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WADC TECHNICAL REPORT 55-30 Pt 3

FINAL REPORT

FOR

OCTOBER 1953 THROUGH SEPTEMBER 1954

ON

# FLUIDS, LUBRICANTS, FUELS AND RELATED MATERIALS

E. Erwin Klaus

Merrell R. Fenske

Petroleum Refining Laboratory

Pennsylvania State University

NOVEMBER 1954

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NOVEMBER 1954


MATERIALS LABORATORY
CONTRACT NO. AF33(038)18193

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

## FOREWORD

This report was prepared by the Pennsylvania State University under USAF Contract No. AF 33(038)-18193. The contract was initiated under Task No. 73313 (formerly RDO No. 613-15, "Hydraulic Fluids and Lubricants MX-1576") and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. R. W. Sneed acting as project engineer.

Research work for the Air Force on Fluids, Lubricants, Fuels and Related Materials by this Laboratory has been a continuous project since March 1941. The work from March 1941 to July 1945 was conducted under National Defense Research Committee Contract OEMsr408. Work from July 1945 to October 1951 was conducted under Navy Contract NOrd 7958(B).

## ABSTRACT

This report describes work carried out on a continuing project to develop improved fluids, lubricants, and fuels for use by the Air Force. The current report deals primarily with the development of high temperature hydraulic fluid and jet engine lubricant and the study of dirtiness characteristics of jet fuel at elevated temperatures.

The hydraulic fluid development goal is a fluid suitable for use at 700°F. for a limited time in a sealed hydraulic unit. The properties of high quality examples of the following chemical classes have been measured; silicones, silicate esters, diesters, pentaerythritol esters, silicone-ester blends, mineral oils, synthetic hydrocarbons, polyglycol ethers, chlorinated aromatic hydrocarbons, and aryl phosphates. The properties measured include: viscosities from 0° to +700°F., thermal stabilities from 500° to 750°F., oxidation and corrosion stability at 347° and 500°F., and operation in a hydraulic pump (vane type) at 500° to 600°F.

The jet engine lubricant goal is a fluid suitable for use for extended periods at 500° to 600°F. bulk oil temperature. The same general chemical classes enumerated for hydraulic fluids have been included in the engine oil studies. Particular emphasis in the jet engine oil studies has been placed on lubricity studies and severe oxidation and corrosion evaluations at 500°F.

Jet fuel dirtiness has been studied from two basic approaches. An attempt has been made to remove the dirty components from a fuel by physical separation techniques. Secondly, a laboratory method of reproducing high temperature dirtiness in jet fuels is being studied.

Coupled with the above programs, some miscellaneous investigations of hydraulic fluid and lubricant problems have been conducted at the request of the Services. In addition, viscosity standards, experimental fluid and lubricant formulations, and reports prepared by this Laboratory have been distributed at the request of industry and the Services.


## PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. Whitmore
Technical Director
Materials Laboratory
Directorate of Research

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## SUMMARY

HIGH TEMPERATURE HYDRAULIC FLUID STUDIES. With respect to high temperature hydraulic fluid development, emphasis is being placed on the actual measurement of properties and the testing of the fluids at high temperatures, as opposed to the extrapolation of fluid behavior as determined at lower temperatures. Preliminary work discussed in this report indicates the value of such a program. That is, significant differences are shown to exist between extrapolated values and determined values in terms of properties such as oxidation and corrosion stability, thermal stability, lubricity level, and viscosity-temperature characteristics.

Base stock components, as well as some finished formulations, representing various chemical classes are being evaluated in these studies. Classes represented in current studies are silicones, silicates, diesters, silicone-diester blends, pentaerythritol esters, mineral oils, synthetic hydrocarbons, polyglycol ethers, chlorinated aromatics, and aryl phosphates.

Low temperature limits have been relaxed for these studies. Also, some materials of construction are eliminated due to the high temperature operational requirements. This allows the reconsideration of some materials eliminated at lower temperatures for reasons such as low temperature behavior, metal corrosion, and rubber swelling.

Apparatus and a procedure for the measurement of the viscosity of fluids and lubricants at temperatures up to 700°F. have been developed. Operation of the viscometer is no more difficult at temperatures in the range of 500° to 700°F. than in a constant temperature bath at 100°F. The standard ASTM viscosity-temperature chart has been extended to include temperatures up to 700°F. and viscosity values down to 0.4 centistoke. Some experimental viscosity values are given. These values point out the deviation of the determined values from the values extrapolated from the standard ASTM viscosity-temperature chart.

It is indicated that high temperature hydraulic systems will be sealed or pressurized units. This tends to shift the primary emphasis in fluid evaluation from oxidation stability to thermal stability. Two types of high temperature thermal stability evaluations are discussed. In one case, decomposition products can escape through a liquid seal. In the second case, all decomposition products are confined in a stainless steel pressure cylinder. This shift in primary emphasis from oxidation to thermal stability is shown to cause a change in the relative positions of the various compounds. Data are presented indicating that a decrease in thermal stability can result from the inclusion of certain additives in a finished formulation.

It is indicated that 700°F. hydraulic systems may have to be designed on the basis of greater inflammability hazards because of the presence of small amounts of decomposition products in the system. The

relative positions of the various classes of compounds listed above, in terms of thermal stability, are shown.

Conventional hydraulic fluids make use of polymeric thickeners to achieve good viscosity-temperature characteristics. Data are presented to indicate that none of the conventional polymeric thickeners is thermally stable at these higher temperatures.

Relatively mild oxidation and corrosion tests at 500°F. have been conducted to show the effect of air leakage into a closed hydraulic system. Essentially all of the compositions tested show a capacity to assimilate small amounts of oxygen without serious deterioration or dirtiness.

Trace dirtiness caused by the use of phenothiazine as an oxidation inhibitor in dibasic acid ester compositions has been studied. The effect of tricresyl phosphate on the thermal, oxidation, and corrosion stability of ester-base compositions has been measured.

A program to study the effect of oil deterioration on the operation of close clearance slide valves in hydraulic systems is described. Trace dirtiness occurring within the stable life of an ester fluid appears to cause no appreciable change in slide valve friction. Relatively severe oxidation of the ester at 500°F. causes a large increase in slide valve friction. The friction increase is attributed to the formation of a hard lacquer-like deposit.

The interrelation of copper-beryllium alloy and the oxidation and corrosion deterioration of several fluids and lubricants is shown. Copper-beryllium appears to have some effect on the oxidation stability of fluids and lubricants. This effect appears to be intermediate between that shown by metals such as copper and bronze and that exerted by metals such as steel and aluminum. The copper-beryllium alloy does not appear to be affected adversely by the test fluids studied.

A mock-up hydraulic system has been constructed for operation at temperatures up to 600°F. A Vickers model VM-100-40-75-10 vane pump, designed for automotive hydraulic steering units, has been found to give satisfactory operation at temperatures up to 600°F. with a mineral oil fluid. The design of the pump minimizes the problems of mechanical failure and allows fluid testing to go forward without a multiplicity of mechanical problems. A fluidized solids bed type of heat exchanger has been used successfully to supply heat to the test fluid cycle without local overheating of the fluid. Observations at 500°F. have been made concerning lubricity, rubber compatibility, oxidative and thermal stability, and shear behavior of the lubricant. In addition to the weight loss sustained by the vanes, two other methods for the evaluation of lubricity of the test fluid have evolved. In the case of rather severe wear, colloidal metal particles appear in the fluid stream. Secondly, the critical wearing areas on the valve plate and the cam ring have been evaluated for surface roughness with a Brush Development Co. surface analyzer. The relative behavior of various fluids proposed for use as high temperature lubricants is discussed. In general, the mineral oils,

esters, and polyglycol ethers show adequate lubricity while the silicates and a silicone-ester blend (SD-17) show poor lubricity at 500°F. in this vane pump. All of the fluids evaluated showed adequate stability for four hours at 550°F. maximum oil temperature in this hydraulic system which is open to the atmosphere.

A survey report, PRL 6.3-Dec53 entitled "Some Properties of Spec. MIL-O-5606 Hydraulic Fluid at Elevated Temperatures" has been issued. High temperature stability properties of Spec. MIL-O-5606 are emphasized. Report PRL 6.3-Dec53 is attached to this report as Appendix A.

HIGH TEMPERATURE JET ENGINE OIL STUDIES. Much of the data obtained in the studies with high temperature hydraulic fluids also finds application in the work carried out on high temperature jet engine oils. However, the jet engine oil requirements are somewhat more severe in that low temperature requirements are retained, more active metals of construction are present, and, because the systems are not readily sealed, oxidation stability is of major importance. Fluid lubricity is also a major requirement of jet engine oil. The classes of chemicals being surveyed as high temperature jet engine oils include, as in the case of the hydraulic fluid survey, the following: silicones, silicate esters, diesters, pentaerythritol esters, monoesters, mineral oils, synthetic hydrocarbons, polyglycol ethers, chlorinated hydrocarbons, and aryl phosphates.

The evaluation of some additional materials for use as lubricity additives in improved lubricants is described. A series of compounds containing an acid hydrogen along with other elements, such as chlorine or sulfur which are present in some conventional extreme-pressure additives, have been studied as additives in ester- and mineral oil-base fluids. In general, these materials are not competitive with the alkyl acid phosphites on the basis of solubility, lubricity improvement, and metal corrosion under the conditions of the Spec. MIL-L-7808 oxidation and corrosion test.

The study of the effect of storage time on neutralization number increase and lubricity of Spec. MIL-L-7808 type fluids containing alkyl acid phosphite additives is discussed. Alkyl acid phosphites made from secondary alcohols give the best storage stability in terms of neutralization number increase. All of the alkyl acid phosphites show increased lubricity after storage in finished blends or neat.

Wear behavior in the Shell four-ball wear tester with M-10 tool steel and heat stabilized 52-100 steel bearing surfaces is compared to that shown by the conventional 52-100 B.P. type bearing surfaces.

Some preliminary work has been carried out in the Shell four-ball wear tester with titanium and titanium alloy test specimens. Hardness values for the various titanium and titanium alloys are given. Indications are that titanium-on-titanium bearing surfaces are extremely difficult to lubricate even at low loads. The majority of the tests have been conducted using a steel-on-titanium or titanium alloy bearing system. Phosphorus-containing additives are not particularly effective for lubrication of these bearing surfaces. It appears that a chemically erosive

additive is required to keep the rotating steel ball free of titanium pick-up from the stationary balls. It would appear that steel-on-titanium bearing loads might be at least as restrictive as steel-on-bronze bearing loads.

A rather extensive study of the phenomenon of "trace dirtiness" in lubricants containing an amine type oxidation inhibitor, such as phenothiazine, is described. Studies to determine the effect of varying concentrations of phenothiazine on the oxidative characteristics of lubricants at test temperatures of 347°, 400°, and 500°F. have been carried out. The emphasis in this study has been directed toward determining what sacrifice in properties may result from obtaining increased fluid stable life by increasing phenothiazine concentration. The data obtained indicate, in general, that it is desirable to obtain as much inherent stability as possible by ester and bulk fluid constituent refining so that the concentration of phenothiazine may be held to a minimum.

The evaluation of fluids with respect to oxidative behavior at 500°F. has been extended to include complete hydraulic fluid and lubricant formulations. The effect of phosphorus-containing lubricity additives on complete lubricant formulations has been emphasized in these studies. The presence of Acryloid polymer in the finished fluid has no effect on the oxidative deterioration of the fluid. All of the phosphorus-containing ester fluids evaluated at 500°F. in an accelerated oxidation test show increased sludging tendencies.

The use of hindered phenol-dialkyl acid phosphite additive combinations has been studied in mineral oil. The dialkyl acid phosphite has been shown previously to have a synergistic effect on oxidation stability of various dibasic acid esters. The dialkyl acid phosphite shows a synergistic effect on the oxidation stability of naphthenic mineral oils containing hindered phenol oxidation inhibitors. As the molecular weight range, or the viscosity level, of the naphthenic-type mineral oil increases, the effect of the hindered phenol-dialkyl acid phosphite inhibitor combination, as well as other conventional oxidation inhibitors, diminishes. With a well refined naphthenic mineral oil of about 10 centistokes at 100°F., the oxidation and corrosion requirements of Spec. MIL-L-7808 can essentially be met with an inhibitor comprising 0.5 weight per cent of a dialkyl acid phosphite and a hindered phenol.

The study of the effect of storage on oxidation and corrosion stability of Spec. MIL-L-7808 ester type lubricants containing phenothiazine and dialkyl acid phosphite additives has been continued.

Oxidation and corrosion studies at 500°F. have been continued. Emphasis is placed on relative oxidation rate and the amount of deterioration noted for a given amount of oxygen assimilated. There is essentially no induction period or stable life at 500°F. Aroclor 1248, two commercial silicate formulations, some polybutene oils, and several pure hydrocarbons have been evaluated under varying degrees of severity. These data supplement the results of similar evaluations of various

fluids discussed in report PRL 5.8-Sep53. Aroclor 1248 and methyl phenyl silicones both show outstanding oxidation resistance at 500°F. The remaining classes of fluids listed previously for hydraulic fluid and jet engine oil studies fall in the same general area with respect to relatively severe oxidation. These materials do, however, show a capacity for the assimilation of substantial amounts of oxygen with what would appear to be tolerable property changes for jet engine use. Further work in high temperature oxidation and corrosion testing is being directed toward ways by which the capacity for oxygen assimilation may be utilized in a lubricant system to best advantage.

The effect of phosphorus-containing lubricity additives on the thermal stability of Spec. MIL-L-7808 type compositions has been studied. Tricresyl phosphate as well as the alkyl acid phosphites and phosphates appear to have some adverse effect on the thermal stability of dibasic acid esters at 500°F. and above.

Several esters of monobasic acids and primary alcohols have been evaluated as base stock materials. These are compared in this report with some of the more common dibasic acid esters.

Several experimental fluids containing phosphorus-type anti-wear additives have been prepared for evaluation in the Ryder gear tester and the panel coking test.

JET FUEL DIRTINESS. A study of jet fuel dirtiness has been undertaken. Both existent and potential values for gum and dirtiness are included in this study. This problem is being studied from two separate approaches. An attempt is being made to remove the dirty components from the fuel by means of physical separation. Secondly, laboratory methods of achieving high temperature dirtiness with actual jet fuels, as well as pure hydrocarbons, is being studied.

For the first phase of this program, JP-4 referee fuel obtained from the Baltimore Refinery of the Esso Standard Oil Company has been used. This fuel exhibits borderline dirtiness. This JP-4 referee fuel has been subjected to physical separation processes including fractional distillation, liquid extraction with a liquid ammonia-methylamine solvent, and silica gel absorption in an attempt to study the dirtiness characteristics of concentrations of the various classes of hydrocarbons present in the fuel.

For the second phase of this program, particular emphasis has been placed on the tendency to form gum and insolubles when subjected to accelerated oxidation or ageing tests. Preliminary results indicate that the solution to the problems as to how and why gum and insolubles form on storage is extremely complex. In general, the degree of dirtiness noted with this JP-4 referee fuel and its various fractions cannot be reproduced with simple pure hydrocarbons in the JP-4 boiling range, or mixtures of these pure hydrocarbons prepared to simulate the composition of JP-4 by hydrocarbon classes. The aromatic-rich fractions of JP-4 show the highest overall gum forming tendencies, while the more paraffinic

fractions show a higher proportion of insolubles in the total gum.

The effect of oxidation inhibitors, dispersants, and oxygenated solvents on JP-4 referee fuel fractions has been studied. The use of oxygenated solvents is the best of these three approaches in reducing insoluble gum formation under severe oxidation conditions.

Simple distillation and silica gel adsorption appear to be effective in removing existent gum from this JP-4 referee fuel. The data indicate that gum may consist of high molecular weight products resulting from oxidation of the original hydrocarbons followed by polymerization or condensation.

A test unit to simulate the thermal history of jet fuel flow from the tank, through the heat exchanger, to the burner nozzle has been designed and built. This unit is designed to circulate fuel at a desired rate and system pressure through a heater, a porous metal filter, and a cooler, in that order. The rate of pressure drop increase across the filter is taken as an indication of fuel dirtiness. Preliminary tests indicate that this tester is capable of differentiating between fuels of different dirtiness characteristics. Some redesign of the unit appears desirable to facilitate cleaning of the metal surfaces between tests.

MISCELLANEOUS STUDIES. Development work on a thin film preservative fluid for hydraulic equipment has been undertaken for the Navy Bureau of Ordnance under Supplemental Agreement S4(53-1095) of Contract AF33(038)18193. Preliminary studies are concerned with the development of a plasticized polymer film containing an effective rust preventive. The primary method used to measure the rust protection is the humidity cabinet type of rust test. Studies have been made with Acryloid and Polybutene polymeric materials, with dibasic acid esters and mineral oil as plasticizers, and with calcium petroleum sulfonate, barium petroleum sulfonate, and alkyl acid phosphate and phosphate rust preventive additives. The effect of film viscosity and solvent concentration on film thickness has been measured. A quantitative method of evaluating the amount of rusting on the test strip is described. The Aminco Aire humidity cabinet has been calibrated with fluids of known rust preventive characteristics.

Several used Spec. MIL-L-6387 hydraulic fluid samples have been inspected. Except for an expected viscosity decrease due to the shear severity of the alternator drive, there appears to be very little change in fluid characteristics. An engine time of 465 hours was indicated for one of the samples.

Shear stability reference polymer HFS-4 has been evaluated and found to be acceptable for use in Spec. MIL-F-5602 shear stability reference fluid.

This Laboratory has cooperated with the Section B, Research Division VII, ASTM Committee D-2 in the evaluation of the permanent viscosity loss due to shear of two non-Newtonian test oils. The data obtained is discussed and compared to similar results obtained with Spec.

MIL-O-5606 hydraulic fluid and Spec. MIL-F-5602 shear stability reference fluid.

This Laboratory has supplied five gallons each of two non-Newtonian fluids (polymer-containing fluids) and one Newtonian mineral oil to Prof. E. B. DuBois of Cornell University for testing in a journal bearing rig. These tests were conducted under an NACA contract. The used samples from this test program have been evaluated by this Laboratory. There is no evidence of permanent viscosity decrease due to shear in these samples. The data from the journal bearing rig show that the non-Newtonian fluids gave a substantially lower friction value than a Newtonian fluid of the same viscosity without causing an appreciable reduction in film thickness of the lubricant in the journal bearing.

Ten four-ounce samples of PML 2815, the low temperature viscosity standard, has been distributed during this period.

Thirteen samples of fluids and lubricants have been formulated by this Laboratory and distributed to the Materials Laboratory and Service contractors as requested.

Copies of several reports have been distributed to industrial organizations at the request of the Wright Air Development Center.

FINAL REPORT FOR THE YEAR
1 OCTOBER 1953 THROUGH 30 SEPTEMBER 1954
ON
CONTRACT AF33(038)18193

## INTRODUCTION

This report comprises a summary of the work which has been carried out under Contract AF33(038)18193 for the year of 1 October 1953 through 30 September 1954. This is the third yearly report on this contract. Studies and investigations contemplated for the future are also outlined.

