in the formulation will control this tendency to form insolubles. The data determined at 400°F confirm earlier data obtained at 347° and 500°F indicating that specific additive combinations may substantially alter the properties of the ester base stock. Small volume (25 milliliters test fluid) tests can be successfully used to evaluate experimental esters available in limited supply.

The use of a controlled atmosphere in the Model C panel coker enhances the value of the coker as a device to predict high temperature dirtiness. The quantitative measurement of oxygen assimilation aids in understanding the mechanism of oxidation at or near the panel surfaces. For the same viscosity level, paraffinic formulations give lower coking values than do naphthenic formulations. The addition of polar additives to mineral oil formulations tends to increase the coke deposit. Coking deposit is reduced when super-refined stocks are used as base stocks for these paraffinic and naphthenic formulations.

Panel deposits decrease with increasing boiling point for these mineral oils. Oxygen assimilation measurements show a reduced oxidation rate for the more volatile of these mineral oils. This suggests that the hot gases formed may act as a buffer to reduce the quantity of air in contact with the hot oil. The increased coke deposit under these conditions indicates a greatly reduced oxygen tolerance for these volatile mineral oils.

The addition of a dithiocarbamate additive to either a mineral oil or ester causes a substantial increase in coke deposit. The inclusion of a dispersant Acryloid in the formulation materially reduces the coke deposit.

A series of successive panel coker studies have been conducted to understand better coking behavior and the contribution of variables governing the deposit. In uninhibited esters, coke formation increases with increased test time or additional incremental tests. At the same time, the rate of oxidation actually decreases. This behavior suggests the formation of deposit precursors as the test proceeds. The neopentyl esters containing inhibitors form about the same amount of deposit in each of the incremental tests. Inhibitor combinations effect a substantial decrease in rate of oxidation compared to an uninhibited fluid or one containing only phenothiazine. However, the coke deposit does not follow the oxygen assimilation pattern. The presence of a dispersant Acryloid effects a decrease in coke deposition.

Additional studies in the single-pass high temperature lube rig are discussed. An increase in deposit for an uninhibited mineral oil and polyolefin hydrocarbon over a storage period of three years suggests a progressive oxidative deterioration of these fluids with a resultant increase in deposit values. A dialkyl acid phosphite in concentrations of 0.5 weight per cent or above in mineral oils or esters causes an increase in deposit in the single-pass rig. This same behavior is shown in other oxidation and deposit type tests. However, studies in the single-pass rig indicate that, in concentrations of 0.1 weight per cent and less, the dialkyl acid phosphite reduces the deposit obtained with the base fluid. Even though the rig is thoroughly cleaned and flushed between tests, the effect of a dialkyl acid phosphite may be seen in the subsequent run. That is, if the fluid for test A contains 0.5 weight per cent dialkyl acid phosphite, the deposit value for a non-additive fluid in test B will be much lower than anticipitated. This suggests extreme sensitivity of the deposit to the dialkyl acid phosphite.

The viscosity or boiling range of the mineral oil tested influences the deposit value. The less volatile, higher boiling fractions show reduced deposit values. The addition of various amounts of a low volatility component to more volatile fraction results in a reduced deposit. The volatility of the fluid does not affect the oxygen assimilation for the fluids tested.

The rate of deposition in the single-pass rig is somewhat different from that shown for the panel cokers. For fluids showing a relatively high deposit value, there appears to be an induction period where rate of formation is low followed by a substantial increase in deposition rate. In fluids exhibiting a relatively low deposit formation, the rate of formation is essentially constant.

The use of a steel or a copper surface in the single-pass rig rates the various test fluids in the same order as that obtained with the aluminum surface conventionally used. The resin and bright stock materials appear to react with the copper surface to some extent.

The blending of mineral oils or esters having different deposit values generally results in an intermediate deposit value. However, when a mineral oil is blended with a polyolefin or a saturated polyolefin, deposit values substantially exceeding the value obtained for either component result.

L. FUTURE WORK. Future studies will emphasize the quantitative measurement of basic properties limiting the capabilities of hydraulic fluids, functional fluids, and lubricants. The data determined from these studies will be directly applicable to aircraft, missiles, and space vehicles in (1) chemical engines, (2) ANP engines, (3) primary, secondary, and auxiliary power sources, (4) engine hydraulics, and (5) control and guidance hydraulic systems.

Efforts to prepare improved fluid and lubricant formulations for extensive laboratory evaluation and hardware testing are continuing. Close coordination and correlation of these three important phases of the fluids and lubricants program are essential to the overall success of the program. This Laboratory plans to pursue a vigorous program of cooperation with the Services; Government Agencies; producers of base stocks, additives, and finished fluid formulations; research and development laboratories; and producers of components and overall weapons systems. Special emphasis will be placed on a cooperative program with WADD, NASA, and industry to determine and define the lubrication and fluid needs in advanced flight vehicles. Because of the extreme demands being made on the hydraulic fluids and lubricants in advanced flight systems, early coordination between fluids and design groups takes on added importance.

Continuing cooperation programs with fluid suppliers will be vigorously pursued to develop new fluids and formulations and to assure a supply of carefully controlled fluid formulations for testing in the initial hardware stages of advanced systems. During the current contract period, approximately 425 gallons of special fluid formulations were prepared by this Laboratory for carefully controlled hardware testing. This program will be continued.

Previous investigation under Air Force Contracts at this Laboratory has shown an excellent high temperature potential for hydraulic fluids and lubricants based on silicones, silanes, esters, mineral oils, and hydrocarbons. Recent Air Force development contracts have produced phenyl ethers and organometallics with a good high temperature potential. All of these fluid classes will be thoroughly evaluated for capability studies in the series of physical and chemical test procedures available. This evaluation will include the following measurements.

1. Liquid range
2. Measured viscosity over the liquid range
3. Low temperature characteristics

4. Volatility (vapor pressure)
5. Lubricity over the high temperature range (four-ball testers and pumps)
6. Oxidative stability (stable life, oxygen tolerance, and oxidation rate)
   - a. Bulk oil tests (347° to 700°F)
   - b. Thin film tests (347° to 500°F)
   - c. Deposition tests (500° to 750°F)
   - d. Successive tests (347° to 500°F)
7. Evaporation rate
8. Metal corrosion under oxidative and thermal conditions
9. Thermal stability (500° to 1000°F)
10. Density
11. Foaming

In the area of mineral oil and hydrocarbon base stocks, substantial progress has been made in the studies of more effective separation and refining processes designed to optimize the properties of specific classes of mineral oils and hydrocarbons. Paraffinic and naphthenic mineral oils and aromatic hydrocarbons are included in these studies. These processes include super-refining for improved inhibitor susceptibility, fractionation for improved viscosity-volatility properties, and deep dewaxing for improved liquid range and low temperature properties. Preliminary studies in these areas have been productive and will be pursued to define the potential of such materials as hydraulic fluids and lubricants and in addition to define better the commercial potential of such materials. Present indications are that these studies may lead to materials suitable for hydraulic applications over the range of -40° to 700°F and above, and lubricant applications over at least as wide a range with a possibility of extending the upper limit depending on the type of lubricant system. Price-wise, these materials should be considerably cheaper than synthetics on a volume production basis.

In the field of esters, cooperative projects with industry to tailor-make molecules of improved liquid range and thermal stability will be continued. Experimental samples from this cooperative program, thus far, have provided neopentyl esters of neopentyl type alcohols and dibasic acids, and neopentyl glycols and monobasic acids which have viscosities at -65°F in the range of 13,000 centistokes and display the good overall stability characteristics of the neopentyl type ester. Work on the development of esters of this type as well as more viscous polyesters and complex esters of the neopentyl type will be continued.

Using the seven classes of fluids already discussed, additive studies will be directed toward the formulation of an additive package designed to optimize stability, lubrication, and corrosion for final application. Preliminary studies point up the necessity of developing a specific additive package for specific fluid types and applications. That is, the best additive package for a given base stock differs considerably for a hydraulic application, a wide range lubricant use, and a high temperature short time application. Effective additive classes will be studied separately and in combinations with particular emphasis on the synergistic or antagonistic effects of the various classes of additives in combination.

Development of fluids and lubricants for advanced flight vehicles places emphasis on capability studies and basic trends in fundamental fluid properties. It is these basic data that will supply guidance in the design and construction of the actual hardware. There are several critical fluid property areas that should be investigated from a more fundamental viewpoint. These areas include lubricity, oxidative stability, and thermal stability.

Basic lubrication studies have been carried out by this Laboratory as a portion of the Air Force contract effort, and as internal research efforts on an academic program for graduate theses research. An intensification of these basic lubricity studies will be pursued. The two classic types of lubrication prevailing between two moving surfaces are characterized as boundary or hydrodynamic. Hydrodynamic lubrication is dependent primarily on the viscosity properties of the lubricant and is, therefore, a physical phenomenon. Boundary lubrication is a surface phenomenon and is dependent on the formation of an easily sheared surface film. This primarily involves surface chemistry. In most practical cases such as the lubrication of gears, hydraulic pumps, heavily loaded journal bearings, and parts of anti-friction bearings, a hybrid condition exists where there is a hydrodynamic (physical) and a boundary (chemical) component.

To improve the understanding of the hydrodynamic component of lubrication for the various fluid classes, viscosity properties will be studied as a function of temperature, pressure, and shear. A basic understanding of these viscosity effects provides a better definition of the relative hydrodynamic component of lubricity under a given set of environmental conditions.

Boundary lubrication effects will be measured in the four-ball wear and E.P. testers in which there is essentially no hydrodynamic lubricity component. The chemical lubricity of the various fluid classes will be measured without a lubricity additive and with addtives of varying polarity (affinity for the metal surface) and mode of chemical attack. The four-ball wear tester provides lubricity values over the range of 167° to 700°F, thereby demonstrating the temperature effect on boundary lubricity. The synergistic and antagonistic behavior of effective additives will be measured for the integrated additive package. In addition to varying the additives and base stock, boundary lubricity studies will be carried out with different metal systems.

With respect to the boundary and hydrodynamic studies, lubricity studies with vane and gear type hydraulic pumps are capable of illustrating both a boundary and a hydrodynamic component of lubricity. Hydraulic pumps have been used as effective lubricity testers under previous Air Force contracts. These pump tests will be integrated into the basic program of lubricity studies. Studies on the mechanism of silicone and silicate lubricity with ferrous alloys which are discussed in this report is an example of the more basic lubricity approach. In addition to the fundamental laboratory studies, correlation with mock-up test devices will be obtained through cooperative test programs with gear and bearing testers currently being evaluated in conjunction with aircraft lubricant development programs.

The complexity of oxidative reactions has been demonstrated in the laboratory by using the series of oxidation tests described above. These complexities are further born out by the lack of correlation between the Spec. MIL-L-7808 or Spec. MIL-L-9236 oxidation and corrosion tests and the behavior of the lubricants in the engine tests. A continuation of the correlation between breakdown in used engine oil and laboratory oxidative severity is proposed. A series of theses have been written by graduate students on the oxidation mechanism and quantitative oxidation results of tests with mineral oils, hydrocarbons, and esters. The agreement of quantitative analysis of oxidation products with the quantitative measure of the oxygen assimilation has been successfully demonstrated in these theses studies. These quantitative oxidation studies will be extended to fluid systems containing oxidation inhibitors and metal catalysts. High temperature tests of the bulk oil, thin film, and successive type will be included in this study. This series of tests with the different fluid types will contribute substantially to the understanding of overall oxidation behavior of the fluids best suitable for high temperature use.

Thermal stability evaluation for the various fluid classes will be continued and expanded along more basic lines. Thermal stability studies generally available are of the type that indicate, by vapor pressure measurement, the point of incipient thermal stability. In the mineral oil field, thermal and catalytic cracking data emphasize the other extreme where a very rapid rate of thermal deterioration occurs. For hydraulic and lubricant application, the rate of thermal decomposition in the temperature range of incipient instability is desired. Preliminary thermal stability studies by this Laboratory have been of this type. These studies will be expanded to include the effect of temperature, environment, metals, and additive package on decomposition rate. In addition, procedures are being developed to characterize quantitatively the type and amount of decomposition products. In preliminary studies of the thermal decomposition of mineral oils, the mechanism of decomposition and the decomposition products appear to vary considerably in this region of incipient thermal instability from those of similar fluids in the region of commercial cracking operations where the cracking rate is high. The results of this proposed study will provide information on the rate of thermal decomposition and the nature of the thermal decomposition products for the various fluid classes.