A series of conferences were held at the Wright-Patterson Air Force Base on May 13 and 14 between Drs. Fenske and Klaus of this Laboratory and representatives of the Materials Laboratory, Power Plant Laboratories, Aircraft Laboratories and Weapons Systems Laboratory. The purpose of these conferences was to define better the high temperature problems currently being encountered, as well as those predicted for the future in hydraulic fluids, engine lubricants, and jet fuels. One of the purposes of these conferences was to formalize the direction of research and development efforts under Contract AF33(038)18193 toward current and future high temperature problems. It was indicated that future work on this contract should be focused on the following three items. These items are listed in order of decreasing priority or urgency insofar as manpower is limiting. They are all important, and the emphasis is subject to change. It was decided, as a result of these discussions, that future quarterly and yearly reports would be written in three separate sections to cover these three major items. This procedure has been followed in quarterly report PRL 5.11-Jun54 and in this yearly report.

(1) The development of a hydraulic fluid for use at temperatures as high as 700°F. is desired. This type of hydraulic fluid would be used in closed hydraulic systems from which oxygen can be excluded. Thus, the thermal stability and the effects of small quantities of oxygen are more important properties than severe oxidation in the presence of large quantities of air or oxygen. The desired life of the fluid at 700°F. is of the order of 5 to 10 hours. It is important that the hydraulic fluid supply adequate lubricity for pump operation and adequate viscosity to control volumetric efficiency and leakage at high temperatures.

(2) The development of a jet engine lubricant for operation in engines having bulk oil temperatures of 500° to 600°F. is desired. In these systems, bearings may be as hot as 750°F. This problem bears many similarities to the development of the 700°F. hydraulic fluid. The major differences are the increased availability of air, increased lubricity demands, and increased operational life in the case of the jet engine oil. If the desired properties can not be achieved in their entirety, the factor to be gained in useful life of the engine by

mechanical improvements such as seals and segmented oil reservoirs will be explored from the point of view of the oil.

(3) A further study of jet fuel dirtiness is desired. Particular emphasis in this study is being placed on the formation of high temperature dirtiness or insolubles in the fuel. This type of dirtiness is being encountered in oil-fuel heat exchangers and in nozzles of the jet engines burning this preheated fuel.

These three items will be emphasized in future work and reports. A fundamental study of high temperature properties of hydraulic fluids, lubricants, and their components has been under way at this Laboratory for several years. Now that specific goals have been set up, these earlier studies will serve as valuable background on which to base more specific investigations. It is recognized that all of the requirements, or property limits, indicated to be desirable for a 700°F. hydraulic fluid or 600°F. jet engine lubricant may not be readily obtained. That is, there may be several fluids which meet the majority of the requirements of the hydraulic fluid and/or lubricant, but may fail other requirements. The requirements failed by the various fluids will probably not be the same. Therefore, it is planned to evaluate thoroughly all compositions that show promise as high temperature fluids and lubricants to determine not only whether they meet the specific requirements set forth but also to determine by what margin these fluids pass or fail all the various requirements. Since not all of the systems into which these high temperature fluids will go have been successfully built as yet, these data should prove helpful to designers and engineers in their present and future work.

Work on JP-4 jet fuel dirtiness has been started within the last nine months by this Laboratory. This work will be continued along the lines discussed in this report.

## I. HIGH TEMPERATURE HYDRAULIC FLUID STUDIES

A. GENERAL. The current need for a hydraulic fluid suitable for use at 500° to 550°F., and the need in the near future for a 700°F. hydraulic fluid have been emphasized in recent discussions with the Materials Laboratory of the Wright Air Development Center. Primary emphasis in the current program at this Laboratory under Contract AF33(038)13199 is the study of fluids suitable for use as both 500° and 700°F. hydraulic fluids. Emphasis has been placed on the actual testing of the fluids at 500° and 700°F. as opposed to obtaining extrapolated values from determinations at lower temperatures.

This emphasis is dictated primarily on the basis of the exploratory studies conducted in the temperature range of 400° to 750°F. with various fluid and lubricant components over the past two years. For example, studies at 347°F. have shown as high as a 20 fold increase in the oxidation stable life of a diester-base fluid over a conventional mineral oil fluid. Tests at 500°F. with the same fluids indicate that the difference in oxidation stability is less than two fold. Similarly, it has been found that materials showing the best oxidation stability at high temperatures do not necessarily show the best thermal stability.

On the basis of these preliminary data, it appears that a detailed evaluation of several classes of fluids and lubricants showing some promise at high temperatures may be profitable. These materials will be completely evaluated to determine by what margin the fluids pass or fail the desired requirements. These data may be of use in the companion development of high temperature hydraulic system components.

A number of complete fluid compositions as well as several classes of base stock components have been chosen for this study. These fluids are listed below:

1. Silicone (methylphenyl silicone and a special General Electric silicone with improved lubricity)
2. Silicate fluids (MLO 8200 from Cronite Chemical Co. and O.S. 45 from Monsanto Chemical Co.
3. Silicone-diester fluid SD-17 developed by the N.A.C.A.
4. Diesters (di-2-ethylhexyl sebacate)
5. Pentaerythritol esters (Hercoflex 600 from Hercules Powder Co.)
6. Mineral Oils (well refined naphthenic neutral fractions of low pour point)
7. Synthetic hydrocarbons (Polybutenes from Standard Oil Co. of Indiana)
8. Polyglycol ethers (Ucons from Carbide and Carbon Chemical Company.
9. Arochlor 1248 (chlorinated biphenyl)
10. Tricresyl phosphate.

These materials will be evaluated for high temperature behavior (500° to 700°F.). The properties of these compositions have been fairly well defined at lower temperatures. It should be emphasized that the low temperature properties have been relaxed for these high temperature applications. That is, 0° to 30°F. are the lower temperature limits considered instead of -65° to -40°F. In addition, the elevated temperature tends to eliminate from consideration rubber and certain active metals as materials of construction. Thus, materials eliminated from consideration as hydraulic fluids for reasons of low temperature fluidity, metal corrosion, rubber swelling, etc. will be reconsidered in these high temperature evaluations.

B. HIGH TEMPERATURE VISCOSITY MEASUREMENT. The actual viscosity of fluids at 500° to 700°F. is important for mechanical design considerations. For example, the volumetric efficiency of pumps, hydraulic pistons, and slide valves, system leakage, and the hydrodynamic component of lubricity are properties that are directly related to the actual viscosity at elevated temperatures. Viscosities have, therefore, been determined at approximately 500° and 700°F. for some of the fluids discussed previously. A constant temperature vapor bath has been constructed for determining viscosities experimentally at temperatures in the range of 300° to 700°F.

The construction details of this constant temperature bath are shown on Figure 1. The constant temperature bath comprises a 1000 ml. Erlenmeyer flask fitted with a cork to support a conventional modified Ostwald viscometer. A constant boiling liquid is placed in the flask and the vapors constantly bathe the viscometer. The cork is also fitted with an air condenser to return the condensed vapor to the flask, and a thermocouple to measure the vapor temperature in close proximity to the viscometer. The heat source for the Erlenmeyer flask comprises a shallow molten metal bath partially filled with Cerrobase alloy (257°F. melting point). The bath is heated by a 750 watt heater clamped directly onto the bottom of the molten metal bath. Current to the heater is controlled manually through a Variac. The entire molten metal bath and Erlenmeyer flask are insulated with 2 inches of asbestos sheet. The actual temperature of the vapor bath is controlled by the boiling point of the liquid used. The two materials used to obtain approximately 500° and 700°F. are biphenyl (490°F. b.p.) and meta terephenyl (707°F. b.p.).

As indicated, the bath is designed to accommodate one viscometer. Operation of the viscometer is no more difficult at 500° and 700°F. than in a constant temperature bath at 100°F. Many of the fluids evaluated show viscosity variation with time at these elevated temperatures. These variations are due to the thermal instability of the fluid and not to any inherent temperature control problems in operating the bath.

Viscosity determinations on various high temperature fluids are shown on Table 1. These data show that most of the 500°F. and essentially all of the 700°F. viscosity values fall below the value predicted by extrapolating lower temperature viscosity values with

the conventional ASTM viscosity-temperature ch... In addition, about half of the materials evaluated at 500°F. and essentially all those evaluated at 700°F. show greater than one per cent viscosity change upon standing in the viscosity bath for 30 minutes at the test temperature. This problem of viscosity change is due to thermal deterioration of the fluid, or to volatility losses of small quantities of light ends. There are no indications of manipulative difficulties with the constant temperature vapor bath.

The extrapolated values for viscosities were determined from "Tables for Determination of A.S.T.M. Slope and Prediction of Viscosities" by L. T. Ary of the Standard Oil Development Co. This Laboratory has also extended the standard A.S.T.M. viscosity-temperature chart to include temperatures up to 700°F. and viscosity values down to 0.4 centistokes. The experimental curves for several of the fluids are illustrated on Figures 2 and 3 from the data given on Table 1. The lower experimental viscosity than the predicted viscosity effectively increases the ASTM slope for the fluid. This effect is illustrated in the following tabulation.

| Test Fluid | ASTM Slope for the Interval (100°-210°F.) | (100°-490°F.) | (100°-707°F.) |
|---|---|---|---|
| Methylphenyl Silicone (PRL 3358) | 0.346 | 0.388 | 0.448 |
| Special Silicone G.E. (PRL 3475) | 0.315 | 0.344 | 0.373 |
| Di-2-Ethylhexyl Sebacate | 0.702 | 0.745 | - |
| Hercoflex 600 (pentaerythritol ester) | 0.717 | 0.775 | 0.857 |
| Humble Pale D (mineral oil, Coastal type) | 0.815 | 0.815 | 0.848 |

The material giving the least deviation from the predicted viscosity at 700°F. is the mineral oil. The ASTM viscosity-temperature relationship used in Figures 2 and 3 was derived emperically using viscosity data from mineral oils. Curves 1 and 2 on Figures 2 and 3 are straight lines connecting the viscosity limits at the low and high temperatures set up as a desirable target for the 700°F. hydraulic fluid. Of the fluids evaluated, only the silicones meet these viscosity values. The other materials studied would require a V.I. improver to meet these properties. Thus far, V.I. improvers of adequate thermal stability and solubility have not been found. A discussion of the thermal stability of V.I. improvers will be given at a later point in this section.

As indicated previously, very few of the materials tested at 707°F. give constant viscosity values. The general trend in viscosity values with time at 707°F. is a decrease. Several exceptions were noted however. Hercoflex 600 shows a slight increase in 707°F. viscosity with time in the viscosity bath. This same trend is evident in the 600°F. thermal stability test. This is attributed to the nature of the thermal decomposition products. Humble Pale D mineral oil also shows an increase in viscosity with increasing time in the viscosity bath. This viscosity

increase is attributed to a volatility loss of the light ends during the test. There was evidence of evaporation and incipient boiling during this 707°F. evaluation. In a sealed system, naphthenic mineral oils of this type show an overall viscosity decrease with time due to thermal cracking or decomposition of a small quantity of the oil.

C. THERMAL STABILITY. It has been indicated that high temperature hydraulic systems will be sealed or pressurized units. In any event, oxygen and air can be excluded or severely limited. This places primary emphasis, therefore, on thermal stability and only secondary importance on oxidation stability. Heretofore, hydraulic fluids have been designed on the basis of free access to the atmosphere through a vent or breather system. In these previous developments, which were also designed for use at lower temperatures, primary emphasis was placed on oxidation stability. This change in the primary stability requirement from oxidation to thermal also changes the relative positions of the various classes of compounds. For example, mineral oils, which show somewhat less oxidation stability than diester fluids, show superior thermal stability.

Two types of thermal stability tests have been conducted. One type of test has been conducted in an all glass system while the second type has been conducted in a stainless steel pressure cylinder. These tests have been described previously in report PRL 5.8-Sep53. Briefly, the tests in the glass tube apparatus are carried out under a nitrogen atmosphere and the tube is sealed by a U-tube containing approximately three milliliters of the test fluid. This liquid seal allows the passage of gas out or air in with pressure changes greater than approximately 0.25 p.s.i. Tests conducted at 500°F. are of 20 hours duration; those conducted at 600°F. and above are of 6 hours duration. The stainless steel pressure cylinder is a completely closed system and any volatile products formed are confined in the cylinder. Tests conducted in the pressure cylinder are for six hours at 600° to 700°F.

1. Thermal Stability of Hydraulic Fluid Compositions. A number of the compositions discussed previously as high temperature hydraulic fluids have been evaluated in these thermal stability tests. The results of these tests are summarized on Table 4. Thermal stability testing is continuing and this summary table will be expanded in subsequent reports. These data allow a direct comparison of the thermal stability properties of the various classes of products considered for high temperature hydraulic fluids. Some of the data are for finished compositions while others are for base stocks.

Thermal stability, in general, can not be enhanced by additives. A decrease in thermal stability can result from the formulation of complete or finished fluids. For example, the use of tricresyl phosphate and alkyl acid phosphites in esters may result in decreased thermal stability. This effect will be discussed later in this report.

The thermal stability data, in general, indicate that it is desirable to design a pressure relief system and a safe method of

Figure 1

APPARATUS USED IN THE DETERMINATION OF HIGH TEMPERATURE VISCOSITIES

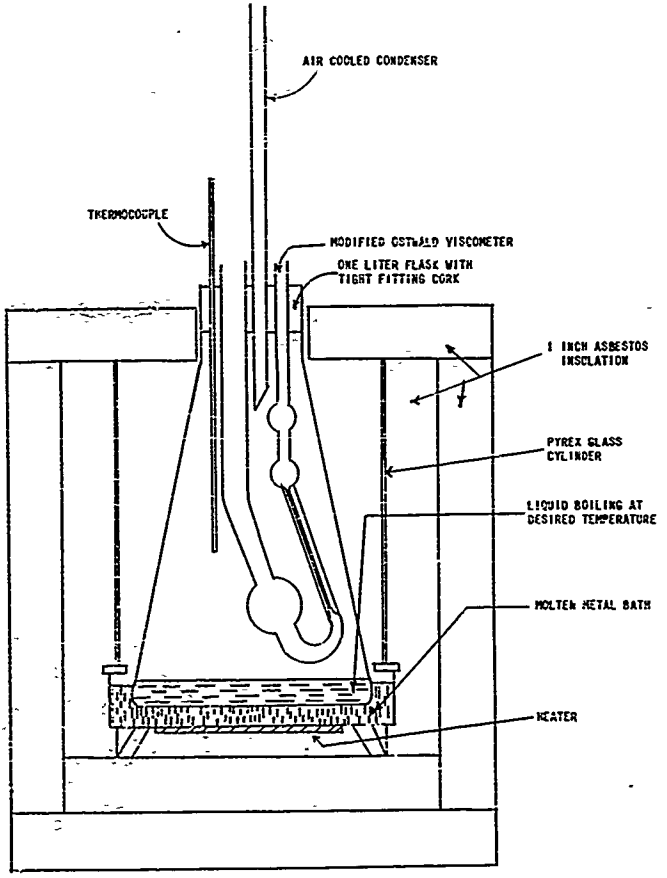


Table 1

## HIGH TEMPERATURE VISCOSITY DETERMINATIONS

THE VISCOSITIES AT 490° AND 707°F. ARE DETERMINED IN A VAPOR BATH CONSISTING OF A 1000 ML. ERLENMEYER FLASK. THE BOILING LIQUIDS USED ARE BIPHENYL (490°F.) AND META TERPHENYL (707°F.). WHERE ONLY A SINGLE VALUE IS GIVEN, THE DEVIATION OR CHANGE IN VISCOSITY IS LESS THAN ONE PER CENT FOR A PERIOD OF 30 MINUTES. WHERE TWO VALUES ARE SHOWN, CHANGE IN VISCOSITY IS OVER A PERIOD OF 30 MINUTES.

| PPL DESIG. | TEST FLUID | CENTISTOKE VISCOSITY AT 0°F. | 100°F. | 210°F. | ASTM SLOPE (210° TO 100°F.) | CS. VISC. AT 490°F. EXPER. | EXTR. (3) | % DEV. (4) | CS. VISC. AT 707°F. EXPER. | EXTR. (3) | % DEV. (4) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| PRL 3358 | METHYLPHENYL SILICONE (D.E.) | 234 | 44.4 | 15.5 | 0.346 | 3.25 | 3.42 | -5 | 1.45-1.37 | 2.30 | -35 |
| PRL 3475 | SILICONE NO. 81405 (G.E.) | 287 | 59.9 | 21.2 | 0.315 | 4.52 | 5.27 | -14 | 2.2-2.0 | 3.02 | -25 |
| PRL 3491 | SILICONE NO. 81451 (G.E.) | 980(2) | 154 | 43.3 | 0.315 | 7.33-7.42 | 8.15 | -9 | -(1) | 4.25 | - |
| PRL 3497 | SILICONE FLUID TYPE 510 (D.C.) | 317 | 75.7 | 29.1 | 0.271 | 6.53 | 7.58 | -13 | 2.85-2.66 | 4.35 | -34 |
| PRL 3519 | SILICONE XF 50 (D.C.) | 363 | 47.9 | 14.4 | 0.396 | 2.65-2.70 | 3.25 | -18 | 1.13 | 1.87 | -40 |
| PRL 3520 | SILICONE RXF 491 (D.C.) | 228 | 17.8 | 5.12 | 0.567 | 1.16 | 1.29 | -10 | 0.562 | 0.78 | -28 |
| PRL 3505 | SILICATE TYPE FLUID (MONSANTO OS-45) | 102 | 12.0 | 3.84 | 0.585 | 0.92-0.87 | 1.08 | -15 | -(1) | 0.67 | - |
| PRL 3455 | TETRA 2-ETHYLHEXYL SILICATE | 60.5 | 6.79 | 2.23 | 0.721 | 0.60-0.58 | 0.67 | -10 | -(1) | 0.44 | - |
| PRL 3506 | SILICATE TYPE FLUID (HLO 8200 ORONITE) | .196 | 32.6 | 11.5 | 0.377 | 2.63-2.59 | 2.99 | -12 | -(1) | 1.84 | - |
| PRL 3529 | 2:1 (VOL.) PRL 3497:DI-2-ETHYLHEXYL SEBACATE + 0.5 WT.% PHENOTHIAZINE | 278 | 42.2 | 14.7 | 0.357 | 3.38 | 3.75 | -10 | -(1) | 2.20 | - |
| PRL 3371 | DI-2-ETHYLHEXYL SEBACATE | 193 | 12.7 | 3.34 | 0.702 | 0.77-0.76 | 0.84 | -8 | -(1) | 0.52 | - |
| PRL 3469 | HERCOFLEX 600 | 615(2) | 22.4 | 4.54 | 0.717 | 0.84-0.82 | 0.96 | -15 | 0.42-0.59 | 0.56 | -27 |
| PRL 3468 | HUMBLE PALE D (NAPHTHENIC MINERAL OIL) | 160,000(2) | 201 | 12.0 | 0.815 | 1.16 | 1.21 | -4 | 0.57-0.66 | 0.62 | -8 |
| PRL 2048 | NECTON 55 (NAPHTHENIC MINERAL OIL) | 19,700(2) | 98.0 | 9.14 | 0.772 | 1.10 | 1.17 | -6 | - | 0.63 | - |
| PRL 3457 | ESSTIC 45 (NAPHTHENIC MINERAL OIL) | 3,900(2) | 44.6 | 5.74 | 0.779 | 0.87-0.86 | 0.98 | -11 | 0.45 | 0.55 | -18 |
| - | 20 WT.% POLYBUTENE B-12 IN NECTON 55 | - | 9252 | - | - | 29-25 | - | - | -(1) | - | - |
| PRL 3440 | POLYBUTENE L-50 | 14,400 | 111 | 12.5 | 0.667 | 1.60 | 1.61 | -1 | - | 0.85 | - |
| PRL 3473 | POLYBUTENE LF-0741 | 804 | 15.4 | 3.10 | 0.829 | 0.62 | 0.69 | -10 | - | 0.42 | - |
| PRL 3474 | POLYBUTENE LF-0742 (HYDROGENATED) | 814 | 15.8 | 3.09 | 0.841 | 0.65-0.63 | 0.68 | -7 | - | 0.41 | - |
| PRL 3507 | UCON LUBRICANT LB-170X | 2,000 | 40.5 | 7.37 | 0.642 | 1.39-1.38 | 1.34 | +4 | -(1) | 0.76 | - |
| PRL 3450 | AROCLOR 1248 | 30,110 | 42.5 | 3.17 | 1.150 | 0.55 | 0.48 | +15 | -(1) | - | - |
| - | TRICRESYL PHOSPHATE | 26,700 | 38.3 | 4.48 | 0.895 | 0.76 | 0.74 | +3 | -(1) | 0.43 | - |
| - | POLYVINYL NAPHTHALENES | 160,000(2) | 133 | 8.16 | 0.897 | 0.00 | 0.93 | -14 | -(1) | 0.49 | - |

(1) A RELIABLE VALUE COULD NOT BE DETERMINED BECAUSE OF DECOMPOSITION OR BOILING.
(2) EXTRAPOLATED VALUE.
(3) DETERMINED FROM "TABLES FOR DETERMINATION OF ASTM SLOPE AND PREDICTION OF VISCOSITIES" BY L. T. EBY OF STANDARD OIL DEVELOPMENT COMPANY.
(4) PER CENT DEVIATION FROM EXTRAPOLATED VALUE.