Long term reliability studies of fluids and lubricants will be continued. Environmental conditions typical of advanced flight systems will of necessity be determined in cooperation with the Wright Air Development Division. Life of the fluid in an operating system is limited in most cases by deterioration due to oxidative, thermal, radiation, or other environmental factors. The first approach to the problem of ultimate fluid life will be a critical study of the temperature coefficient of reaction rate under thermal conditions and again under oxidation conditions in an environment duplicating as closely as possible the conditions in the advanced weapons system. In the case of thermal stability, a plot of test time versus temperature for lines of constant property change, or degree of reaction, will provide a method of extrapolating fluid life. In terms of oxidation, a plot of stable life versus test temperature provides an estimate of fluid life at a given temperature. At temperatures above the stable life, a plot of the time required to assimilate the amount of oxygen necessary to exceed the oxygen tolerance provides a similar life curve. The environmental conditions are extremely important in predicting a fluid life based on oxygen tolerance or on stable life (induction period). Preliminary studies show that fluid life based on induction period, or oxygen tolerance, may vary by a factor of 2 to 10 depending on environmental conditions and their effect on the additive package. Quantitative evaluation of oxidation products and depletion of additives have been used in previous studies as measured quantities to predict the remaining fluid life. These techniques will be coupled with tests involving changes in environment and additive package to optimize a fluid formulation and test system for a given base fluid. Similar studies will be conducted with the various fluid types showing promise for the specific conditions existing in a particular application.

In many cases, extrapolation of high temperature properties as described above results in a longer stable life than is found at the lower temperature. Frequently, this decrease in stable life is affected by secondary reactions completely different from the reaction measured in the accelerated tests. Storage life of Spec. MIL-L-7808 is an example of this phenomenon. In general, these low temperature reactions affecting stability occur due to the chemical action of the additives with other reaction products which accelerate overall property changes at low temperatures. Dynamic testing will be used wherever possible to check out the low temperature behavior predicted from the high temperature studies. The dynamic tests will in all cases attempt to simulate the predicted end use. In many cases, static or storage conditions in the simulated test environment will best duplicate intended usage. Periodically, sufficient sample will be withdrawn from the static or dynamic endurance test to evaluate property changes and determine the remaining stable life of the fluid. Measurement of low temperature deterioration phenomena will be attempted in this fashion. When clues to the nature of the specific secondary reactions that cause accelerated deterioration are found, these reactions will be studied specifically to understand better the nature of such a reaction and its effect on overall storage or long time stability.

A vacuum source and control system suitable for control at pressures down to 0.05 mm. Hg pressure is being built for use with a vacuum boiling point apparatus for measuring dynamic vapor pressures to temperatures of 750°F. A second unit is being designed for this vacuum source to study the behavior of fluids for extended times at elevated temperatures. This unit will be designed to study the rate of loss of fluid at elevated temperatures and low pressures through relatively small openings. This is essentially a study in diffusion or effusion. This technique is suggested as a method of lowering fluid consumption in systems where pressure seals are impractical. Both of these units will be used to evaluate all of the high temperature fluid types. With the completion of these units, facilities will be available for simulating altitudes of 200,000 feet and attaining 1000°F under thermal conditions or 800°F under oxidative conditions. The fluid classes listed above will be evaluated in these facilities to determine the maximum temperature capability under thermal and oxidative conditions. Preliminary tests with these fluid classes indicate that many of the fluid types have limiting capabilities for thermal stability in the region of 700° to 800°F and for oxidation in the region of 600° to 700°F.

High temperature testing of fluids and lubricants has been a relatively recent development. As a result, test procedures have not yet been standardized as CRC, ASTM, or Federal Spec. VV-L-791 methods. The lack of standard test methods and the introduction of general reproducibility problems due to the high temperatures presents a problem on the basis of interlaboratory reproducibility and hence correlation of data from various sources for different fluid classes. Studies will be continued in an attempt to develop and refine more quantitative and reproducible test procedures for the measure of high temperature lubricity, density, viscosity, thermal stability, fluid volatility, oxidation (stable life, oxygen tolerance, and oxidation rate), and corrosion. A cooperative test program appears to be an effective way of evaluating the interlaboratory reproducibility of the finalized test procedures developed in this program.

II. MISCELLANEOUS

A. EXPERIMENTAL HIGH TEMPERATURE HYDRAULIC FLUID SAMPLES. Several samples of an experimental high temperature hydraulic fluid have been prepared and distributed for evaluation. The fluid comprises a highly refined naphthenic white oil as a base stock, an oxidation inhibitor, an antiwear additive, and an antifoam agent. This fluid is designated as MLO 7243 or MLO 7277. Fluids with these two designations are identical.

The composition and properties of this fluid are discussed in report WADC TR 55-30 Pt VI. A discussion of some of the results obtained in the evaluation of this fluid is included in report WADC TR 55-30 Pt VII. A further discussion of this fluid is in Section D of this report.

Additional samples of this fluid have been distributed to the following organizations:

Boeing Airplane Company Seattle, Washington	65 gallons
Republic Aviation Corporation Farmingdale, Long Island New York	50 gallons
Sundstrand Aviation Division of Sundstrand Corporation Rockford, Illinois	30 gallons
Lockheed Aircraft Corporation Georgia Division Marietta, Georgia	30 gallons
Lockheed Aircraft Company Burbank, California	10 gallons
National Aeronautics and Space Administration Cleveland, Ohio	10 gallons
Cook Technological Center Morton Grove, Illinois	5 gallons
Monsanto Chemical Company 1700 S. Second Street St. Louis, Missouri	1 gallon
Minnesota Mining and Manufacturing Company St. Paul, Minnesota	1 gallon

Douglas Aircraft Company Charlotte, North Carolina	1 quart

A second experimental hydraulic fluid has been prepared and samples distributed to various organizations for evaluation. This formulation has the same additive package mentioned above for the MLO 7243 or MLO 7277 fluid. The base stock for this fluid, however, is a relatively narrow boiling cut from a paraffinic mineral oil. This material is the prototype for a deep dewaxed mineral oil which will have a liquid range of approximately -65° to >700°F. The samples furnished thus far have not been deep dewaxed. That is, they have the same overall stability and performance characteristics as the dewaxed oil except for the low temperature properties. This fluid is designated as either MLO 7459 or MLO 7460. A discussion of the properties and evaluation of this fluid is in Section D of this report.

Samples of this type of fluid have been sent to the following organizations for evaluation.

Vickers Incorporated Detroit 32, Michigan	30 gallons
Boeing Airplane Company Seattle, Washington	15 gallons
Republic Aviation Corporation Farmingdale, Long Island New York	10 gallons
Linear, Incorporated Philadelphia, Pennsylvania	1 pint

B. <u>FLUIDS FOR GEAR TESTER</u>. Five gallons each of three fluids (MLO 7450, MLO 7451, and MLO 7452) have been sent to the Western Gear Corporation, Lynwood, California for evaluation in the Universal Gear and Spline Tester.

C. <u>MISCELLANEOUS OIL SAMPLES</u>. Eleven gallons of MLO 7341 and six gallons of MLO 7392 have been sent to the National Aeronautics and Space Administration for evaluation as high temperature lubricants. These are complete formulations with base stocks comprising a super-refined paraffinic neutral and a paraffinic resin, respectively.

Fifteen gallons of a naphthenic white oil have been sent to the Monsanto Chemical Company, Everett, Massachusetts. This is an oil of the type used as the base stock for the MLO 7243 fluid discussed above.

Ten gallons of MLO 7464 have been furnished to the Wright Air Development Division, WCLTR-LL. MLO 7464 is a naphthenic white oil of the type used as a base stock for Spec. MIL-H-5606 hydraulic fluids.

A one-quart sample each of MLO 7430 and MLO 7431 has been sent to the California Research Corporation, Richmond, California for evaluation as reactor coolants. These materials are narrow boiling fractions from partially hydrogenated aromatic hydrocarbons.

D. DISTRIBUTION OF STANDARD FLUIDS. This Laboratory distributes several fluids for use in calibration on an interlaboratory basis. Two of these fluids are used to calibrate the Shell four-ball wear tester. One of the fluids is used as a low temperature viscosity standard.

1. Standard Fluids for Wear Tester. Eight-ounce samples of two fluids (PRL 3207 and PRL 3462) are furnished as wear tester standards. These fluids comprise a good non-additive lubricant and a lubricant containing an antiwear additive. Past experience has indicated that good interlaboratory reproducibility may be expected with these oils. These standards have been furnished to the following organizations during the period covered by this report.

Convair
Division of General Dynamics Corporation
Ft. Worth, Texas

Republic Aviation Corporation
Farmingdale, Long Island
New York

Douglas Aircraft Company
Santa Monica, California

2. Low Temperature Viscosity Standard. A four-ounce sample of the low temperature viscosity standard (PRL 2815) is furnished. PRL 2815 is calibrated for use at -40° and -65°F. The primary purpose of this standard is the establishment of a common temperature scale for viscosity determinations at these low temperatures. This standard has been used by many organizations over a period of years with very satisfactory results. Samples of this standard have been furnished to the following organizations during the period covered by this report.

Lehigh Chemical Company
Chestertown, Maryland

Royal Lubricants Company
Hanover, New Jersey

Vickers, Incorporated
Detroit 32, Michigan

Materials Laboratory, WCLTR-L
Wright Air Development Center
Wright-Patterson Air Force Base, Ohio

SURVEY OF HYDRAULIC FLUIDS, LUBRICANTS, AND WORKING FLUIDS FOR AERONAUTIC AND ASTRONAUTIC APPLICATIONS

ACKNOWLEDGEMENT. MUCH OF THE BACKGROUND FOR THIS REPORT HAS COME FROM CONTRACTS AF33(616)2851 AND AF33(616)5460.

This report relates to the following three areas:

(a) hydraulic fluids
(b) lubricants
(c) working fluids

Each of these areas will be discussed separately, with emphasis on the materials currently available on a commercial basis, and the materials under development for advanced applications. In the development program, the need for research in specific areas will be indicated.

I. Hydraulic Fluids.

The following military specifications for hydraulic fluids represent the basic groups, or types, of hydraulic fluids that are available. The fluid type and useful temperature range are tabulated below.

Temp. Range, °F.	Base Stk.	Spec. No.	Use
-90 to +200	Mineral oil	MIL-F-25598	Hydraulic and missile oil
-65 to +275	Mineral oil	MIL-H-5606A	Hydraulic oil
-65 to +400	Ester	MIL-L-6387	Hydraulic oil
-65 to +400	Silicate	MIL-H-8446A	Hydraulic oil

Current research is directed to the development of hydraulic fluids for use above 400°F. Examples of the desired temperature range of operation are: (a) from -65° or 0° to 550° or 700°F ; (b) 0° or 30° to 850°F.

The principal fluids that appear suitable are: special types of mineral oils, aromatic hydrocarbons, silicones, silanes, and phenyl ethers.

The results of the principal investigators for the Air Force work are described in a paper by George Baum entitled "Air Force Development Programs in Hydraulic Fluids" presented at the "Conference on Lubricants," 17-19 February 1959 at Dayton, Ohio. This paper is included in Volume II of WADC Technical Report 59-244.

The relative values of the different fluid types are listed in Table 112.

Long range research in this area was reviewed at a conference on "High Temperature Polymer and Fluid Research" held at Dayton, Ohio during the interval 26-28 May 1959. Preprints of the conference were available. The principal fluid types reviewed in this conference were organo-metallics, aromatic materials, and inorganic coordination compounds.

II. Lubricants.

The following are specifications for aircraft lubricants.