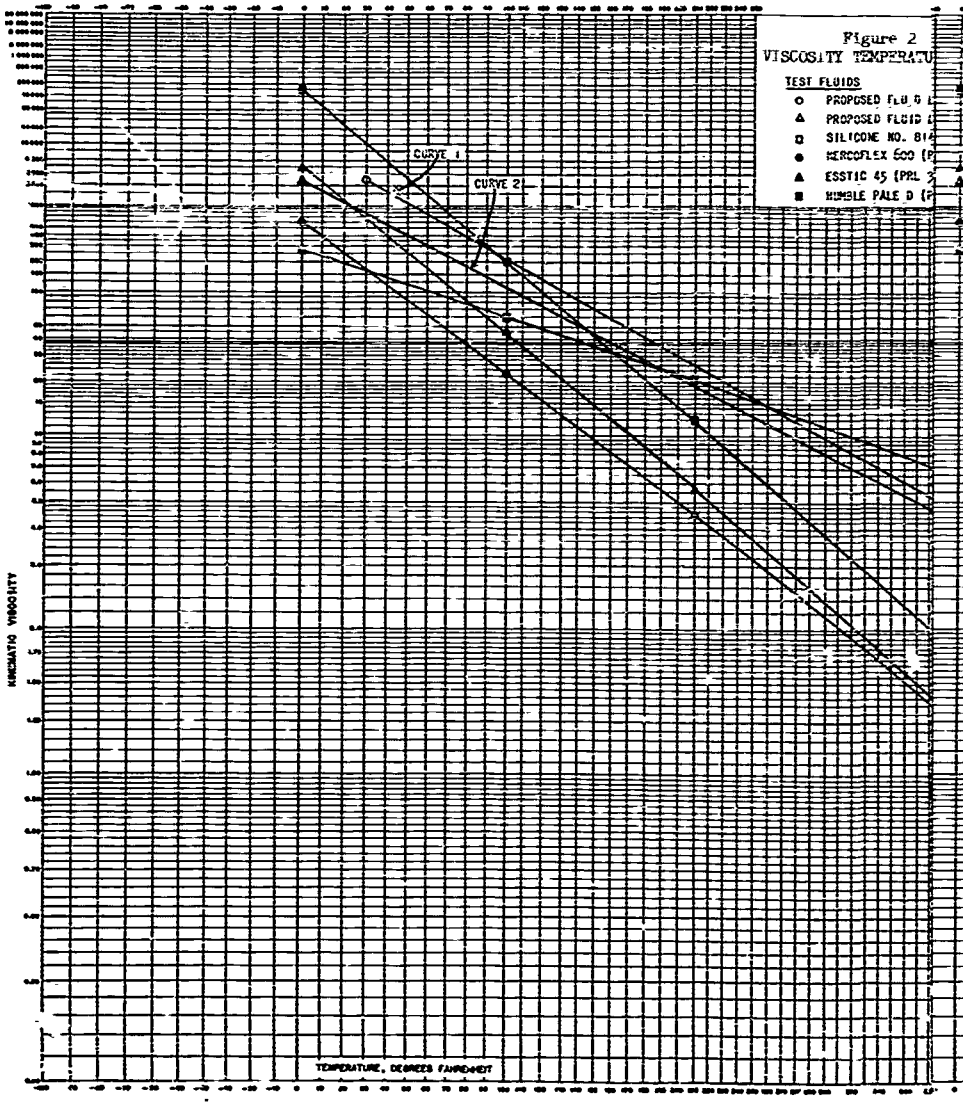


Figure 2
VISCOSITY TEMPERATU
TEST FLUIDS
PROPOSED FLUID
PROPOSED FLUID
SILICONE NO. 81
HERCOFLEX 600 (P
ESSTIC 45 (PRL
HUMBLE PALE D (P
CURVE 1
CURVE 2
KINEMATIC VISCOSITY
TEMPERATURE, DEGREES FAHRENHEIT

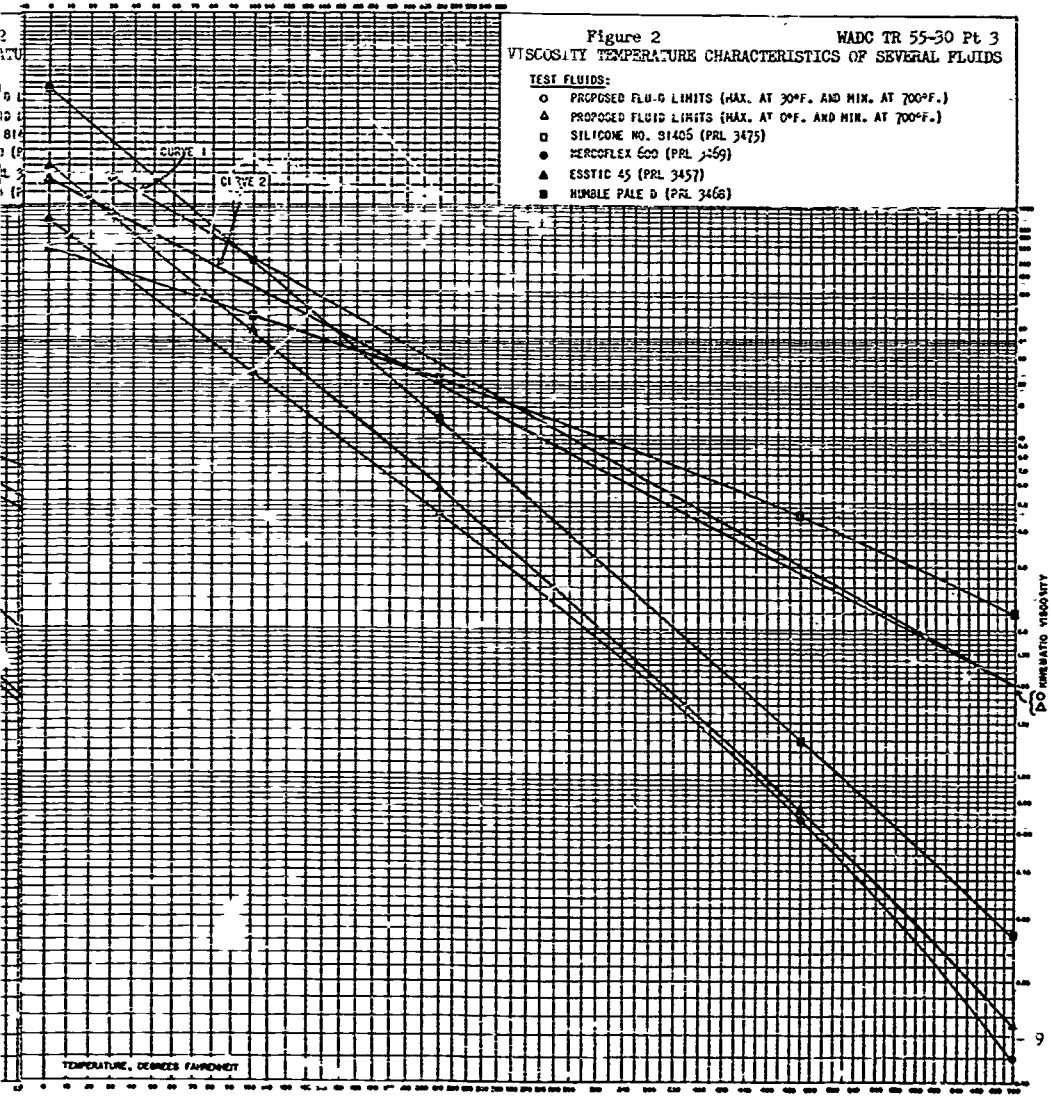



Figure 2 WADC TR 55-30 Pt 3

VISCOSITY TEMPERATURE CHARACTERISTICS OF SEVERAL FLUIDS

TEST FLUIDS:

- ○ PROPOSED FLUID LIMITS (MAX. AT 30°F. AND MIN. AT 700°F.)
- △ PROPOSED FLUID LIMITS (MAX. AT 0°F. AND MIN. AT 700°F.)
- □ SILICONE NO. 81405 (PRL 3475)
- ● MERCOFLEX 600 (PRL 3469)
- ▲ ESSTIC 45 (PRL 3457)
- ■ HUMBLE PALE D (PRL 3468)

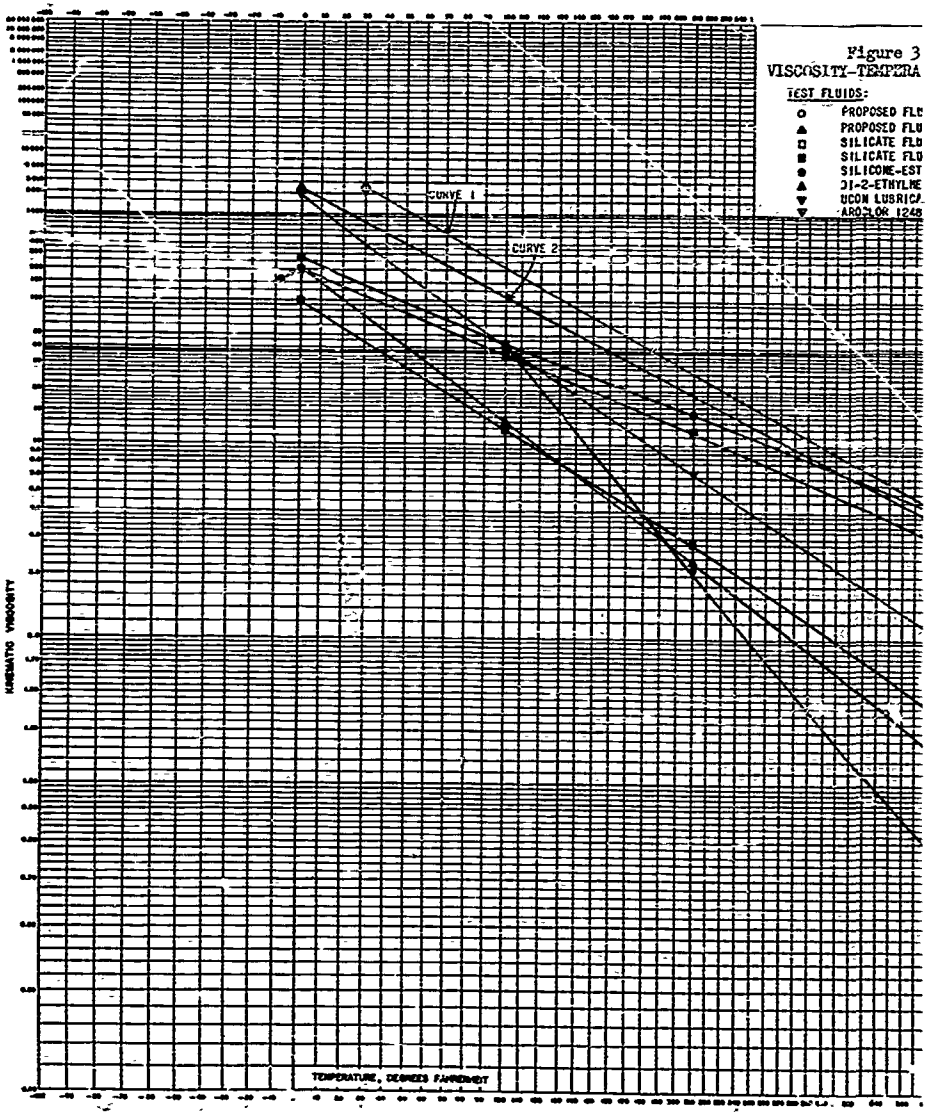
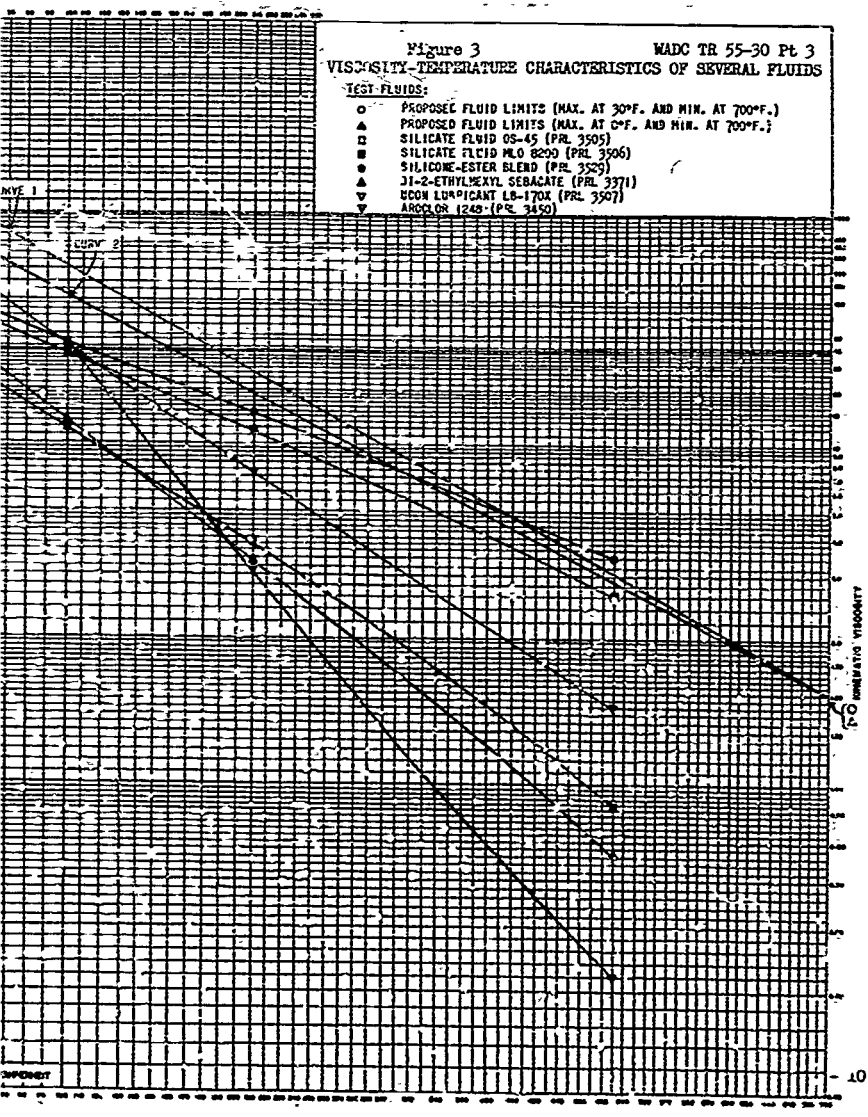


Figure 3
VISCOSITY-TEMPERA
TEST FLUIDS:
PROPOSED FLU
PROPOSED FLU
SILICATE FLU
SILICATE FLU
SILICONE-EST
DI-2-ETHYLHE
UCON LUBRICA
AROCLOR 1248
CURVE 1
CURVE 2
KINEMATIC VISCOSITY
TEMPERATURE, DEGREES FAHRENHEIT

Figure 3

VISCOSITY-TEMPERATURE CHARACTERISTICS OF SEVERAL FLUIDS



discharging volatile inflammable material from the hydraulic system during all stages of operation for all high temperature hydraulic systems. This would apply to a 550°F. system as well as a 700°F. system. It can be seen from the data on Table 4 that all of the materials tested form volatile decomposition products at 700°F. under an inert atmosphere. These volatile products are, in general, organic fragments of the original molecule. As smaller organic fragments, they quite probably represent a higher degree of inflammability than does the parent compound. It is believed, therefore, that 500° and 700°F. hydraulic systems will have to designed on the basis of a greater inflammability hazard than is indicated by the inflammability properties of an unused or "fresh" high temperature hydraulic fluid formulation.

It is apparent from the data on Tables 2, 3, 4 and 5 that none of the fluid formulations are free from some thermal deterioration at 700°F. and few, if any, are entirely thermally stable at 550°F. Thus, it would appear that the relative rates and products of thermal deterioration will play an important role in the selection of the most satisfactory high temperature hydraulic fluids.

Tests conducted in the pressure cylinder in the presence of stainless steel and previous 500°F. thermal stability tests in glass equipment containing copper, steel, silver, magnesium, and aluminum indicate that, at least for certain fluids, there may be an increase in severity of the test when metals are present. The increase in test severity in the presence of metals appears to be more noticeable in the case of esters than for some of the other types studied. Studies of thermal stability at temperatures above 500°F. with metal catalysts will be continued to determine the magnitude of the metal-catalyst effect. Data from the pressure cylinder indicate more severe viscosity changes, in general, than the data from the glass equipment. In addition to the presence of metal surfaces in the pressure cylinder test, the volatile products are kept in the system resulting in more severe viscosity changes.

Aroclor 1248 shows the best thermal stability properties of the various materials tested thus far. Aroclor 1248 is a chlorinated biphenyl which exhibits good non-inflammability properties. This material appears to be thermally stable at 700° and 750°F. as shown on Table 2.

Methylphenyl silicones (Dow Corning 701 and 510 types), silicones prepared by General Electric with improved lubricity properties, and naphthenic mineral oils (Nectons 45 and 55 and Esstic 45) show reasonably good thermal stability at 700°F. On the basis of thermal stability alone, and a 10 hour fluid life at the 700°F. temperature, the silicones, mineral oils, and Aroclor 1248 shown on Table 4 have sufficient stability to warrant further investigation. These fluids have all been investigated at 700°F. in the pressure cylinder and glass apparatus.

Hercoflex 600 (a pentaerythritol ester) shows the best stability of the organic esters evaluated. In the glass equipment, stability looks promising in the 650° to 700°F. range. Pressure rise in the pressure cylinder is quite rapid at 650°F., however. In this pressure cylinder test, the viscosity stability is good and volatility loss is low. Further studies with the Hercoflex 600 are planned in order to evaluate the amount of starting material involved in the thermal decomposition to form gaseous products at 700°F. The thermal stability properties of Hercoflex 600 are very good in both tests at 600°F.

Studies shown on Table 4 indicate that the remainder of the materials tested show reasonable thermal stability in the 550° to 600°F. range. These materials include di-2-ethylhexyl sebacate, tricresyl phosphate, Ucon Lubricant LB-170X (a polyglycol ether), O.S. 45 (a silicate formulation), MLO 8200 (a silicate formulation), Indopol (a low molecular weight polybutene), and SD-17 formulation (a silicone-di-2-ethylhexyl sebacate blend). The two silicate fluids, O.S. 45 and MLO 8200, are commercial fluids prepared by Monsanto Chemical Co. and Cronite Chemical Co., respectively. Tests with typical silicate ester base stocks indicate that some of the changes noted on thermal stability may be due to the polymer or other additives in the formulation.

Data for tetra ($C_6$-$C_8$) silicate (di-2-ethylhexyl di-2-ethylbutyl silicate) and tetra-2-ethylhexyl silicate are shown on Table 5. These data indicate somewhat better thermal stability in terms of viscosity change than the O.S. 45 and MLO 8200 formulations. The stability of di-2-ethylhexyl sebacate dictates the thermal deterioration of the Silicone-di-2-ethylhexyl sebacate blend (SD-17).

Polybutene (Indopol L-50) represents a synthetic hydrocarbon in the form of a polymerized olefin. Additional polybutene fractions are shown on Table 5. Polybutene LF-0742 is a hydrogenated sample of Polybutene LF-0741. All of these polybutenes have about the same thermal stability properties. Hydrogenation does not significantly alter the thermal stability. Depolymerization of these polymers becomes appreciable in the 600° to 650°F. temperature range. Additional synthetic hydrocarbons will be evaluated since materials of the polybutene type appear to be somewhat cleaner in oxidation tests than naphthenic mineral oil fractions.

Thermal stability tests in the pressure cylinder have been conducted with some typical halogenated non-inflammable fluid constituents. These data are shown on Table 2.

Alkazene 42 and Aroclor 1248 are constituents of the ethyldibromobenzene-base hydraulic fluid (PRL 3209) developed to meet Spec. MIL-F-7100. Alkazene 42 is ethyldibromobenzene; Aroclor 1248 is a chlorinated biphenyl; and Fluorolube FS is a polymer of trifluoromonochloroethylene. The pressure cylinder test was chosen for these thermal stability studies primarily as a means of confining the thermal decomposition products.

Table 2

THERMAL STABILITY OF NON-INFLAMMABLE LUBRICANTS

Tests Conducted in Pressure Cylinder of 46 ml. Capacity Using a 20 ml. Charge of Test Fluid

| Test Fluid | Test Temp., °F. | Test Time, Hrs. | Pressure After Test, p.s.i. at Test Temp. | Pressure After Test, p.s.i. at Room Temp. | Neut. No. Increase | % Change in Cs. Visc. at 100°F. |
|---|---|---|---|---|---|---|
| Alkazene 42 | 500 | 6 | 29 | 0 | 0.0 | +2 |
| Alkazene 42 | 600 | 4 | 250 | 45 | 6.1 | +29 |
| Fluorolube-FS | 500 | 6 | 33 | 0 | -0.5 | -2 |
| Fluorolube-FS | 600 | 6 | 100 | 6 | 1.0 | -10 |
| Fluorolube-FS | 650 | 4-3/4 | 270 | 3 | 2.4 | -49 |
| Aroclor 1248 | 600 | 6 | 27 | 0 | 0.0 | 0 |
| Aroclor 1248 | 650 | 6 | 35 | 0 | 0.0 | -1 |
| Aroclor 1248 | 700 | 6 | 40 | 0 | 0.0 | +3 |
| Aroclor 1248 | 750 | 6 | 60 | 4 | 0.3 | +12 |

The Alkazene 42 shows reasonably good thermal stability at 500°F. but decomposes fairly rapidly at 600°F. Fluorolube-FS exhibits a thermal stability of the same order of magnitude as the Alkazene 42. That is, Fluorolube begins to show a high rate of thermal decomposition at about 600°F. It should be emphasized that Fluorolube-FS is a perhalo-compound. Very good thermal stability properties are normally attributed to perhalo-compounds. The Aroclor 1248 which has been discussed previously does give very good thermal stability properties even at 750°F. It should be noted that Aroclor 1248 is not a perhalo-compound but does contain carbon, hydrogen and chlorine in each molecule.

These thermal stability data indicate that some of the non-inflammable hydraulic fluid components exhibit a threshold of thermal decomposition of the same order of magnitude as the other synthetic fluids evaluated in this series of tests.

2. Thermal Stability of Polymeric V.I. Improvers. The conventional Spec. MIL-O-5606 and MIL-L-6387 hydraulic fluids achieve their excellent viscosity-temperature characteristics by the use of viscous polymeric thickeners. Acryloid has been used in these two specification fluids. Acryloid is a polymerized ester of methacrylic acid. Polybutene is another conventional polymeric additive used in hydraulic fluid and lubricant applications where the base stock is a hydrocarbon.

These two polymeric additives have been evaluated for use in high temperature hydraulic fluids. The results of the studies with Acryloids have previously been discussed in yearly report PRL 5.8-Sep53. Thermal stability tests with Polybutene-thickened mineral oils are shown on Table 3.

The thermal stability tests with Polybutene-thickened mineral oil at 500° and 600°F. indicate a thermal stability superior to that of the Acryloid-thickened mineral oil or ester fluids. The Polybutene-thickened oil shows very little viscosity change due to thermal effects at 500°F. At 600°F., a large viscosity decrease is noted for Polybutene blends without indication of appreciable decomposition, i.e., the only change noted is viscosity decrease. The viscosity decrease noted with Polybutene-thickened mineral oils at 600°F. is of the same order of magnitude as the viscosity change noted with Acryloid at 500°F. The Acryloid-thickened blends begin to show signs of chemical decomposition of the ester linkage of the Acryloid at 600°F. Chemical decomposition of the Polybutene thickener begins at 650°F. and becomes a serious problem at 700°F.

Table 3

THERMAL STABILITY OF POLYBUTENE-MINERAL OIL BLENDS AT HIGH TEMPERATURES

Tests Conducted in Glass Test Tubes Under a Nitrogen Atmosphere. Test Time is 6 Hours. Fluid Charge = 25 Gms.

| Test Fluid | Test Temp., °F. | % Visc. Due to Polybutene | % Change in Visc. at 100°F. | Liquid Loss, Wt.% | Neut. No. Increase |
|---|---|---|---|---|---|
| 20 Wt.% Polybutene B-12 in Necton 55 | 600 | 99 | -65 | 0 | 0.0 |
| 20 Wt.% Polybutene B-12 in Necton 55 | 650 | 99 | -98 | 8 | 0.0 |
| 5 Wt.% Polybutene B-12 in Necton 45 | 700 | 50 | -85 | 5 | 0.0 |
| Polybutene B-12 | 700 | 100 | - | 90 | 0.7 |

It can be noted from the data that 90 per cent of the Polybutene polymer decomposes to a volatile gas after 6 hours at 700°F. The decomposition product under these conditions appears to be the isobutylene from which the Polybutene was prepared. These data indicate that Polybutene offers about 100°F. advantage over Acryloid thickener in both the point of thermal viscosity loss and actual chemical decomposition.

Polybutene is not as versatile a polymer as Acryloid in several respects. The solubility of Polybutene in esters, for example, is very limited. The improvement of viscosity-temperature properties of a given base stock for a given degree of thickening is better for the Acryloid polymer. Solubility in dibasic acid esters is also a problem with high viscosity silicone polymers. Thus, a thickener and V.I. improver for use with hydraulic fluids at 550° and 700°F. is still desired.

Polyesters have been used as thickeners for hydraulic fluids and lubricants. A series of Paraplex polyesters (Paraplex AP-52, G-25, and G-25-HV) have been evaluated previously by this Laboratory. The higher molecular weight material compared favorably with Acryloid HF-25 in terms of blending efficiency (i.e., V.I. improvement for a given degree of thickening) and viscosity-shear properties. This series of polyesters contained some ester linkages of a secondary alcohol and, therefore, were less thermally stable than the simple dibasic acid esters of the di-2-ethylhexyl sebacate type.

The data for Paraplex AP-52 shown on Table 5 indicates a viscosity loss and a rupture of the ester linkage in a 500°F. thermal stability test. An experimental polyester containing all ester linkages of primary alcohols has been prepared by the Rohm and Haas Co. This polyester (AC 3385) has been evaluated in the thermal stability test at 500° and 600°F. as shown on Table 5. At 500°F., the polyester shows good stability and at 600°F. the incipient thermal breakdown of the ester linkage is of the same order of magnitude as for di-2-ethylhexyl sebacate under the same test conditions. Thus, the AC 3385 type polyester appears to have adequate thermal and viscosity stability for a 500° to 550°F. hydraulic fluid. Polyesters of this type will be evaluated more extensively as larger samples become available.

A viscous resin fraction extracted from Pennsylvania crude oil has also been considered as a thickener for high temperature hydraulic fluids. Preliminary tests indicate that these resins show good viscosity stability in 500°F. thermal stability tests. Thermal stability tests with these resins will be conducted at higher temperatures.

3. Effect of Phosphorus-Containing Lubricity Additives on Thermal Stability. The effect of tricresyl phosphate and various alkyl acid phosphites on the thermal stability of dibasic acid esters is shown on Tables 77 and 78 and is discussed in some detail in the section on jet engine lubricants. Since some hydraulic fluid formulations do contain tricresyl phosphate, it should be noted here that tricresyl phosphate does have a small adverse effect on the thermal stability of dibasic acid esters at 500°F.

D. OXIDATION AND CORROSION CHARACTERISTICS. It has been indicated that oxidation in high temperature hydraulic systems will be limited by using closed units. Thus, for hydraulic system applications, relatively small quantities of oxygen would be in contact with the fluid at the elevated operating temperatures. These small quantities of oxygen would, however, be in contact with the fluid at the elevated temperature for sufficient time to cause essentially complete oxygen assimilation with many of the proposed fluid types. Due to the closed system and elevated temperature, the effect of oxidation should be considered in a different manner from previous lower temperature hydraulic fluid and lubricant studies.

For temperature ranges up to about 400°F., oxidation stability of a fluid is generally measured as the length of an induction period during which the fluid absorbs little or no oxygen, and exhibits

Table 4

## SUMMARY OF THERMAL STABILITY OF VARIOUS TYPES OF FLUIDS AT HIGH TEMPERATURES

TESTS CONDUCTED IN GLASS TEST TUBES CONSIST OF A TWENTY-FIVE GRAM CHARGE OF TEST FLUID. THE TEST TUBES ARE 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.
TESTS CONDUCTED IN THE STAINLESS STEEL PRESSURE CYLINDER CONSIST OF A 20 ML. CHARGE OF TEST FLUID. THE TOTAL VOLUME OF THE CYLINDER IS 46 ML. 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 PRESSURE CYLINDER THE NITROGEN PRESSURE AT 600°F IS ABOUT 20 P.S.I. GAGE.

| PRL NO. | FLUID | TEST TEMP., °F. | TEST TIME, HRS. | TYPE OF APPARATUS (3) | CENTISTOKE VISCOSITY AT 100°F. ORIG. | FINAL | % CHANGE | % LOSS IN WT. (1) | NEUT. NUMBER (MG. KOH/GM. OIL) ORIG. | FINAL | MAX. SYSTEM PRESS., P.S.I. | FINAL PRESS. AT ROOM TEMP., P.S.I. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3103 | DI-2-ETHYLHEXYL SEBACATE | 500 | 20 | GLASS | 12.8 | 12.8 | 0 | 2.0 | 0.1 | 2.8 | - | - |
| 3371 | DI-2-ETHYLHEXYL SEBACATE | 600 | 6 | GLASS | 12.7 | 11.3 | -13 | 2.0 | 0.1 | 25.3 | - | - |
| 3371 | DI-2-ETHYLHEXYL SEBACATE | 600 | 6 | P.C. | 12.7 | 11.9 | -6 | - | 0.1 | 31.5 | 72 | 0 |
| 3371 | DI-2-ETHYLHEXYL SEBACATE | 650 | 6 | GLASS | 12.7 | SOLID | - | 6.0 | 0.1 | 126 | - | - |
| 3371 | DI-2-ETHYLHEXYL SEBACATE(2) | 650 | 6 | P.C. | 12.7 | SOLID | - | - | 0.1 | 216 | 265 | 25 |
| 3057 | HERCOFLEX 600 | 500 | 20 | GLASS | 22.1 | 22.4 | +1 | 2.0 | 0.0 | 0.4 | - | - |
| 3057 | HERCOFLEX 600 | 600 | 6 | GLASS | 22.1 | 22.4 | +1 | 0.3 | 0.1 | 2.1 | - | - |
| 3057 | HERCOFLEX 600 (PENTA-ERYTHRITOL ESTER) | 600 | 6 | P.C. | 22.1 | 21.6 | -2 | - | 0.1 | 7.2 | 35 | 6 |
| 3057 | HERCOFLEX 600 | 650 | 6 | GLASS | 22.1 | 23.1 | +5 | 0.0 | 0.1 | 14.2 | - | - |
| 3057 | HERCOFLEX 600 | 650 | 2.5 | P.C. | 22.1 | 21.0 | -5 | - | 0.1 | 47.0 | 270 | 72 |
| 3057 | HERCOFLEX 600 | 700 | 6 | GLASS | 22.1 | 27.1 | +23 | 16.0 | 0.1 | 6.8 | - | - |
| 2031 | NECTON 37 | 500 | 20 | GLASS | 15.5 | 15.8 | +2 | 2.0 | 0.3 | 0.3 | - | - |
| 2053 | NECTON 42 | 600 | 6 | GLASS | 32.4 | 32.9 | +1 | 2.0 | 0.2 | 0.2 | - | - |
| 3457 | ESSTIC 45 (MINERAL OILS) | 600 | 6 | P.C. | 44.6 | 42.7 | -4 | - | 0.0 | 0.4 | 25 | 0 |
| 2054 | NECTON 55 | 650 | 6 | GLASS | 98.0 | 82.9 | -12 | 0.0 | 0.0 | 0.2 | - | - |
| 2053 | NECTON 42 | 700 | 6 | GLASS | 32.4 | 16.2 | -50 | 2.0 | 0.2 | 0.2 | - | - |
| 2782 | NECTON 45 | 700 | 6 | P.C. | 44.7 | 20.1 | -55 | - | 0.0 | 0.1 | 158 | 23 |
| 2054 | NECTON 55 | 750 | 6 | GLASS | 99.0 | 31.0 | -68 | 0.0 | 0.0 | 0.4 | - | - |
| - | TRICRESYL PHOSPHATE | 500 | 20 | GLASS | 38.3 | 41.4 | +8 | 2.0 | 0.2 | 3.5 | - | - |
| - | TRICRESYL PHOSPHATE | 600 | 6 | GLASS | 38.4 | 41.8 | +8 | 0.0 | 0.2 | 2.8 | - | - |
| - | TRICRESYL PHOSPHATE | 600 | 6 | P.C. | 38.4 | 51.1 | +33 | 0.2 | 0.2 | 12.9 | 30 | - |
| 3325 | SILICONE 701 (DOW CORNING) | 500 | 20 | GLASS | 7.23 | 7.45 | +2 | 0.0 | 0.0 | 0.0 | - | - |
| 3325 | SILICONE 701 (DOW CORNING) | 600 | 6 | GLASS | 7.23 | 7.80 | +7 | 0.0 | 0.0 | 0.3 | - | - |
| 3325 | SILICONE 701 (DOW CORNING) | 600 | 6 | P.C. | 7.29 | 7.72 | +6 | - | 0.0 | 0.0 | 36 | 6 |
| 3497 | SILICONE 510 (DOW CORNING) | 600 | 6 | P.C. | 75.7 | 58.9 | -22 | - | 0.1 | 0.1 | 31 | 0 |
| 3325 | SILICONE 701 (DOW CORNING) | 700 | 6 | GLASS | 7.28 | 7.67 | +5 | 18.0 | 0.0 | 0.2 | - | - |
| 3497 | SILICONE 510 (DOW CORNING) | 700 | 6 | P.C. | 75.7 | 54.4 | -28 | - | 0.1 | 0.1 | 55 | 0 |
| 3497 | SILICONE 510 (DOW CORNING) | 700 | 6 | GLASS | 75.7 | 50.2 | -34 | 4.0 | 0.1 | 0.1 | - | - |

(CONCLUDED ON FOLLOWING PAGE)