Temp. Range, °F	Base Stk.	Spec. No	Use
-65 to +200	Mineral oil	MIL-0-6081B	Jet engine lube
-65 to +350	Ester	MIL-L-7808	Jet engine lube
-65 to +350	Ester	MIL-L-25336	Jet engine lube and high gear loading oil
-65 to +350	Ester	MIL-L-7499	Jet engine lube and extreme pressure oil
-65 or -40 to +450	Ester	MIL-L-9236A	Jet engine lube

Current research is directed toward the development of lubricants for operation at 500° to at least 800°F. In all cases, operation at the lowest possible temperature is desired. While the goal of -65°F is desirable, it may be necessary to sacrifice low temperature performance to get the high temperature capability. The same general fluid types mentioned for hydraulic fluids are applicable to lubricant use, with some modifications. These modifications relate mostly to the additive package and not to the base stock type. The principal differences between hydraulic and lubricant applications reside in the increased oxidative and lubricity demands for lubricants. The relative rating of the different lubricant types are also in Table 112.

III. Working Fluids.

This nomenclature is used to denote fluids used in devices for generating power, such as those in Rankine or heat cycles, or those that are necessary as coolants in a power producing operation.

The AEC has done substantial work in this area, and is perhaps one of the better sources of information. However, it must be recognized that this AEC work is limited to atomic powered devices.

An extensive survey of working fluid capabilities is not available. For this reason the questionnaire in Appendix A was prepared and circulated. Being cognizant of this deficiency, the following WADC groups are working in this area:

(a) Aeronautical Accessories Laboratory
(b) Materials Laboratory
(c) Propulsion Laboratory

The WADC Propulsion Laboratory has contract AF33(616)6232 in operation at Southwest Research Institute. Under this contract, the following properties are being tabulated, for the materials listed:

Properties

Specific heat
Thermal conductivity
Viscosity of liquid and vapor
Density
Melting and boiling points

Properties

- Vapor pressure
- Latent heats, fusion and vaporization
- Mollier diagrams
- Critical properties
- Nuclear cross section
- Dielectric constants

Materials

- Sulfur
- Rubidium
- Mercury and mercury 204
- Phosphorus
- Aluminum bromide
- Lithium
- Potassium
- Cesium
- Helium
- Argon
- Kryton
- Hydrogen

IV. Results of Survey on Hydraulic Fluids, Lubricants, and Working Fluids.

The questionnaire in Appendix A was sent to 45 people. The object of sending this questionnaire was to crystallize the problem areas and evaluate their relative importance. These people represent government and industrial organizations working in aeronautics, missiles, and space craft.

Replies were received from 29 people, or a return of 64 per cent. These people or organizations are listed in Table 113. It should be noted that the largest proportion of replies emphasizes space operations. The predominant problem area in hydraulic fluids, lubricants, and working fluids pertains to high temperatures.

Hydraulic Fluids. Table 114 lists survey results on hydraulic fluids. Eleven organizations listed hydraulic fluid operations at 700°F. and higher, and 5 of these were above 1000°F. Several of these also wanted operability down to -60° to -80°F.

Another item of considerable concern was fluid leakage," indicating the importance of seals in hydraulic systems.

Lubricants. Table 115 lists survey results on lubricants. Fourteen organizations listed the need for lubricants operating above 700°F. Regarding the time at these high operating temperatures 10 of the replies cited 5 minutes to 15 hours above 700°F. One reply related to 1000 hours at 500°F. Three replies cited 1 to 2 years in the range of 1500° to 1800°F.

Other items of concern were reliability, seals, radiation resistance, lack of an atmosphere, lubricity, and bearing materials. Comments regarding lubricity were substantial, and included these problem areas: lubrication with fuels, inorganic lubricants, effect of lubricants on metal fatigue, lubrication with low viscosity fluids, the use of gas bearings, liquid metal lubricants, lubrication in the presence of cryogenics and corrosive materials such as nitric acid, the effects of high vacuum and inert atmospheres, and the effects of additives in new environments.

Working Fluids. Table 116 lists survey results on working fluids. Ten of the replies indicated operating temperatures in excess of 1000°F; of these 6 were in excess of 2000°F, and one listed 4500°F plus.

Several replies suggested mercury, sulfur, and the alkali metals as well as helium and argon.

Nuclear and solar energy appear about equally favored as energy sources, with nuclear becoming more important at the higher power requirements.

Many replies were concerned with the confining, handling, and corrosion properties of the working fluid.

V. Recommendations.

Hydraulic Fluids and Lubricants. These are discussed together because of their similar properties and uses.

(1) An adequate, realistic, and fundamental study of the critical properties of hydraulic fluids and lubricants at high temperatures is needed. Some of these properties are: lubricity, thermal stability, oxidative behavior, and corrosivity, together with such physical properties as: liquid range, bulk modulus, foaming characteristics, and liquid dynamics.

Comparative, standardized, and realistic evaluation procedures, comparable to those in existence for currently used fluids, do not now exist. The lack of end item hardware places the emphasis on fundamental studies at this time. As a result of this survey, it is evident that high temperatures dominate the future applications of hydraulic fluids and lubricants.

The possibility of NASA initiating and coordinating the necessary work to attain these objectives should be examined.

(2) Since the demands on hydraulic fluids and lubricants, based on preliminary design considerations, in many cases approach or appear to exceed the stability limits of the fluids, there is need for unprecedented cooperation between fluid and lubricant developments on the one hand, and hardware developments on the other. Thus far, all of the optimum properties for fluid and lubricant applications have not been found for a single fluid. The desirability of compensating for

fluid properties by mechanical design is suggested by current research and development experience.

Experimental hardware and mock-up equipment are being developed and tested for many advanced vehicles, but there appears to be no well defined mechanism for disseminating and coordinating the results of all this effort. NASA could be the facility for doing this.

(3) Development work on new chemical structure appears to be covered adequately by existing programs.

Working Fluids. Nuclear or solar energy appears the most promising as a source for producing power. Accordingly, the working fluid has to be selected with these two sources in mind. To attain space power, it is necessary to formulate target specifications for working fluids applicable to these energy sources.

The working fluid will be either a gas cycle (heater and cooler), or a liquid-vapor cycle (boiler and condenser) based on the present state of our knowledge.

For the gas cycle, it is recommended that an energetic program be initiated to improve gaseous heat transfer. The use of particulate solids, in the gas or fluidized by the gas, can provide very substantial increases in gaseous heat transfer coefficients.

A competent facility should be established to define the important fluid properties, including the thermodynamic values, for fluids that offer promise, but are otherwise inadequately defined for use in a power cycle.