Table 4 (Concluded)

| PRL NO. | FLUID | TEST TEMP., °F. | TEST TIME, hrs. | TYPE OF APPARATUS (3) | CENTISTOKE VISCOSITY AT 100°F. ORIG. | FINAL | % CHANGE | % LOSS IN WT. (1) | NEUT. NUMBER (MG. KOH/GM. OIL) ORIG. | FINAL | MAX. SYSTEM PRESS., P.S.I. | FINAL PRESS. AT ROOM TEMP., P.S.I. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3475 | SILICONE NO. 81406 | 600 | 6 | P.C. | 59.9 | 53.7 | -10 | - | 0.1 | 0.3 | 25 | 0 |
| 3491 | SILICONE NO. 81451 | 600 | 6 | P.C. | 154 | 133 | -13 | - | 0.1 | 0.3 | 36 | 0 |
| 3475 | SILICONE NO. 81406 | 700 | 6 | GLASS | 59.9 | 60.2 | 0 | 2.0 | 0.1 | 6.5 | - | - |
| 3475 | SILICONE NO. 81406 | 700 | 6 | P.C. | 59.9 | 46.3 | -23 | - | 0.1 | 2.5 | 106 | 15 |
| 3491 | SILICONE NO. 81451 | 700 | 6 | P.C. | 154 | 90.5 | -41 | - | 0.1 | 13.4 | 160 | 35 |
| 3507 | UCON LUBRICANT LB-170X | 500 | 20 | GLASS | 40.5 | 39.7 | -2 | 0.0 | 0.0 | 0.1 | - | - |
| 3507 | UCON LUBRICANT LB-170X | 500 | 20 | P.C. | 40.5 | 37.1 | -8 | - | 0.0 | 0.1 | 36 | 0 |
| 3507 | UCON LUBRICANT LB-170X | 600 | 6 | GLASS | 40.5 | 18.5 | -54 | 34.0 | 0.0 | 2.4 | - | - |
| 3507 | UCON LUBRICANT LB-170X | 600 | 1-1/2 | P.C. | 40.5 | 20.8 | -49 | - | 0.0 | 0.8 | 281 | 52 |
| 3505 | OS-45 SILICATE FLUID | 500 | 20 | GLASS | 12.0 | 9.20 | -23 | 2.0 | 0.2 | 2.2 | - | - |
| 3505 | OS-45 SILICATE FLUID | 600 | 6 | GLASS | 12.0 | 7.98 | -34 | 0.0 | 0.2 | 3.1 | - | - |
| 3505 | OS-45 SILICATE FLUID | 600 | 6 | P.C. | 12.0 | 7.06 | -41 | - | 0.2 | 1.4 | 85 | 6 |
| 3505 | OS-45 SILICATE FLUID | 700 | 3/4 | P.C. | 12.0 | 6.91 | -42 | - | 0.2 | 4.0 | 275 | 25 |
| 3506 | MLO 8200 SILICATE FLUID | 500 | 20 | GLASS | 32.6 | 30.0 | -8 | 4.0 | 0.1 | 0.2 | - | - |
| 3506 | MLO 8200 SILICATE FLUID | 600 | 6 | GLASS | 32.6 | 23.7 | -27 | 2.0 | 0.1 | 0.1 | - | - |
| 3506 | MLO 8200 SILICATE FLUID | 600 | 6 | P.C. | 32.6 | 14.2 | -56 | - | 0.1 | 0.0 | 51 | 8 |
| 3506 | MLO 8200 SILICATE FLUID | 700 | 2-1/4 | P.C. | 32.6 | 10.3 | -68 | - | 0.1 | 0.2 | 279 | 51 |
| 3416 | SILICATE FLUID (MLO 5277) | 600 | 6 | GLASS | 27.9 | 24.3 | -13 | 2.0 | 0.1 | 0.0 | - | - |
| 3416 | SILICATE FLUID (MLO 5277) | 600 | 6 | P.C. | 27.9 | 16.6 | -40 | - | 0.1 | 0.1 | 35 | 0 |
| 3450 | AROCLOR 1248 | 600 | 6 | GLASS | 42.1 | 44.0 | +4 | 0.0 | 0.1 | 0.0 | - | - |
| 3450 | AROCLOR 1248 | 600 | 6 | P.C. | 42.1 | 42.1 | 0 | - | 0.1 | 0.1 | 27 | 0 |
| 3450 | AROCLOR 1248 | 650 | 6 | P.C. | 42.1 | 41.8 | -1 | - | 0.1 | 0.1 | 35 | 2 |
| 3450 | AROCLOR 1248 | 700 | 6 | P.C. | 42.1 | 43.3 | +3 | - | 0.1 | 0.0 | 40 | 0 |
| 3450 | AROCLOR 1248 | 750 | 6 | P.C. | 42.1 | 47.2 | +12 | - | 0.1 | 0.4 | 60 | 4 |
| 3440 | POLYBUTENE (INDOPOL L-50) | 600 | 6 | GLASS | 111.1 | 97.6 | -12 | 4.0 | 0.0 | 0.0 | - | - |
| 3440 | POLYBUTENE (INDOPOL L-50) | 600 | 6 | P.C. | 111.1 | 40.6 | -63 | - | 0.0 | 0.0 | 138 | 0 |
| 3440 | POLYBUTENE (INDOPOL L-50) | 650 | 6 | GLASS | 111.1 | 34.3 | -69 | 10.0 | 0.0 | 0.0 | - | - |
| 3529 | 2:1 SILICONE:DI-2-ETHYLHEXYL SEBACATE (BY VOLUME) + 0.5 WT.% PHENOTHIAZINE (SO-17) | 500 | 20 | GLASS | 42.2 | 44.9 | +7 | 0.0 | 0.1 | 0.3 | - | - |
| | | | | | | 25.4 | -40 | 0.0 | 0.1 | 11.0 | - | - |
| | | 600 | 6 | P.C. | 42.2 | SOLID | -- | - | 0.1 | 11.4 | 60 | 3 |

(1) PER CENT LOSS IN WEIGHT IS GOOD TO ± 2.0% OR 0.5 GRAMS.
(2) THIS TEST WAS CONDUCTED WITH A 5 ML. CHARGE OF TEST FLUID.
(3) TESTS CONDUCTED IN GLASS TEST TUBES DESIGNATED AS "GLASS". TESTS CONDUCTED IN STAINLESS STEEL PRESSURE CYLINDERS INDICATED AS "P.C.".

Table 5

THERMAL STABILITY OF VARIOUS FLUIDS AT HIGH TEMPERATURES

TESTS ARE CONDUCTED USING A 25 GRAM CHARGE OF TEST FLUID. TESTS AT 500°F. ARE CONDUCTED FOR A 20 HOUR PERIOD; 600°F. TESTS ARE FOR A 6 HOUR PERIOD. THE TEST TUBES USED ARE SEALED WITH A U TUBE CONTAINING APPROXIMATELY 0 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.

| PRL NO. | TEST FLUID | TEST TEMP., °F. | CENTISTOKE VISCOSITY AT 100°F. ORIG. | FINAL | % CHANGE | % LOSS IN WEIGHT | NEUT. NUMBER (MG. KOH/GM. OIL) ORIG. | FINAL |
|---|---|---|---|---|---|---|---|---|
| 3440 | INDOPOL POLYBUTENE L-50 | 600 | 111 | 97.6 | -12 | 4 | 0.0 | 0.0 |
| 3473 | POLYBUTENE LY-0741 | 600 | 15.4 | 14.4 | -6 | 10 | 0.0 | 0.1 |
| 3474 | POLYBUTENE LF-0742 (HYDROGENATED) | 600 | 15.8 | 14.1 | -11 | 8 | 0.0 | 0.0 |
| 3454 | TETRA ($C_6$-$C_8$) SILICATE | 600 | 5.04 | 5.05 | 0 | 2 | 0.0 | 0.1 |
| | | 700 | 5.04 | 5.48 | +9 | 8 | 0.0 | 1.1 |
| 3455 | TETRA (2-ETHYLHEXYL) SILICATE | 600 | 6.79 | 6.74 | -1 | 0 | 0.0 | 0.1 |
| | | 700 | 6.79 | 7.02 | +3 | 8 | 0.0 | 0.8 |
| 3075 | PARAPLEX AP-52 | 500 | 53.0 | 30.5 | -42 | 0 | 1.3 | 42.5 |
| 3488 | AC-3305 POLYESTER | 500 | 83.3 | 99.8 | +20 | 0 | 0.2 | 2.8 |
| | | 600 | 83.3 | 69.4 | -17 | 0 | 0.2 | 17.6 |

essentially no change in physical properties. The length of the stable life, or induction period, is influenced primarily by additives (oxidation inhibitors) in this temperature region.

At temperatures of 500°F. and above, this characteristic induction period no longer exists or is extremely short lived. These data have been emphasized in the previous yearly reports PRL 5.4-Sep52 and PRL 5.8-Sep53. The presence of oxidation inhibitors at 500°F. and above may, however, slow down the rate of oxygen assimilation. It should be emphasized that in a sealed system at elevated temperatures the primary consideration is not necessarily the induction period or the rate of oxidation, but in many cases it may be the amount of the property change resulting from a given amount of oxygen assimilated. In a sealed system this amount of oxygen should be small.

1. Oxidation and Corrosion Characteristics of High Temperature Hydraulic Fluids. To simulate oxidation at elevated temperatures and limited oxygen, a 24-hour test at 500°F. at a low rate of air circulation (0.6 liters per hour) has been used. On the basis of a five gallon capacity hydraulic system, this 24 hour test introduces the equivalent of approximately 90 cubic feet of air under standard conditions of temperature and pressure (32°F. and 760 mm. Hg pressure).

The results of these low air rate oxidation tests at 500°F. for the high temperature hydraulic fluid formulations and base stocks are shown on Table 6. These data indicate that the amount of available oxygen assimilated at 500°F. varied from approximately 2 to 60 per cent. This value can be converted to the equivalent volume of air used in a 5 gallon hydraulic fluid system by simply taking the indicated percent of 90 cubic feet which is equivalent to the total amount of air passed through the sample.

These data indicate that Aroclor 1248 uses essentially no oxygen. The methylphenyl silicones absorb considerably less oxygen than do the mineral oils, esters, and silicates. The silicates, mineral oils, esters, tricresyl phosphate, and polyglycol ethers absorb from about 20 to 40 per cent of the available oxygen in this test. The high absorption values for Indopol Polybutene polymer L-50 and the Necton 45 are believed to be attributed to oxidation in the vapor section of the tube due to the relatively high volatility of these products. This phenomenon has been noted consistently with high volatility hydrocarbon materials.

The viscosity stability of all of the test fluids appears to be adequate. Neutralization number changes vary according to chemical composition. There is no correlation between neutralization number increase and metal corrosion. The Aroclor 1248 shows some copper corrosion. Tendencies toward copper corrosion have been noted for all of the oxidation tests at 347°F. and above for Aroclor 1248 without the use of basic inhibitors. Tricresyl phosphate shows moderate copper corrosion but excessive steel corrosion under these mild oxidation conditions. Di-2-ethylhexyl sebacate shows borderline copper corrosion. The two silicate formulations show evidence of steel corrosion. The

corrosion value for O.S. 45 is higher than that for MIL 8200. None of the corrosion values could be considered serious in view of the 10 hour life indicated for these high temperature hydraulic fluids.

Dirtiness is generally a critical problem in high temperature systems. The only fluids evaluated that show no evidence of sludge and/or dirtiness are the two methylphenyl silicones and Aroclor 1248. The SD-17 silicone-diester composition shows a large sludge value considering the test severity. It is interesting to note that the sludge formed by the SD-17 blend is 23 times that formed by the ester component, which shows the poorer oxidation stability of the two components that are present in SD-17. This same phenomenon has previously been reported by this Laboratory in PRL 5.8-Sep53 for other similar silicone-diester blends. Tricresyl phosphate also shows a fairly large value of sludge formation coupled with a high viscosity increase.

Dirtiness in the ester, silicate, polyglycol ether (Ucon), synthetic hydrocarbon, and mineral oil is all of approximately the same order of magnitude. A trace is the designation given to dirtiness values up to 0.05 weight per cent. Above this value the dirtiness is expressed numerically to the nearest 0.1 weight per cent. Experience with Spec. MIL-L-7808 jet engine oil indicates that dirtiness of this order of magnitude may cause some problems with respect to filter plugging and deposits. It may be desirable, therefore, to evaluate filter porosity, and the behavior of close tolerance moving parts under realistic conditions in the early development stages of high temperature hydraulic system components.

Oxidation tests with relatively slow rates of air circulation are continuing with fluids representative of various chemical classes. More specific evaluations have been conducted with esters typical of current Spec. MIL-L-6387 and MIL-L-7808 quality materials. These evaluations have been directed toward the effect of oxidation and lubricity additives on oxidation and corrosion stability.

2. Phenothiazine Dirtiness. Phenothiazine is being used widely as an oxidation inhibitor for synthetic hydraulic fluids and lubricants of the ester type. Phenothiazine has been found to be effective in extending the induction period of esters substantially in the temperature range up to 350° and 400°F. At 500°F. the phenothiazine is effective in esters only to reduce the rate of oxidation. Phenothiazine and other amine inhibitors have been found to cause darkening of the fluid and trace dirtiness in ester fluids within the stable life of the fluid. This problem will be discussed in more detail under the high temperature jet engine oil development studies. Some of the data are summarized here to illustrate the manner in which additives may be undesirable in high temperature hydraulic fluids for sealed systems.

Data are tabulated on Table 7 to show the effect of increasing phenothiazine dirtiness as a function of phenothiazine concentration in a 347°F. oxidation and corrosion test. All of the test fluids were oxidized to a point slightly beyond the induction period. None of the

Table 6

OXIDATION AND CORROSION PROPERTIES FOR VARIOUS FLUIDS AT 500°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-6387.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME = 24 HOURS; AIR RATE = 0.6 LITERS PER HOUR;
TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

| TEST FLUID (COMPOSITIONS IN WT.%) | PRL 3207 DI-2-ETHYLHEXYL SEBACATE + 0.5 PHENOTHIAZINE | PRL 3197 SILICONE 510 | PRL 3529 SILICONE-DIESTER BLEND (SD-17) | PRL 3325 SILICONE 710 | PRL 3505 SILICATE FLUID OS-45 | PRL 3506 SILICATE FLUID ML-O 8200 |
|---|---|---|---|---|---|---|
| LIQUID CHARGED, GRAMS | 90.0 | 95.5 | 94.0 | 101.5 | 86.5 | 89.0 |
| LIQUID LOSS, WT.% | 2 | 1 | 1 | 1 | 4 | 4 |
| APPROX. AMOUNT $O_2$ SUPPLIED, GMS.(1) | 3.78 | 3.78 | 3.78 | 3.78 | 3.78 | 3.78 |
| APPROX. AMOUNT $O_2$ USED, GMS.(1) | 1.36 | 0.53 | 1.13 | 0.38 | 1.67 | 1.21 |
| APPROX. % $O_2$ USED | 36 | 14 | 30 | 10 | 44 | 32 |
| MOLES $O_2$ USED/426 GMS. FLUID(2) | 0.20 | 0.07 | 0.16 | 0.05 | 0.24 | 0.18 |
| % CHANGE IN CENTISTOKE VISCOSITY | | | | | | |
| AT 130°F. | +7 | +18 | 0 | +20 | -15 | -58 |
| AT 0°F. | +17 | +23 | -1 | +28 | +9 | -48 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | | | |
| ORIGINAL | 0.1 | 0.0 | 0.1 | 0.1 | 0.0 | 0.1 |
| FINAL | 6.0 | 0.0 | 5.3 | 0.1 | 0.5 | 0.0 |
| WT.% INSOLUBLE MATERIAL | 0.1 | NONE | 2.3 | NONE | 0.1 | TRACE |
| FINAL CATALYST CONDITION | | | | | | |
| APPEARANCE | | | | | | |
| COPPER | CORRODED | DULL | DULL | DULL | BRIGHT | DULL |
| STEEL | DULL | DULL | DULL | DULL | CORRODED | DULL |
| ALUMINUM | DULL | DULL | DULL | DULL | BRIGHT | BRIGHT |
| WT. LOSS (MG./SQ. CM.) | | | | | | |
| COPPER | 0.23 | +0.04 | 0.02 | 0.12 | 0.06 | 0.03 |
| STEEL | +0.02 | +0.02 | 0.02 | 0.02 | 0.42 | 0.11 |
| ALUMINUM | 0.01 | 0.04 | 0.00 | 0.02 | 0.03 | 0.00 |

(1) AMOUNT OF $O_2$ 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 $O_2$ USED IS DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR $O_2$.
(2) THE MOLS OF $O_2$ FOR 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE AMOUNT OF $O_2$ ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYLHEXYL SEBACATE IS 426.

(TABLE CONCLUDED ON NEXT PAGE)

Table 6 (Concluded)

OXIDATION AND CORROSION PROPERTIES FOR VARIOUS FLUIDS AT 500°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-6387.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME = 24 HOURS; AIR RATE = 0.6 LITERS PER HOUR;
TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

| TEST FLUID (COMPOSITIONS IN WT.%) | PRL 3057 MERCOFLEX 600 + 0.5 PHENOTHIAZINE | PRL 2702 NECTON 45 (MINERAL OIL) | NECTON 45 + 1.0 PHENYL-α-NAPHTHYL-AMINE | PRL 3410 INDOPOL POLYBUTENE L-50 | PRL 3508 AROCLOR 1248 | TRICRESYL PHOSPHATE |
|---|---|---|---|---|---|---|
| LIQUID CHARGED, GRAMS | 97.0 | 87.0 | 87.0 | 81.0 | 137.0 | 114 |
| LIQUID LOSS, WT.% | 0 | 0 | 0 | 3 | 0 | 0 |
| APPROX. AMOUNT $O_2$ SUPPLIED, GM.(1) | 3.78 | 3.78 | 3.78 | 3.78 | 3.78 | 3.78 |
| APPROX. AMOUNT $O_2$ USED, GMS.(1) | 0.98 | 2.04 | 0.87 | 2.27 | 0.08 | 1.17 |
| APPROX. % $O_2$ USED | 26 | 54 | 23 | 60 | 2 | 31 |
| MOLES $O_2$ USED/426 GM. FLUID(2) | 0.13 | 0.31 | 0.13 | 0.38 | 0.01 | 0.14 |
| % CHANGE IN CENTISTOKE VISCOSITY | | | | | | |
| AT 130°F. | +12 | +12 | +11 | +15 | +1 | +232 |
| AT 0°F. | +29 | - | - | +69 | - | - |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | | | |
| ORIGINAL | 0.1 | 0.1 | 0.1 | 0.0 | 0.0 | 0.1 |
| FINAL | 0.6 | 1.1 | 0.4 | 0.6 | 0.0 | 40.0 |
| WT.% INSOLUBLE MATERIAL | TRACE | TRACE | TRACE | TRACE | NONE | 0.9 |
| FINAL CATALYST CONDITION | | | | | | |
| APPEARANCE | | | | | | |
| COPPER | DULL | COATED | COATED | DULL | CORRODED | CORRODED |
| STEEL | DULL | DULL | DULL | DULL | DULL | CORRODED |
| ALUMINUM | DULL | DULL | DULL | DULL | BRIGHT | DULL |
| WT. LOSS (MG./SQ. CM.) | | | | | | |
| COPPER | 0.04 | +0.10 | +0.10 | +0.02 | 0.60 | 1.18 |
| STEEL | 0.01 | 0.02 | +0.02 | 0.02 | 0.03 | 11.30 |
| ALUMINUM | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.03 |

(1) AMOUNT OF $O_2$ 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 $O_2$ USED IS DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR $O_2$.
(2) THE MOLS OF $O_2$ FOR 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE AMOUNT OF $O_2$ ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYLHEXYL SEBACATE IS 426.

inhibited blends were carried as far beyond the stable life as the 20 hour test with uninhibited ester.

These data indicate increasing sludge formation with increasing phenothiazine concentration. These data indicate that for a limited amount of oxidation which might be anticipated by a sealed, or partially sealed system, the probability of dirtiness or sludge formation would increase directly with increasing phenothiazine oxidation inhibitor.

Table 7

EFFECT OF PHENOTHIAZINE CONCENTRATION ON OXIDATION AND CORROSION PROPERTIES OF DI-2-ETHYLHEXYL SEBACATE AT 347°F.