Electrostatics. When any fluid is moved relative to a surface, there can be an electrical separation into positive and negative charges. These charges can cause explosions where explosive mixtures exist. They can rupture or impair the operation of equipment, in the absence of explosive conditions because of their violence. In combustors, these discharges could be the cause of erratic combustion.

Unless adequate studies are underway to define the role of electrostatic phenomenon in aeronautic and astronautic equipment, it is recommended that work be done in this area.

NACA Sub-Committee on Lubrication and Wear. As a result of the present survey, it appears that the "Review of Needs for Basic Research in the Fields of Lubrication and Wear" reviewed at the July 9, 1958 meeting of the NACA sub-committee on lubrication and wear are still pertinent recommendations. This review is attached as Appendix B.

Table 112

RELATIVE RATING OF VARIOUS FLUID TYPES FOR EXTREME TEMPERATURE CONDITIONS

Rating System: 1 = Excellent; 2 = Good; 3 = Fair; 4 = Poor.

PROPERTY	MINERAL OILS (1)		AROMATIC(1) HYDROCARBON	<------ESTERS------>			CHLORINATED AROMATIC	SILICONE	IMPROVED LUBRICITY SILICONE	PHENYL ETHERS
	PARAFFINIC	NAPHTHENIC		SPEC.-7808 TYPE	NEOPENTYL TYPE	SILICATE				
VISCOSITY-VOLATILITY	2	3	4	1	1	1	4	1	1	3
VISCOSITY-TEMPERATURE	2	3	4	2	2	2	4	1	1	4
LOW TEMPERATURE FLUIDITY	2	3	4	1	2	1	4	1	1	4
THERMAL STABILITY	2	2	1	4	3	3	1	2	2	1
OXIDATION RATE	3	3	2	3	3	3	1	2	2	2
OXYGEN TOLERANCE	1	2	3	4	4	4	3	3	4	3
METAL CORROSION	1	1	1	4	4	3	3	2	3	1
LUBRICITY	1	1	2	1	1	4	3	4	3	3
INFLAMMABILITY	3	3	3	3	3	3	1	3	3	3

(1) SUPER-REFINED AND DEEP DEWAXED.

Table 113

ORGANIZATIONS PARTICIPATING IN SURVEY ON HYDRAULIC FLUIDS, LUBRICANTS, AND WORKING FLUIDS

Army Ballistic Missile Agency, Propulsion and Mechanics Branch, Redstone Arsenal, Alabama (2 Replies)

National Aeronautics and Space Administration, Ames Research Center, Moffett Field, California

National Aeronautics and Space Administration, Langley Research Center, Langley Field, Virginia

National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio

National Aeronautics and Space Administration, Liquid Fuel Rocket Engines Section, Washington, D. C.

National Aeronautics and Space Administration, Auxiliary Power Units Program, Washington, D. C.

National Aeronautics and Space Administration, Space Flight Development, Nuclear Engines Branch, Washington, D. C.

Office of Naval Research, Bureau of Aeronautics, Department of the Navy, Washington, D. C.

Office of Naval Research, Garfield Thomas Water Tunnel, Ordnance Research Laboratory, University Park, Pennsylvania

United States Air Force, Wright Air Development Center, Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio

The Garrett Corporation, AiResearch Manufacturing Company, Los Angeles, California

General Electric Company, Aerodynamics Suboperation Department, Cincinnati, Ohio

General Electric Company, Development Laboratory, Cincinnati, Ohio

General Electric Company, Electrical Propulsion Section, Cincinnati, Ohio

General Electric Company, ANP Division, Cincinnati, Ohio

General Electric Company, Flight Propulsion Laboratory Department, Cincinnati, Ohio

General Electric Company, Small Aircraft Engine Department, West Lynn, Massachusetts

General Motors Corporation, Allison Division, Research Department, Indianapolis, Indiana

General Motors Corporation, Allison Division, Engineering Department, Indianapolis, Indiana

Hughes Aircraft Company, Controls Department, Culver City, California

Hughes Aircraft Company, Materials and Processes Lab., Culver City, California

Hughes Aircraft Company, Engineering Department, Culver City, California

North American Aviation, Inc., Rocketdyne Division, Canoga Park, California (2 Replies)

Republic Aviation Corporation, Research and Development Department, Farmingdale, Long Island, New York

Thompson Ramo Wooldridge, Inc., Thompson Products Division, Engineering Department, Cleveland, Ohio

United Aircraft Corporation, Hamilton Standard Division, Windsor Locks, Connecticut (2 Replies)

Table 114

SURVEY RESULTS ON HYDRAULIC FLUIDS

A total of 29 questionnaires were received from
the organizations listed in Table 113.

1 = Most Important; 5 = Lease Important

Problem Areas in Properties and Applications	No. of Replies Indicating the Following Ratings 1	2	3	4	5	Total Answers
Hydraulic Fluids, General Rating	4	3	7	2	3	19
Hydraulic Applications						
Manned Aircraft	6	2	5	1	4	18
Space craft	11	2	4	0	1	18
Missiles	5	7	2	4	1	19
Rockets	5	6	4	2	0	17
Hydraulic Fluid Properties						
High Temperature	12	5	2	1	1	21
Low Temperature	2	6	0	5	4	17
High Pressure	5	4	2	4	4	19
Lubricity	2	1	7	4	4	18
Bulk Modulus	1	3	5	3	7	19
Inflammability	1	4	6	2	5	18
Hydraulic Systems						
Gear Pump	2	5	3	3	2	15
Vane Pump	1	3	4	4	3	15
Piston Pump	3	2	6	3	1	15
Fluid Leakage	9	4	3	1	1	18
Environment	4	7	5	0	3	19
Materials of construction	3	3	3	1	4	14

Table 115

SURVEY RESULTS ON LUBRICANTS

A total of 29 questionnaires were received from the organizations listed on Table 113.