Test Procedures and Techniques in Accordance with Spec. MIL-L-6387.
Test Temperature = 347 ± 3°F.; Test Time as Indicated; Air Rate = 10 ± 1 Liters Per Hour; Test Fluid = 100 ml.; Test Conducted with a 1 Inch Square each of Steel, Cadmium-Plated Steel, Aluminum, Copper and Magnesium.

| Test Fluid | Di-2-Ethylhexyl Sebacate (PRL 3371) | | | | | |
|---|---|---|---|---|---|---|
| Phenothiazine Concentration, Wt.% | None | 0.1 | 0.25 | 0.5 | 1.0 | 2.0 |
| Test Time, Hours | 20 | 25 | 63 | 159 | 194 | 424 |
| Approx. Stable Life, Hours | - | 21 | 46 | 152 | 180 | 424 |
| % Change in Cs. Visc. at 130°F. | +30 | +7 | +24 | +15 | +12 | +7 |
| Neut. No. Increase, Mg. KOH/Gm. Fluid | 10.6 | 3.8 | 15.3 | 12.2 | 32.4 | 3.8 |
| Wt.% Oil Insolubles - | None | Trace | 0.2 | 0.4 | 2.1 | 1.5 |

More severe oxidation tests were conducted at 500°F. to study further the effect of phenothiazine concentration on dirtiness in di-2-ethylhexyl sebacate. These data are shown on Table 8. It can be seen that the effect of the phenothiazine is to reduce the rate of oxygen assimilation under a given set of test conditions. The tests in this case were continued to about the same degree of severity on the basis of oxygen assimilated. These conditions are somewhat more severe than would be anticipated in a sealed hydraulic system. Under these test conditions, there is a strong trend toward more dirtiness with the presence of, or increase in concentration of. phenothiazine.

Table 8

THE EFFECT OF PHENOTHIAZINE CONCENTRATION ON OXIDATION AND CORROSION CHARACTERISTICS OF DI-2-ETHYLHEXYL SEBACATE AT 500°F.

Test Procedures and Techniques in Accordance with Spec. MIL-L-6387.
Test Conditions Include: Test Temperature = 500 ± 5°F.; Air Rate = 5 ± 0.5 Liters per Hour; Test Time = 30 Hours; Test Fluid Charged = 100 ml.; Catalyst = A 1 Inch Square of each Metal Indicated.

| Test Fluid | Di-2-Ethylhexyl Sebacate (PRL 3371) | | | |
|---|---|---|---|---|
| Phenothiazine Concentration, Wt.% | None(1) | 0.5 | 1.0 | 2.0 |
| Wt.% Volatile Products | 7 | 9 | 7 | 1 |
| Mols $O_2$/426 Gms. Fluid | 1.3 | 1.3 | 1.2 | 1.0 |
| % Change in Cs. Visc. at 130°F. | +39 | +116 | +56 | +32 |
| Neut. No. Increase, Mg, KOH/Gm. Fluid | 19.8 | 16.7 | 13.2 | 7.5 |
| Wt.% Oil Insolubles | 0.1 | 0.8 | 10.9 | 10.8 |
| Wt. Loss (Mg./Sq. Cm.) | | | | |
| Copper | 0.04 | 0.07 | +0.17 | +0.18 |
| Steel | +0.62 | +0.23 | 0.05 | +0.05 |
| Aluminum | 0.00 | 0.00 | 0.00 | 0.00 |

These data indicate that trace dirtiness of the type now noted with the use of Spec. MIL-L-7808 in the region of 200° to 350°F. may be encountered with relatively small quantities of oxygen at 500°F. due to the presence of phenothiazine. For use in sealed systems, a small concentration of a hindered phenol type inhibitor to protect the hydraulic fluid in shelf life storage but which gives essentially no apparent high temperature oxidation protection, may be more desirable for esters than phenothiazine or other amine type inhibitors.

3. Effect of Tricresyl Phosphate on High Temperature Hydraulic Fluid Dirtiness. Tricresyl phosphate is a commonly used lubricity additive in hydraulic fluids and jet engine lubricants. The advantages of tricresyl phosphate in esters as a lubricity aid at 500°F. in the Vickers vane type power steering pump are demonstrated in this report. The effect of tricresyl phosphate, as well as various alkyl acid phosphates and phosphites, on the oxidation stability of esters at 500°F. has been determined. This study will be discussed in some detail in the section on jet engine oils. The effect of tricresyl phosphate on phenothiazine-inhibited di-2-ethylhexyl sebacate in 500°F. oxidation tests is summarized on Table 9.

Table 9

EFFECT OF TRICRESYL PHOSPHATE ON OXIDATION AND CORROSION AT 500°F.

Test Conditions: Test Time = 20 Hrs.; Air Rate = 5 ± 0.5 l./hr.; Test Fluid Charged = 100 ml.; Catalyst = a 1 Inch Square of Each Metal. Test Fluid = 0.5 Wt.% Phenothiazine in Di-2-Ethylhexyl Sebacate.

| Tricresyl Phosphate, Wt.% | - | 1.0 | 5.0 |
|---|---|---|---|
| % Visc. Change at 130°F. | | | |
| Oil Insol. Removed | +44 | +37 | +118 |
| Isopentane Insol. Removed | +4 | +12 | +79 |
| Neut. No. Increase, Mg. KOH/Gm. Fluid | 15.3 | 14.2 | 15.2 |
| Wt.% Oil Insolubles | 0.1 | 2.2 | 3.6 |
| Catalyst Loss (Mg./Sq. Cm.) | | | |
| Copper | 0.08 | 0.36 | 0.05 |
| Steel | 0.00 | 0.06 | +0.07 |
| Aluminum | 0.00 | 0.13 | +0.04 |

These data show that under oxidation conditions the tricresyl phosphate contributes substantially to fluid dirtiness at 500°F. This dirtiness effect in 347°F. oxidation and corrosion tests has not been clearly demonstrated. At 500°F., however, tricresyl phosphate produces considerably more insolubles than phenothiazine.

The undesirable effects of these additives demonstrated by Tables 7, 8 and 9 show that, at 500°F., it is not a simple problem to obtain from additives a sizeable safety factor in lubricity and oxidation without jeopardizing certain other fluid properties. These data point up the desirability of knowing the minimum requirements of the service application at high temperatures in order to develop the best overall fluid.

4. Slide Valve Sludging Tests. The Wright-Air Development Center, Materials Laboratory, requested this Laboratory to study the effect of oil oxidation on the operation of close clearance slide valves in hydraulic systems. It was indicated that hydraulic slide valves are made to close tolerances and are located, in some cases, in the hot portion of the hydraulic system. In many cases, the slide valve must move freely after remaining in one position for extended periods in the presence of the hydraulic fluid at elevated temperatures. Thus, the slide valve appears to be one of the more critical areas for sludge or lacquer formation to cause malfunctioning of the hydraulic system. The average clearance between the piston lands and the cylinder barrel is of the order of 0.0001 to 0.0002 inch on the radius.

Two complete slide valves were obtained from North American Aviation, Inc. through the Wright Air Development Center. This

Laboratory does not have adequate control equipment for operating the slide valves as a portion of a hydraulic system mock-up. In addition, operating temperatures above those of conventional hydraulic systems were desired for this laboratory investigation. Operation of the slide valve at high temperatures was simulated by removing the barrel and piston assembly from the housing and immersing this assembly in a bath of hydraulic fluid exposed to accelerated oxidation conditions. The piston-barrel assembly was mounted in such a manner that the piston could be moved back and forth in the barrel during the oxidation test with a balance arrangement for the quantitative measurement of the force necessary to effect piston movement.

The construction details of the constant temperature bath, the slide valve holder, and the piston yoke and balance arrangement are given in report PRL 5.8-Sep53. The apparatus is designed to operate over a temperature range of 100° to 600°F. The unit can be used for thermal stability tests as well as oxidation and corrosion tests. The air for oxidation, and the inert atmosphere (nitrogen) for thermal stability, can be introduced under the surface of the test fluid or passed through the free space above the test fluid. Problems encountered in moving the piston with a small unbalanced force are discussed in report PRL 5.8-Sep53. With proper alignment and adjustment, an unbalanced force of 5 to 10 grams is sufficient to move the piston in either direction with a typical unused hydraulic fluid.

The tests were conducted at the indicated temperatures using a fluid charge of 500 ml. This quantity of fluid was sufficient to immerse totally the slide valve assembly in the fluid. A total air rate of 20 liters per hour was introduced at the rate of 10 liters per hour through each of two steel inlet tubes located about midway between the end of the bath and the end of the slide valve. The location of the air inlet tubes is indicated in Figure 7 of report PRL 5.8-Sep53. The inlet tubes were extended to within one-quarter of an inch of the bottom of the test fluid reservoir. In this manner, the fluid receives adequate stirring from the air stream. A value of 20 liters per hour total air has been chosen to match the severity of the slide valve oxidation test with that of the more conventional Spec. MIL-L-7808 type oxidation test conventionally used by this Laboratory for oxidation and corrosion tests at 347° to 500°F.

Thermal stability tests were conducted by sweeping nitrogen over the top of the fluid and by bubbling nitrogen into the fluid in the same manner described above for air. Bubbling the nitrogen through the liquid does not appear to be an adequate test procedure for thermal stability. In some cases where nitrogen was bubbled through the fluid, there were signs of significant oxidation of the fluid. A test illustrating this phenomenon is included on Table 10. The method of passing nitrogen over the surface of the fluid is preferred for thermal stability tests. Between tests, the slide valve was cleaned by heating and brushing the coated parts of the slide valve in a solvent consisting of a 50-50 mixture by volume of benzene and pyridine. This solvent was fairly effective in removing the sludge and lacquer-like coatings from the barrel and piston assembly. It should be emphasized, however, that the coatings were not completely removed in any of the tests, although in

most cases, the coatings were effectively removed from the piston lands and cylinder barrel where clearance is critical.

Two general patterns have been followed in the slide valve exercise during testing. In one case, the slide valve was measured every hour for the force necessary to produce motion in the piston, while in the second type test, the piston was allowed to remain stationary for essentially the entire test and exercising was attempted only at the end of the test period.

The data taken from the various slide valve tests are shown on Table 10 and Figure 4. The data on Table 10 illustrate both the oil oxidation behavior and the slide valve exercise characteristics. In this series of tests, a value of over 500 grams required to remove the piston is considered as failure or unsatisfactory behavior. The normal value for moving the piston with a fresh ester-base oil is 10 to 20 grams. Thus, it can be seen that a 50 fold friction increase is considered the criterion of failure.

The properties of viscosity and neutralization number change and sludge formation are indicative of oxidative deterioration. Probably the most important of these property changes to the operation of a slide valve is the sludge formation. The metal test bath does not lend itself to quantitative cleaning for sludge measurement. Therefore, the measurement of isopentane insolubles has been used to give a relative value for oxidative deterioration. It can be seen by comparing the oil insoluble sludge with the isopentane insoluble material in 500°F. oxidation tests for di-2-ethylhexyl sebacate, as given in report PRL 5.8-Sep53, that the isopentane insolubles greatly exceed the oil insolubles at low values for sludge. Isopentane insolubles might be called potential sludge, in this case. The isopentane values are listed, therefore, as an approximate indication of sludge formation.

The tests on Table 10 are listed in chronological order. This is an important point for discussing the results. The annular clearance of the new slide valve assembly was of the order of 0.0001 to 0.0002 inch on the radius. At the end of test 12, with the same slide valve, the clearance was of the order of 0.0010. It can also be noted in the sequence of tests that 10 and 11 are more severe than tests 3 and 4 using the same test fluids but tests 3 and 4 failed where tests 10 and 11 did not. The piston cylinder wall dimensions were not measured after each individual test. On the basis of weight loss of the piston and cylinder barrel and visual observation, it is estimated that data for tests 9 through 12 appear to be much better than predicted from the previous tests. As a further check, a test with the phenothiazine inhibited di-2-ethylhexyl sebacate has been conducted with a second slide valve piston and barrel assembly. The initial clearance for the piston and barrel assembly is 0.0001 to 0.0002 inch on a radius. The data for test 13 show the failure anticipated from tests 3 and 4. Thus, the conclusions must be drawn carefully from these data to allow for the change in clearance during the tests.

Tests 1 and 2 are designed to simulate the severity of Spec. MIL-L-7808 oxidation and corrosion tests. The values of the oxidized oil indicate the same severity as the Spec. MIL-L-7808 oxidation and corrosion test. The piston in test 1 was exercised hourly compared with exercising only at the beginning and end of test 2. Both tests show little or no increase in the amount of force necessary to move the piston during the course of the test. The piston and barrel show some evidence of staining but no evidence of sludging and lacquering during the test.

Tests 3 and 4 are 500°F. oxidation and corrosion tests designed in severity to simulate the Spec. MIL-L-7808 type test at 500°F. using 5 liters of air per hour, i.e., the tests described in Tables 26 through 33 of report PRL 5.8-Sep53. Tests 3 and 4 caused a rapid increase in friction and in the force necessary to operate the piston in 10 to 15 hours of test time. The force necessary to operate the piston as a function of time is shown on Figure 4. The piston could be moved with difficulty at the termination of the 500°F. test. On cooling to room temperature, the piston was stuck and had to be driven from the barrel.

It was also noted that the deposits from these tests were in the form of a lacquer on the metal parts. This lacquer could be chipped off with a fingernail. The troublesome build-up of deposits appeared to be in the exposed portion of the piston barrel. There was not much evidence of lacquering in the close clearance portions between the piston lands and the cylinder barrel. Following test 4, a method was devised for removing the piston from the cylinder barrel while hot to prevent the sticking encountered on cooling. This was done by changing the method of clamping the cylinder barrel to the bottom of the bath.

Tests 5 and 6 are 500°F. thermal stability tests with phenothiazine-inhibited di-2-ethylhexyl sebacate. Test 5 was conducted by bubbling nitrogen at a total rate of 10 liters per hour (5 liters per hour from each tube) through the fluid. This resulted in fluid property changes indicative of oxidation rather than thermal stability. The air-fluid contact at the fluid surface was not effectively excluded by the test in which the nitrogen is bubbled through the fluid. The level of final neutralization number and sludge formation are indicative of oxidative deterioration.

Test 6 was conducted with a nitrogen rate of 20 liters per hour passing over the surface of the liquid. The fluid properties from test 6 are of the same order of magnitude as those expected from a simple thermal stability test conducted in a sealed glass tube under similar conditions of temperature and time. It has been noted in tests of the type where the gas is passed over the surface of the liquid rather than bubbled through it that there may be a temperature gradient of 10° to 20°F. between the bottom of the fluid and the surface.

There is a considerable increase in friction noted in the slide valve assembly in test 5 where oxidative deterioration is indicated. There is no evidence of increased friction in the slide valve assembly for test 6 which appears to be a purely thermal stability test.

Test 7 was conducted as a rough check on the results from test 5. In this test, 5 liters of air were passed over the surface of the test fluid. There is evidence of considerable oil oxidation in this test, indicating that it is not necessary to bubble the air directly into the oil to obtain oxidation. This test is obviously less severe in terms of oxidative deterioration than the tests in which larger volumes of air are bubbled directly into the oil. Test 7 does cause the formation of the same type of hard lacquer-like coating on the metal parts and does result in a high increase in friction in the slide valve.

Test 8 is an oxidation test conducted at 400°F. to determine the effect of temperature on sludge character and slide valve friction. The 400°F. test produced sludge without much evidence of the hard lacquer formation noted on the metal parts in the 500°F. test. There was no indication of increased slide valve friction in this 400°F. test.

It should be noted from the data on Table 10 that each additional test requires more severe conditions to cause failure of the slide valve. This fact should be taken into consideration in the discussion of tests 8 through 12, particularly. The gradual change in slide valve failure with sludge formation is attributed to the gradual increasing clearance in the slide valve piston barrel assembly brought about by fluid corrosion as noted on Table 10 and by mechanical erosion in the cleaning process of the lacquered parts. The 400°F. test produced a large quantity of soft sludge but little evidence of hard lacquer-like deposits on the metal. This is believed to be significant.

Tests 9, 10, 11 and 12 have been conducted at 500°F. with a complete ester-base formulation (PRL 3161), a well refined naphthenic mineral oil fraction, and phenothiazine-inhibited di-2-ethylhexyl sebacate. These tests were continued to a point of very severe oxidation and sludge formation. In all of these tests, an objectionable type of lacquer-like coating was observed on the slide valve surfaces These tests, in general, did not show the expected friction increase. This is believed to be due to the increased clearance of the piston in the cylinder-barrel. As a check on the importance of bearing clearance, test 13 has been conducted with phenothiazine-inhibited di-2-ethylhexyl sebacate at 500°F. using a new slide valve assembly of 0.0001 to 0.0002 inch clearance. Failure in this test was similar to the type of failures noted with tests 3 and 4.

No appreciable change in slide valve friction has been noted with phenothiazine-inhibited di-2-ethylhexyl sebacate within the stable life of the fluid in a Spec. MIL-L-7808 oxidation and corrosion test. Relatively severe oxidation of the ester at 500°F. causes a large increase in slide valve friction. The friction increase is attributed to the formation of a hard lacquer-like deposit. Friction increase in the slide valve appears to be a strong function of piston-cylinder barrel clearance. An increase in annular clearance from 0.0002 to 0.001 inch may mean the difference between friction increase and no change in friction under the same 500°F. oxidation and corrosion conditions. Severe oxidation of the ester at 400°F. does not result in increased slide valve friction probably because of the lack of lacquer formation on the slide valve surfaces.

Studies with mineral oil and PRL 3161 ester-base lubricants were carried out after the annular clearance of the slide valve was increased by wear. Thus, a critical evaluation could not be made. It is evident, however, that under 500°F. oxidation conditions, the mineral oil and PRL 3161 do not appear to be much worse than the ester in the formation of a hard lacquer type coating.

It should be emphasized that these tests were conducted in a static fluid bath. That is, there was no flow through the slide valve. Under these static conditions, there is no indication that the trace dirtiness noted with Spec. MIL-L-7808 fluids and sometimes attributed to phenothiazine is causing increased friction. Under flow conditions trace dirtiness could be more troublesome since the small piston-barrel wall clearance would be expected to act as a filter to remove solids from any leakage through the annular clearance.

No further work is contemplated on the slide valve piston and barrel assembly unless requested by the Air Force. It would appear that a new piston and barrel would be required for each test, at least in the case where the test shows a large friction increase or metal coating. A test of this type might be developed around a Bosch diesel fuel injection pump piston and barrel assembly. These assemblies would lend themselves to the same type balance apparatus used for the slide valve. It is indicated that the Bosch piston and barrel assembly are manufactured to a select fit of 0.00004 inch tolerance. This fit is better than the 0.0001 inch value noted for the slide valves.