1 = Most Important; 5 = Least Important

Problem Areas in Properties and Applications	No. of Replies Indicating the Following Ratings					Total Answers
	1	2	3	4	5	
Lubricant Applications						
Manned Aircraft	3	5	8	2	1	19
Space craft	14	2	3	0	0	19
Missiles	3	5	7	2	0	17
Rockets	8	5	3	2	0	18
Lubricant Properties						
High Temperature	13	5	2	1	1	22
Low Temperature	4	4	4	3	3	18
Lubricity	8	4	3	1	0	16
Thermal Stability	9	8	1	2	0	20
Oxidative Stability	2	6	4	1	2	15
Radiation Resistance	8	9	1	0	1	19
Lubricant Systems						
Materials of Construction	5	2	1	1	0	9
Reliability	14	7	1	1	0	23
Seals	9	2	1	0	1	13
Bearing Materials	7	6	1	2	3	19
Speed	1	6	5	3	5	20
Loadings	1	7	3	3	5	19
Lubricant Systems in Space						
Lack of Atmosphere	8	5	3	3	3	22
Lack of Gravity	1	5	6	1	9	22
High Temperatures	10	9	1	1	1	22
Low Temperatures	6	6	3	2	3	20

Table 116

SURVEY RESULTS ON WORKING FLUIDS

A total of 29 questionnaires were received from
the organizations listed in Table 113.

1 = Most Important; 5 = Least Important

Problem Areas in Properties and Applications	No. of Replies Indicating the Following Ratings					Total Answers
	1	2	3	4	5	
Working Fluids General	9	6	0	1	0	16
Working Fluids for						
Nuclear Reactor	10	4	2	0	1	17
Solar Collector	9	5	3	0	1	18
Thermoelectric	5	2	3	0	4	14
For Gas Turbine Power Generation						
Heat Transfer	6	10	1	1	1	19
Entropy Diagram	8	5	4	0	0	17
Thermal Stability	6	4	4	2	1	17
Confining, Handling, and Corrosion	12	4	2	1	0	19
Gas Cycle	3	5	8	0	1	17
Vapor Liquid Cycle	10	5	1	0	1	17
Liquid + Second Working Fluid	4	5	4	2	2	17
For Heater, Turbine, Condenser System						
Heater	6	8	3	0	0	17
Turbine	3	6	5	2	0	16
Condenser	11	1	3	2	1	18
Compressor	4	3	3	4	1	15
Lack of Gravity Effect on Thermodynamic Engine	10	4	4	1	1	20
Better Definition of Fluids for Thermodynamic Engines	5	4	2	0	0	11
For 5 KW Power Generation						
Nuclear	13	1	1	0	0	15
Solar	3	6	5	0	0	14
Thermoelectric	1	4	5	0	3	13

APPENDIX I

A. QUESTIONNAIRE ON WORKING FLUIDS

Name:

Title of Organization:

Date:

Does your organization have problems and/or applications in the following areas:

(a) Hydraulic fluids
(b) Coolants
(c) Working fluids
(d) Primary power system lubricants
(e) Secondary power system lubricants
(f) Auxiliary power system lubricants

* - * - * - * - * - * - * - *

Please rate the answers to these questions by using a scale of 1 to 5 to evaluate their importance as you see it. Rating 1 should be the most important and 5 the least. If the applications are all of equal importance, please rate them by assigning the same number to more than one application. In addition, please indicate specific limiting conditions wherever possible.

I. Fluids

Please rate the following applications with respect to importance and the need to do more research and development work.

(1) Hydraulic, general ( )

Comments:

(2) Hydraulic, specific, with respect to:

(a) Temperatures ( ) high, or ( ) low (give specific values in °F.)

(b) Pressures, high ( ) and values.

(c) Lubricity ( ) with what rubbing combinations.

(d) Leakage and sealing problems ( ) with respect to what materials.

(e) Bulk modulus ( )

(f) Inflammability ( )

(g) Type of pump, vane ( ), gear ( ), piston ( ), constant or variable delivery.

(h) Environment with respect to ambient pressure, temperature and atmosphere, name ( )

(i) New materials of construction, name ( )

(j) Other (state and rate)

Comments:

(3) Hydraulic applications for:

(a) Manned aircraft ( )

(b) Spacecraft ( )

(c) Unmanned aircraft, missiles ( )

(d) Unmanned spacecraft, rockets ( )

Comments:

(4) Coolants, or for transferring heat ( )

- (a) Nuclear reactors ( )
- (b) Solar collectors ( )
- (c) Thermoelectric coolants ( )
- (d) Please give temperature ranges over which coolants are to be used and the nature of the environment ( )
- (e) Other (state and rate)

Comments:

(5) Media for generating power by expanding vapors via turbines ( )

Importance of:

- (a) Heat transfer characteristics ( )
- (b) Favorable temperature-entropy diagram ( )
- (c) Thermal stability ( )
- (d) Confining, handling and corrosion ( )
- (e) Other (state and rate)

Comments:

(6) With respect to (5), what is your evaluation of:

(a) The fluid being a gas throughout the cycle ( )

(b) The fluid capable of changing from liquid to vapor and back to liquid ( )

(c) Being liquid and then transferring its heat to another working fluid ( )

Comments:

(7) In generating space power by a heater (boiler), turbine, condenser (cooler) arrangement (a so-called thermodynamic engine), do you think the most important problems, with respect to fluid properties, reside in:

(a) The boiler or heater ( )

(b) The turbine ( )

(c) The radiator or cooler ( )

(d) The compressor, if the working fluid is a gas ( )

(e) Other (state and rate)

Comments:

(8) Please evaluate the lack of gravity as a serious deterrent to developing power via a thermodynamic engine ( ), in hydraulics ( ), and in lubrication ( ).

Comments:

(9) If a thermodynamic engine is used, what are your opinions of practical and operational temperatures and pressures in:

(a) The heater or boiler (T= °F ; P= psia.)

(b) The radiator or cooler (T= °F ; P= psia.)

Comments:

(10) In a thermodynamic engine for space craft, what are your (first three) preferences for the working fluid, and briefly state why.

Comments:

(11) Should a research and development program be undertaken to find and define better working fluids for thermodynamic engines for space craft? ( )

Comments:

(12) In generating over 5 kilowatts of electric (or mechanical) power for spacecraft, please evaluate the following methods:

(a) Nuclear ( )

(b) Solar ( )

(c) Thermoelectric ( )

(d) Others

Comments:

II. Lubricants and Lubrication

(1) Do the principal problems in lubricants and lubrication reside in:

(a) Manned aircraft ( )

(b) Manned spacecraft ( )

(c) Unmanned aircraft, missiles ( )

(d) Unmanned spacecraft, rockets ( )

Comments:

(2) Are improvements in lubricants needed with respect to:

(a) Operability at low temperatures ( ); limiting viscosity ____cs.; limiting temperature ____ °F

(b) Operability at high temperatures ( ); limiting viscosity ____ cs.; limiting temperature ____ °F

(c) Better lubricity ( ) and define rating system.