5. Interrelation of Copper-Beryllium Alloy and Oxidation and Corrosion Deterioration. The Materials Laboratory of the Wright Air Development Center has requested that this Laboratory investigate the effect of copper-beryllium alloy on the oxidation stability of hydraulic fluids and lubricants as well as the corrosive effect of the fluids on the alloy. The Materials Laboratory has furnished this Laboratory with fifty, one-by-one inch test specimens of copper-beryllium alloy. It has been indicated that copper-beryllium is one of the metals of construction of high temperature hydraulic systems. It is the purpose of this preliminary study to compare copper-beryllium with pure copper.

The corrosion of copper-beryllium alloy in the Spec. MIL-L-6387 oxidation and corrosion test is shown on Table 12. Corrosion values for various other metals of construction are also shown for comparison. These data indicate that there is no significant corrosion of the copper-beryllium alloy under these test conditions. It should be noted that copper also shows no significant corrosion in this test.

The effect of copper-beryllium on the stable life of di-2-ethylhexyl sebacate at 347°F. has been determined. Test fluids contain 0.1 or 0.5 weight per cent phenothiazine as the anti-oxidant. The test fluids have been subjected to a stable life test at 347°F. That is, the test is continued until fluid samples indicate a rapid increase in neutralization number with test time. Stable life values obtained, along with similar values for steel and aluminum, are shown in Table 11 and Figure 5.

Table 10

SUMMARY OF TESTS MADE WITH A SLIDE VALVE

TESTS CONDUCTED USING A 500 ML. CHARGE OF TEST FLUID. TEST TEMPERATURE AND AIR RATE OR NITROGEN RATE AS INDICATED.
INITIAL PISTON CYLINDER CLEARANCE IS APPROX. 0.0001 TO 0.0002 INCH. CLEARANCE AFTER TEST 12 IS 0.0010 TO 0.0011 INCHES.
TEST APPARATUS IS SHOWN ON FIGURES 6 AND 7 OF REPORT PRL 518-SEP53.
TEST FLUID PRL 3486 = DI-2-ETHYLHEXYL SEBACATE + 0.5 WT.% PHENOTHIAZINE.
PRL 3161 = SPEC. MIL-L-7808 TYPE SYNTHETIC GEAR LUBRICANT.
NECTON 55 = HIGHLY REFINED NAPHTHENIC MINERAL OIL.

| TEST FLUID | <- - - - - - - - - - - - - - - - PRL 3486 - - - - - - - - - - - - - - - -> | | | | | | | | PRL 3161 | < -PRL 3486-> | | NECTON 55 | PRL 3486 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TEST NUMBER | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13(2) |
| TYPE OF TEST | OXID. | OXID. | OXID. | OXID. | THERMAL STAB. | THERMAL STAB. | OXID. | OXID. | OXID. | OXID. | OXID. | OXID. | OXID. |
| TEST TEMPERATURE, °F. | 347 | 347 | 500 | 500 | 500 | 500 | 500 | 400 | 500 | 500 | 500 | 500 | 500 |
| TEST TIME, HOURS | 72 | 72 | 11 | 14-1/2 | 20 | 20 | 20 | 96 | 27 | 48 | 24 | 44 | 22 |
| AIR RATE, LITERS PER HOUR | 20 | 20 | 20 | 20 | - | - | 5(1) | 20 | 20 | 20 | 20 | 20 | 20 |
| NITROGEN RATE, LITERS PER HOUR | - | - | - | - | 10 | 20(1) | - | - | - | - | - | - | - |
| FREQUENCY OF MEASUREMENT OF PISTON FRICTION | HOURLY | AT END OF TEST | HOURLY | HOURLY | HOURLY | HOURLY | HOURLY | HOURLY | HOURLY | HOURLY | HOURLY | HOURLY | HOURLY |
| % CHANGE IN FLUID VISCOSITY AT 130°F. | +2 | +2 | +42 | +58 | +42 | +10 | +27 | +144 | SOLID | SOLID | SOLID | SOLID | SOLID |
| 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 | 0.1 | 0.2 | 0.1 |
| FINAL | 1.3 | 1.2 | 11.5 | 11.0 | 9.6 | 3.2 | 9.3 | 32.3 | 79.0 | 35.0 | 22.6 | 4.2 | 18.9 |
| WT.% ISOPENTANE INSOLUBLE MATERIAL | 0.3 | 0.3 | 2.6 | 5.1 | 3.2 | 0.5 | 1.5 | 8.5 | 4.6 | 26.0 | 30.7 | 29.9 | 20.9 |
| OPERATION OF SLIDE VALVE UPON TERMINATION OF TEST | SAT. | SAT. | UNSAT. | UNSAT. | SAT. | SAT. | UNSAT.(3) | SAT. | SAT. | SAT. | SAT. | SAT. | UNSAT. |
| WT. IN GRAMS REQUIRED TO MOVE PISTON ORIGINAL | 10 | 15 | 10 | 10 | 15 | 10 | 10(3) | 15 | 20 | 10 | 20 | 20 | 20 |
| FINAL | 10 | 15 | FAILED | FAILED | 120 | 10 | FAILED(3) | 15 | 100 | 15 | 30 | 20 | FAILED |
| WT. LOSS AFTER VALVE IS CLEANED, MGS. PISTON | 0.6 | 0.5 | 0.0 | 1.0 | 0.9 | 0.1 | +0.2 | +0.5 | +2.9 | 5.2 | 6.5 | 0.0 | 53.4 |
| BARREL | 0.6 | 0.0 | 0.0 | 13.3 | 18.6 | 0.2 | +1.7 | +2.2 | +8.7 | 0.6 | 17.4 | 0.6 | 96.7 |

(1) NITROGEN OR AIR WAS SWEPT OVER THE LIQUID SURFACE.
(2) THIS TEST WAS CONDUCTED WITH A NEW SLIDE VALVE.
(3) OPERATION WAS SATISFACTORY AT 19 HOURS, BUT UNSATISFACTORY AT 20 HOURS.

Figure 4

EFFECT OF FLUID OXIDATION ON SLIDE VALVE OPERATION AT 500°F.

TEST FLUID = 0.5 WT.% PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE (PRL 3207)
o = DATA FOR TEST NO. 3 ON TABLE 10.
Δ = DATA FOR TEST NO. 4 ON TABLE 10.

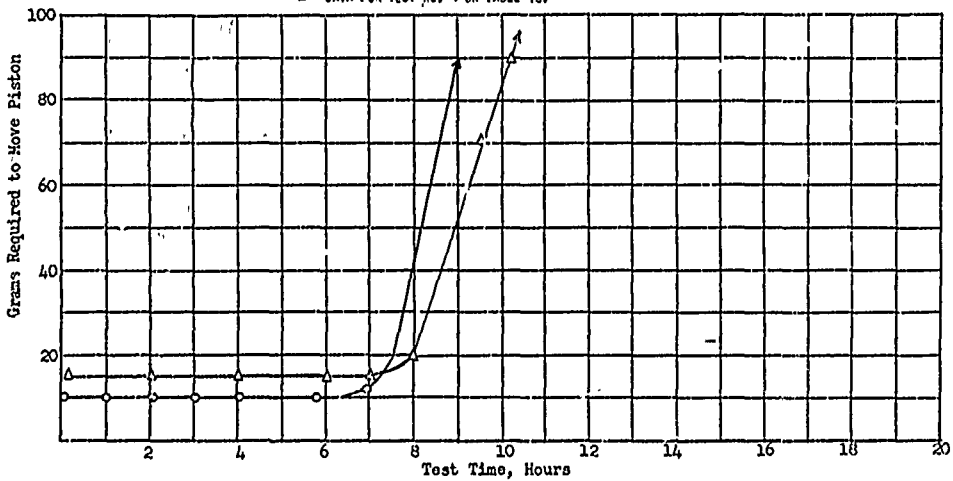


Table 11

EFFECT OF COPPER-BERYLLIUM ON THE STABLE LIFE
OF DI-2-ETHYLHEXYL SEBACATE

| Catalyst Metal | Approx. Stable Life, Hrs. 0.1 Wt.% Phenothiazine | 0.5 Wt.% Phenothiazine |
|---|---|---|
| No Catalyst | 125 | 350 |
| Copper | 20 | 210 |
| Copper-Beryllium | 30 | 300 |
| Steel | 115 | - |
| Aluminum | 120 | - |

These data indicate that copper-beryllium alloy does effect a reduction in the stable life of phenothiazine-inhibited di-2-ethylhexyl sebacate. However, this reduction appears to be somewhat less than that incurred with copper catalyst.

These tests have been continued past the stable life of the test fluid. That is, the final neutralization number and the viscosity increase are relatively high, indicating oxidative deterioration of the test fluid. It is interesting, therefore, to observe the corrosive effect of the test fluids on the catalyst metals. A summary of the properties of the test fluids and the catalyst corrosion is shown in Table 13.

In these tests, the copper-beryllium tends to be coated. The copper becomes somewhat corroded. It should be remembered that these tests were continued beyond the stable life of the test fluid.

Specification MIL-L-7808 oxidation and corrosion tests (347°F., 72 hours) have been carried out with some synthetic gear lube type fluids in the presence of copper-beryllium catalyst metal. A description of the test fluids used follows:

(1) PRL 3207 is a di-2-ethylhexyl sebacate-phenothiazine blend.

(2) PRL 3161 is a Spec. MIL-L-7808 type synthetic gear lube containing tricresyl phosphate.

(3) PRL 3313 is a commercially prepared synthetic fluid containing tricresyl phosphate and Ortholeum 162

(4) PRL 3313A has the same composition as PRL 3313 but was prepared from stocks available at this Laboratory.

A summary of the fluid properties and catalyst conditions following the test is shown on Table 14.

With test fluids PRL 3207 and PRL 3161, there is no corrosion of any of the catalyst metals, and copper-beryllium appears to have no effect on the oxidative behavior of the test fluids under these conditions.

It will be noted that, in the case of PRL 3313 and PRL 3313A test fluids, the original neutralization number is relatively high. These two samples had been stored in sealed containers at room temperature for approximately 18 months prior to the test shown. The phenomenon of neutralization number increase with storage time for fluids containing acid phosphate type additives (Ortholeum 162) has been discussed in previous reports. Test fluid PRL 3313A shows high copper corrosion but no copper-beryllium corrosion. Test fluid PRL 3313 shows high copper-beryllium corrosion. It should be pointed out that this commercial batch of PRL 3313 has shown a tendency to corrode metals in previous tests. That is, tests conducted with this fluid when it was first received by this Laboratory showed copper, steel, and magnesium corrosion under the Spec. MIL-L-7808 oxidation and corrosion conditions.

Tests have been conducted at 500°F. for 20 hours with di-2-ethylhexyl sebacate containing 0.5 weight per cent phenothiazine (PRL 3207). The results of these tests are shown on Table 15. Their relation to the copper-beryllium catalyst are the same as those discussed previously for test fluid PRL 3207 at 347°F.

The investigation of the effect of copper-beryllium on hydraulic fluids and lubricants has been extended to include mineral oil compositions. The test fluid for these studies is a highly refined naphthenic mineral oil (Voltesso 36, PRL 3456) having a viscosity of approximately 9 centistokes at 100°F. The tests have been conducted at 347°F. for 72 hours. In one series of tests, a hindered phenol type of anti-oxidant (Paranox 441) is used. In the second set of tests, a hindered phenol type of inhibitor (Antioxidant 2246) combined with dimethyl acid phosphite is used. The effect of this inhibitor combination on the oxidation stability of mineral oils is discussed in the section of this report concerned with jet engine lubricants. A summary of the results obtained in these mineral oil studies is shown in Table 16.

It should be noted that the tests with the fluid containing only Paranox 441 as the oxidation inhibitor appear to have exceeded the stable life of the test fluid. That is, the viscosity change and the neutralization number increase indicate incipient oxidation. Only copper shows any appreciable amount of corrosion in these tests. Copper-beryllium, either alone or in conjunction with the other metals is not corroded under these test conditions.

In the tests containing the dimethyl acid phosphite, the test fluid is stable to oxidative deterioration for the 72 hour test period. The coating noted for the catalyst metals is typical for fluids containing dimethyl acid phosphite.

In conclusion, the data indicate that copper-beryllium alloy does have some effect on the oxidation stability of hydraulic fluids and

Table 12

EFFECT OF METALS ON OXIDATION AND CORROSION CHARACTERISTICS OF DI-2-ETHYLHEXYL SEBACATE

Test Procedures and Techniques in Accordance with Spec. MIL-L-6387
Test Conditions Include: Test Temperature = 347 ± 3°F.; Test Time = 72 Hours; Air Rate = 10 ± 1 Liters per Hour; Test Fluid Charged = 100 ml.; Catalyst = a 1 Inch Square each of Metals Indicated.
Test Fluid: PRL 3207 = Di-2-Ethylhexyl Sebacate + 0.5 Wt.% Phenothiazine

| Test Fluid | PRL 3207 | | |
|---|---|---|---|
| Liquid Loss, Wt. % | 3 | 3 | 2 |
| % Change in Viscosity: | | | |
| at 130°F. | +3 | +3 | +1 |
| at 0°F. | +6 | +7 | +2 |
| Neut. No. (Mg. KOH/Gm. Oil): | | | |
| Original | 0.1 | 0.1 | 0.1 |
| Final | 1.5 | 0.8 | 1.4 |
| A.S.T.M. Union Color: | | | |
| Original | 2 | 2 | 2 |
| Final | >8 | >8 | >8 |
| Wt. % Insoluble Material | 0.3 | 0.5 | 0.3 |
| Final Catalyst Condition: | | | |
| Appearance: | | | |
| Copper | Dull | - | - |
| Steel | Dull | - | - |
| Aluminum | Dull | - | - |
| Magnesium | Dull | - | - |
| Lead-Indium | Dull | - | - |
| Lead | - | Corroded | - |
| Copper-Beryllium | - | - | Dull |
| Wt. Loss (Mg./Sq. Cm.): | | | |
| Copper | +0.02 | - | - |
| Steel | +0.03 | - | - |
| Aluminum | +0.02 | - | - |
| Magnesium | +0.01 | - | - |
| Lead-Indium | +0.06 | - | - |
| Lead | - | 9.74 | - |
| Copper-Beryllium | - | - | 0.05 |

Figure 5

COMPARISON OF THE OXIDATION STABILITY OF DI-2-ETHYLHEXYL SEBACATE AT 347°F. IN THE PRESENCE OF COPPER AND COPPER-BERYLLIUM CATALYST METALS

TESTS CONDUCTED IN ACCORDANCE WITH THE PROCEDURES AND TECHNIQUES OF SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F.; TEST TIME AS INDICATED; AIR RATE = 10 ± 1 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE OF METAL INDICATED.
TEST FLUID PRL 3371 = DI-2-ETHYLHEXYL SEBACATE.

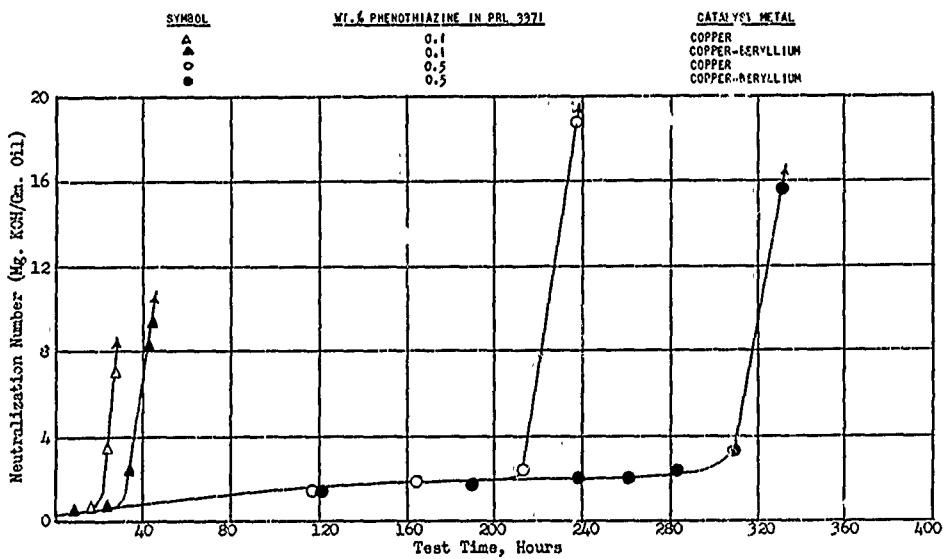


Table 13

COMPARISON OF THE OXIDATION STABILITY OF DI-2-ETHYLHEXYL SEBACATE AT 347°F. IN THE PRESENCE OF COPPER AND COPPER-BERYLLIUM

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-6387.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F.; TEST TIME AS INDICATED; AIR RATE = 10 ± 1 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF THE METALS INDICATED.

| TEST FLUID | DI-2-ETHYLHEXYL SEBACATE (FAL 337°) | | | |
|---|---|---|---|---|
| PHENOTHIAZINE CONC., WT.% | 0.1 | 0.1 | 0.5 | 0.5 |
| TOTAL TEST TIME, HOURS | 27 | 44 | 287 | 380 |
| APPROX. STABLE LIFE, HOURS | 20 | 30 | 214 | 310 |
| TEST TIME BEYOND STABLE LIFE, HOURS | 7 | 14 | 73 | 70 |
| % CHANGE IN VISCOSITY | | | | |
| AT 150°F. | +12 | +17 | +103 | +81 |
| AT 0°F. | -28 | +42 | +272 | +222 |
| NEUT. NO. (MG. KOH/GM. OIL): | | | | |
| ORIGINAL | 0.1 | 0.1 | 0.1 | 0.1 |
| FINAL | 7.0 | 9.3 | 36.5 | 36.9 |
| A.S.T.M. UNION COLOR: | | | | |
| ORIGINAL | 2 | 2 | 2 | 2 |
| FINAL | >8 | >8 | >8 | >8 |
| WT.% OIL INSOLUBLE MATERIAL | 0.1 | 0.1 | 1.9 | 1.1 |
| FINAL CATALYST CONDITION | | | | |
| APPEARANCE | | | | |
| COPPER | DULL | - | CORRODED | - |
| COPPER-BERYLLIUM | - | DULL | - | COATED |
| WT. LOSS (MG./SQ. CM.) | | | | |
| COPPER | 0.12 | - | 0.21 | -- |
| COPPER-BERYLLIUM | - | +0.02 | - | +0.29 |

Table 14

SOME STUDIES OF THE EFFECT OF COPPER-BERYLLIUM ON OXIDATION AND CORROSION PROPERTIES OF VARIOUS FLUIDS AT 347°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-6387.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F.; TEST TIME = 72 HOURS; AIR RATE = .0 ± 1 LITERS PER HOUR; CATALYST = A 1 INCH SQUARE EACH OF METALS INDICATED.
TEST FLUID: PRL 3207 = 0.5 WT.% PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE.
PRL 3161 = SPEC. MIL-L-7808 TYPE FLUID CONTAINING 5.0 WT.% TRICRESYL PHOSPHATE.
PRL 3313 = COMMERCIALLY PREPARED GEAR LUBRICANT CONTAINING 5.0 WT.% TRICRESYL PHOSPHATE AND 0.5 WT.% ORTHOLEUM 162.
PRL 3313A = SAME COMPOSITION AS PRL 3313 BUT PREPARED FROM STOCKS AVAILABLE AT THIS LABORATORY.