(d) Radiation stability ( )

(e) Thermal stability ( ); limits in temperature ____ °F ; time at maximum temperature ____ °F

(f) Oxidative stability ( ); maximum temperature ____ °F ; environment _____; approximate gas flow rate through critical areas _____ ft.^{3}/min.

(g) Sealing media ( ); name ____________.

(h) New materials of construction ( ); name ____________.

(i) Others (state and rate)

Comments:

(3) Do you believe that the lubrication of machinery in space will differ significantly from that in aircraft ( ) because of:

(a) The need for greater reliability ( )

(b) Radiation ( )

(c) Higher ( ) or lower ( ) temperatures

(d) The lack of an atmosphere ( )

(e) The lack of gravity ( )

(f) Greater speeds ( ) and loadings ( ) on bearings

(g) More unusual combinations of bearing materials ( )

(h) Others (state and rate)

Comments:

(4) In what areas involving lubricant application, do you currently lack engineering and research data?

B. REVIEW OF NEEDS FOR BASIC RESEARCH IN THE FIELD OF LUBRICATION AND WEAR

I. The operating conditions, not necessarily occurring simultaneously, under which lubrication and control of friction and wear must be effected in aeronautical and space mechanisms are as follows:

A. Speeds

Extremes of sliding, oscillating, and rolling speeds varying from imperceptibly small rates to those approaching the speed of sound in solids.

B. Temperatures

Extremes from those approaching absolute zero to those equal to the maximum permissible operating temperature of the solids used in the structure of the mechanisms.

C. Atmospheres

Extremes from complete absence of any atmosphere or presence of inert gases or liquids, to presence of high concentrations of highly reactive gases and liquids or highly ionized gases or plasmas.

D. Radiation and Fields

Nuclear radiations of intensity of the order of those in a nuclear reactor, electric and magnetic fields of intensity of the order of those in an atomic particle accelerator, photon radiation of the order of intensity of that in space in the solar system, secondary radiations generated by ionizing particles in space, and gravitational and accelerational force fields varying from zero to several hundred times the force level of the earth's gravitational field.

E. Times

Reliable operating times from the order of a millisecond to several hundred days, operating lives of several thousand days, and shelf lives of several years.

II. The basic problem areas, and the broad problems to be solved in them, generated by the operating conditions defined in part I, are as follows:

A. Materials

Present materials are deficient in their properties under the anticipated conditions. We particularly need to improve the capabilities of lubricants under extremes of temperature. We need basic information of methods of defining and obtaining improved physical and surface fatigue properties of materials for rolling-contact bearings under various conditions of lubrication.

B. Hydrodynamic and Hydrostatic Lubrication

Research on suitable techniques for lubrication at high speeds and/or extremes of temperature is needed. Hydrostatic gas bearings and hydrodynamic effects in rolling bearings are examples.

C. Boundary Lubrication

Under many of the operating conditions, hydrodynamic lubrication will be minimized and the boundary lubrication component will be more critical. More attention should then be paid to the metallurgy of the wearing parts, the chemistry of the lubricant, and the interaction of the bearing surfaces, the lubricant, and the environment. We need to develop methods for forming and maintaining beneficial surface films under dynamic conditions, under static conditions, at extremes of temperature and speed, without deterioration of the bearings, seals, or gear surfaces.

D. Wear

Destructive wear is a major problem under conditions of extreme temperatures and high speeds. We need methods for separating wear into its major components of metal transfer, mechanical abrasion, and chemical attack, and means for preventing their destructive action.

III. The types of applications where these problems are currently most severe, together with an indication of the most urgent problems in these applications, to be solved by basic research, are as follows:

A. Lubricants

Detailed information is needed on the nature and extent of the chemical and physical processes in aero- and astronautical devices that degrade the lubricant's useful life or render it inoperative.

Research along these lines is needed on the following materials:

1. Conventional lubricants at high temperature - mechanism of degradation and means of inhibiting it.

2. Non-conventional lubricants at high and low temperatures - synthesis, development and evaluation of.

    a. Organometallics
    b. Liquid metals
    c. Solid lubricants
    d. Gases

3. Non-conventional fluids at extremely low temperatures- evaluation and development of applications of.

III. 3. (continued)

- a. Liquified gases
- b. Components of high energy propellant combinations.

4. All lubricants under the effects of radiation.

5. All lubricants for their compatibility with unconventional atmospheres in service.

B. Rolling Contact Bearings

Research is needed in three fundamental areas:

1. Mechanism of rolling contact bearing operation
   - a. Lubrication (especially the hydrodynamic lubrication component).
   - b. Physical, metallurgical and chemical factors affecting failures between highly-loaded, closely-fitted surfaces subjected to relative sliding and rolling.
2. Rolling contact fatigue
   - a. Fundamental study of sub-surface rolling fatigue
   - b. Detection of impending fatigue failure of bearings in service.
   - c. Effect of surface conditions on sub-surface fatigue
   - d. Effect of lubricants
   - e. Effect of temperature
3. Development of rolling contact bearing materials for service under extremes of temperature and in unconventional atmospheres.

C. Seals:

1. Research is required to find new materials capable of withstanding a much higher surface temperature at the contact face at high rubbing speeds.
2. Seal materials for containing high energy propellants must be developed. Fundamental stability data on adequate materials in the presence of these materials should be obtained.
3. Fundamental information for seal design should be developed to replace the present empirical design procedures.

D. Gears

1. High temperature gear materials should be developed and investigations conducted to determine adequate compatibility of existing and future lubricants with the new high temperature materials.

2. Some applications require that gears be lubricated by nonconventional, highly reactive fluids, or liquified gases. Work should be done on evaluating the compatability of possible gear material with these fluids.

E. Gas Bearings

Analytical and experimental studies of gas lubricated bearings, including instability factors and load capacities, are necessary.

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