| FLUID | PRL 3207 | | PRL 3161 BATCH 5380 | | PRL 3313 BATCH 593' | PRL 3313A | |
|---|---|---|---|---|---|---|---|
| LIQUID LOSS, WT.% | 3 | 2 | 2 | 3 | 3 | 4 | 3 |
| % CHANGE IN VISCOSITY | | | | | | | |
| AT 130°F. | +3 | +1 | +5 | +5 | +20 | +4 | +8 |
| AT 0°F. | +6 | +2 | +7 | +6 | SOLID | +14 | +14 |
| NEUT. NO. (MG. KOH/GM. OIL): | | | | | | | |
| ORIGINAL | 0.1 | 0.1 | 0.2 | 0.2 | 7.2 | 5.1 | 5.1 |
| FINAL | 1.5 | 1.4 | 2.2 | 1.5 | 7.4 | 5.0 | 5.3 |
| A.S.T.M. UNION COLOR | | | | | | | |
| ORIGINAL | 2 | 2 | 2 | 2 | 2 | 3 | 3 |
| FINAL | >8 | >8 | >8 | >8 | >8 | >8 | >8 |
| WT.% OIL INSOLUBLE MATERIAL | 0.3 | 0.3 | 0.2 | 0.1 | 0.9 | 1.9 | 0.3 |
| FINAL CATALYST CONDITION | | | | | | | |
| APPEARANCE | | | | | | | |
| COPPER-BERYLLIUM | - | DULL | - | DULL | CORRODED | - | DULL |
| COPPER | DULL | - | DULL | - | - | CORRODED | - |
| STEEL | DULL | - | DULL | - | - | DULL | - |
| ALUMINUM | DULL | - | DULL | - | - | DULL | - |
| MAGNESIUM | DULL | - | DULL | - | - | CORRODED | - |
| WT. LOSS (MG./SQ. CM.) | | | | | | | |
| COPPER-BERYLLIUM | - | 0.05 | - | +0.02 | 27.0 | - | +0.05 |
| COPPER | +0.02 | - | +0.05 | - | - | 30.00 | - |
| STEEL | +0.03 | - | +0.05 | - | - | 0.00 | - |
| ALUMINUM | +0.02 | - | 0.02 | - | - | 0.00 | - |
| MAGNESIUM | +0.01 | - | +0.05 | - | - | 0.81 | - |

Table 15

THE EFFECT OF VARIOUS METALS ON THE OXIDATION AND CORROSION PROPERTIES OF DI-2-ETHYLHEXYL SEBACATE AT 500°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-6387.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME = 20 HOURS; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF THE METALS INDICATED.

| TEST FLUID | 0.5 WT.% PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE (PRL 3426) | | |
|---|---|---|---|
| LIQUID RECOVERED, GRAMS | 90.5 | 69.5 | 89.5 |
| LIQUID LOSS, WT.% | 7 | 2 | 1 |
| APPROX. AMOUNT $O_2$ SUPPLIED, GMS.(1) | 26.2 | 26.2 | 26.2 |
| APPROX. AMOUNT $O_2$ USED, GMS.(1) | 5.8 | 4.6 | 5.2 |
| MOLES $O_2$ USED/MOLE FLUID (426 GRAMS) | 0.86 | 0.68 | 0.77 |
| % CHANGE IN VISCOSITY | | | |
| AFTER REMOVAL OF OIL-INSOLUBLE MATERIAL(2) | | | |
| AT 130°F. | +44 | +33 | +20 |
| AT 0°F. | +48 | +68 | +38 |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) | | | |
| AT 130°F. | +4 | +15 | +12 |
| NEUT. NO. (MG. KOH/GM. OIL): | | | |
| ORIGINAL | 0.1 | 0.1 | 0.1 |
| FINAL | 15.4 | 12.5 | 7.1 |
| WT.% OIL INSOLUBLE MATERIAL(2) | 0.1 | 0.2 | 10.6 |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 4.8 | 3.6 | 11.8 |
| FINAL CATALYST CONDITION | | | |
| APPEARANCE | | | |
| COPPER | DULL | - | - |
| STEEL | DULL | - | - |
| ALUMINUM | BRIGHT | - | - |
| COPPER-BERYLLIUM | - | COATED | - |
| LEAD | - | - | CORRODED |
| WT. LOSS (MG./SQ. CM.) | | | |
| COPPER | 0.10 | - | - |
| STEEL | 0.07 | - | - |
| ALUMINUM | 0.00 | - | - |
| COPPER-BERYLLIUM | - | +0.10 | - |
| LEAD | - | - | 7.42 |

(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 OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR $O_2$.

(2) 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.

(3) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL AND THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF OXIDIZED FLUID (FROM WHICH OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.

Table 16

THE EFFECT OF A COPPER-BERYLLIUM CATALYST ON THE OXIDATION AND CORROSION CHARACTERISTICS OF A NAPHTHENIC TYPE MINERAL OIL AT 347°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-6387.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 2°F.; AIR RATE = 10 ± 1 LITERS PER HOUR; TEST TIME = 72 HOURS; TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF THE METALS INDICATED.

| TEST FLUID | <- - - - - - - - - VOLTESSO 35 (PRL 3436) - - - - - - - - - -> | | | | |
|---|---|---|---|---|---|
| ANTI-OXIDANT, WT.% | <-----1.0 PASANOX 441-----> | | | 1.0 ANTIOXIDANT 2246 + 0.5 DI-METHYL ACID PHOSPHITE | |
| LIQUID LOSS, WT.% | - | 0 | 0 | 1 | 0 |
| % CHANGE IN VISCOSITY | | | | | |
| AT 130°F. | +45 | +23 | +18 | +2 | +3 |
| AT 0°F. | +202 | +117 | +81 | +4 | +6 |
| NEUT. NO. (MG. KOH/GM. OIL): | | | | | |
| ORIGINAL | 0.1 | 0.1 | 0.1 | 0.3 | 0.3 |
| FINAL | 4.6 | 6.6 | 4.0 | 0.9 | 0.7 |
| A.S.T.M. UNION COLOR: | | | | | |
| ORIGINAL | 2 | 2 | 2 | 1 | 1 |
| FINAL | >8 | >8 | >8 | >8 | >8 |
| WT.% OIL INSOLUBLE MATERIAL | 1.1 | 1.4 | 0.2 | 1.6 | 1.3 |
| FINAL CATALYST CONDITION | | | | | |
| APPEARANCE | | | | | |
| COPPER-BERYLLIUM | - | DULL | DULL | - | COATED |
| COPPER | CORRODED | - | - | COATED | - |
| STEEL | DULL | DULL | - | DULL | - |
| ALUMINUM | BRIGHT | DULL | - | BRIGHT | - |
| MAGNESIUM | BRIGHT | DULL | - | COATED | - |
| WT. LOSS (MG./SQ. CM.) | | | | | |
| COPPER-BERYLLIUM | - | 0.02 | 0.02 | - | +0.36 |
| COPPER | 0.24 | - | - | +0.18 | - |
| STEEL | 0.00 | 0.04 | - | 0.05 | - |
| ALUMINUM | 0.00 | 0.04 | - | 0.02 | - |
| MAGNESIUM | +0.02 | 0.03 | - | +0.43 | - |

lubricants of the types evaluated. This effect appears to be intermediate between that exerted by metals such as copper and bronze and that shown by metals such as steel and aluminum. The copper-beryllium alloy does not appear to be affected adversely by the types of hydraulic fluids used in this study under the test conditions outlined.

E. HIGH TEMPERATURE HYDRAULIC PUMP TESTS. One of the deterrents to testing hydraulic fluids and hydraulic system components at elevated temperatures is the current lack of an adequate high temperature hydraulic pump to circulate the fluid through the system. There are indications that with current aircraft hydraulic pumps, operation at temperatures of 300°F. and higher may result in mechanical problems which retard or prohibit fluid testing. Many of the mechanical problems in aircraft hydraulic pumps at high temperatures result from differential metal expansion and seal problems. As a result of these problems, high temperature pump testing must be done with other types of hydraulic pumps and/or by indirect evaluation using current aircraft pumps. Both of these approaches to the problem have been studied by this Laboratory.

A discussion of the indirect testing techniques in a Vickers piston type aircraft hydraulic pump is found in report PRL 5.8-Sep53. In this study, the viscosity, volatility, and lubricity levels of ester-base hydraulic fluids and lubricants (Specs. MIL-L-7808 and MIL-L-6387) at 400° to 600°F. were matched using hydrocarbon-base fluids at 100° to 250°F. Also in this study, Vickers Model PF-17-3911-10ZEL piston pumps were found to operate satisfactorily at 200°F. and 3000 p.s.i. with fluids of one centistoke viscosity and with other properties matching the diester fluids and lubricants at 500° to 600°F. These data indicate that a Vickers piston pump will operate satisfactorily with fluids of one centistoke viscosity. Thus, it appears that metallurgical and mechanical changes to compensate for temperature effects are required, but that no major change in tolerances at the operating temperature, or bearing loadings, would be required over current model pumps to operate at 500° to 550°F. with current dibasic acid ester hydraulic fluids and jet engine lubricants.

The current studies are an extension of the above work to an actual mock-up hydraulic system in which all of the components, including the pump, are operated at temperatures of 500°F. and higher.

1. Design and Construction Details of the High Temperature Pump Test Stand. A flow diagram of the high temperature pump test stand is shown on Figure 6. The system design is simple and the high pressure portion of the cycle short. The entire test unit, with the exception of the pump, is mounted in a 17 by 38 by 45 inch box which consists of an angle iron frame with 1/4 inch Transite board sheathing. This box serves a two-fold purpose. It protects the operator from the hot oil system and from hot oil spray in case of a hydraulic line failure. The Transite box also acts as insulation for the test unit. With the exception of the oil heater, there has been no attempt to insulate individual portions of the system within the Transite box.

The hydraulic pump is surrounded by a separate Transite box to act as insulation and protection for the operator. The hydraulic lines (about 10 inches long) leading from the pump enclosure to the larger test system enclosure are insulated separately with asbestos gauze. The test unit is located so that either of two pump drive units can be used. The units consist of one two-speed motor with a power output of 5 horsepower at 1800 r.p.m. and 10 horsepower at 3600 r.p.m. and a single speed motor delivering a power output of 7.5 horsepower at 3600 r.p.m.

The high pressure portion of the cycle extends from the pump to the high pressure orifice. This test unit has a double bypass system. With valves 1 and 2 (Figure 6) in the open position, the pump flow is directed back to the reservoir without passing through the remainder of the test system. That is, with both valves 1 and 2 open, a pump rate can not be measured since the system flow under these conditions does not pass through the orifice used to measure flow rate. With valve 1 closed and valve 2 open, the fluid is bypassed around the pressure loading orifice into the normal test cycle. The discharge pressure of the pump is measured by the pressure gage located in the loading orifice holder immediately upstream of the orifice.

The heat exchanger in the pump test system utilizes a bed of fluidized solids. Construction details for this heat exchanger are shown on Figure 7. A wiring diagram for the heat exchanger is shown on Figure 8. The fluidized solids bed consists of the annular space between the 10 inch steel pipe shell and the four inch steel tubing dummy section. Two concentric coils of 1/2 inch stainless steel tubing wound to a 6 and 8 inch diameter, respectively, to give a total of 50 linear feet of tubing, are located in the fluidized solids section. The bottom of the fluidized solids section consists of a porous brass plate to allow the fluidizing air to pass through. The fluidized bed is filled to a height of 16 inches with alumina of 100 to 150 micron size. The exhaust air from the fluidized solids section passes through a cyclone precipitator to remove the entrained alumina particles. Fluidizing air is metered into the bed at a rate of 3 cubic feet per minute.

Ten 500 watt strip heaters are clamped directly on the outer shell of the fluidized bed. The distribution of the heaters and the wiring diagram for the heating circuits are shown on Figure 8. The heater controls are designed to give continuous variation between 0 and 5000 watts heating capacity with reasonably even heat distribution over the outer shell wall. The entire heat exchanger is insulated with one-inch laminated asbestos paper. There is a one inch air space between the heaters and the asbestos insulation. Provision is made for measuring the temperatures of the fluidized bed by means of iron-constantan thermocouples located on the heating shell, in the fluidized bed midway between the heating shell and the outer coil, and in the fluidized bed between the two concentric coils.

The temperature of the test oil from the heat exchanger is measured at the outlet by means of an iron-constantan thermocouple. The oil flow from the heat exchanger passes through an orifice and filter and then is returned to the reservoir. This second orifice

is a sharp edged type used to measure flow rate. The pressure drop across the orifice is measured by means of pressure gages located in the orifice case immediately upstream and downstream of the orifice. The filter element is constructed from 80 mesh stainless steel screen. The reservoir is an approximately one gallon capacity section of 6 inch diameter Pyrex pipe. The temperature of the oil from the reservoir is measured by means of a recording thermometer and reported as pump inlet temperature.

The heat exchanger and orifice flow meter represent a marked departure from the equipment employed in the other PRL pump test stands which have been described in previous reports from this Laboratory. The reasons for the choice of these units and their operating characteristics, therefore, deserve further comment.

The high temperature pump test stand is designed to simulate, as far as possible, the situations existing temperature-wise in actual operation. Therefore, care must be taken in the manner of heating the fluid in the pump test system. This is particularly true in the range of 400° to 500°F. bulk oil temperatures. These temperatures are close to the level of incipient thermal instability of many of the synthetic lubricants. Oxidation stability is critical in this temperature range for both mineral oil- and ester-type fluids. The use of electrical immersion heaters in direct contact with the fluid has been found to be generally unsatisfactory. Even with forced circulation, the surfaces of the electrical immersion heaters become sufficiently hot to cause local thermal cracking of some synthetic lubricants even though the bulk oil temperature is controlled at 50° to 150°F. below the point of thermal instability.

The use of a heat exchanger of the type described eliminates or minimizes this local overheating problem. The use of a fluidized solids bed heat exchanger reduces the fire hazard and the sealing problems normally involved in a liquid or vapor type heating medium. The fluidized solids bed exchanger is competitive with liquid-liquid heat exchangers in terms of overall efficiency and heat transfer coefficient. Data on the amount of heat required in the heat exchanger to maintain various test temperatures in the pump test system are shown on Table 17. These data are dependent on the energy input to the fluid by the hydraulic pump. The thermocouple temperatures listed are for the indicated thermocouple locations on Figures 6 and 7.

The flow rate is measured by the pressure drop across an orifice in this high temperature system. Flow diversion to a graduated cylinder and the displacement type flow meter have been used to measure flow on low temperature PRL hydraulic pump stand systems. The flow diversion method is undesirable at high temperatures because of the hazard to the operator. The use of displacement meters is undesirable at high temperatures because of the increased system holdup and heat loss involved.

Two orifice sizes have been used in this study. The calibration curves of flow rate versus pressure drop are shown on Figure 9. These two orifice sizes cover adequately the range in flow rates

obtained with the Vickers vane power steering pump. The orifice flow meter is essentially independent of viscosity. Viscosity is only a 0.2 power function of pressure drop in turbulent flow through a sharp edged orifice. The use of the orifice flow meter has proven to be satisfactory for these tests.

2. Vickers Vane Type Hydraulic Steering Pump. The pump used for these 500°F. tests is a Vickers model VT4-100-40-75-10 vane pump. This type of pump is commonly used in automotive hydraulic steering units. This pump has a displacement of 4 g.p.m. at 1200 r.p.m. This is a mass produced, industrial type, pump consisting of essentially all steel parts. The configuration of the wearing parts of this Vickers vane power steering pump are shown in Figures 10 and 11. The indicated pump parts are identified on Table II.

The essential wearing parts of this pump consist of a slotted steel rotor (H) and 12 hardened steel vanes (J), a steel cam ring (G), and two hardened steel valve plates. One of the valve plates (E) is a separate part, whereas the second valve plate is an integral part of, and forms the face of the pump body (L). These parts fit together in a compact unit in which the rotor and vanes are situated in the elliptical shaped cam ring with the two valve plates on either side of the cam ring as shown in Figure 11. When the pump is assembled the relative positions of the valve plate and cam ring with respect to the pump body are determined by two removable pins (K) which are situated in the pump body and are radially placed 180° apart. The pins project through corresponding holes in the cam ring and into the valve plate. As a consequence, no relative movement between the valve plates and cam ring occurs.

The assembled pump contains two rubber "O" ring seals (D), which are designed to eliminate oil leakage from the pump. One ring seal is recessed in a circular slot in the pump body and seals the pump between the cam ring and the pump body. The second "O" ring fits into a recessed groove in the cover and seals the pump between the cam ring and the pump cover. In addition to being hydraulically loaded, the pump is spring loaded by the control valve assembly and spring (C) which is contained in the pump cover and which forces the valve plate (E) against the cam ring. The rotor and cam ring are so designed that as the rotor rotates in the elliptical cam ring, the centrifugal action forces the vanes out against the inner surface of the cam ring. The vanes are subsequently extended to their maximum position where the radius of the ellipse is a maximum. Conversely, the vanes extend out of the rotor the least when the radius of the ellipse is a minimum.

The valve plates and cam ring are so plated with respect to each other that the change from minimum to maximum radius of the cam ring coincides with the valve plate inlet ports. The change from maximum to minimum radius of the cam ring coincides with the valve plate exit ports. The radius of the cam ring remains constant between ports.

The control valve assembly contains a spring loaded pressure relief valve which normally opens when the pump outlet pressure reaches

700 p.s.i. and allows fluid to be by-passed from the pump outlet to the reservoir. However, for the series of tests discussed in this report the by-pass port to the reservoir was plugged (T). In other words, although the pump actually contains a pressure relief valve, the system was so constructed that the valve could not operate.

The rotor is driven by the drive shaft (S) which is mounted in the pump body and is supported by two bearings (N) and (P). The drive shaft seal assembly (O) consists of a spring loaded lip type rubber seal in a stamped steel container. The rubber member fits snugly on the drive shaft and eliminates oil leakage from the pump to the atmosphere along the drive shaft.

The operation of the pump is as follows: fluid enters the pump inlet port (H) and is drawn into the pump unit at suction line pressure through two ports in the pump body. The pump body inlet ports communicate with a recessed portion of the valve plate (E) through three holes drilled in the cam ring (G). This enables the fluid to enter the pump unit from both sides of the cam ring. The vanes are forced out against the inside surface of the cam ring by centrifugal force generated by the rotor which is revolving at the driven speed of the pump. As the vanes move past the valve plate inlet ports a portion of the fluid is entrapped and delivered to the discharge ports in the valve plate (E). The fluid is subsequently discharged through the pump discharge port (F) to the external hydraulic system at full line pressure. This vane pump was chosen for use in evaluating high temperature fluids for two reasons: first the pump parts are all steel and are loaded hydraulically and centrifugally, i.e., there are no fixed clearance parts in the pumping mechanism; and second the Vickers V105A vane pump of similar design has been used successfully in the past by this laboratory as a lubricity tester.

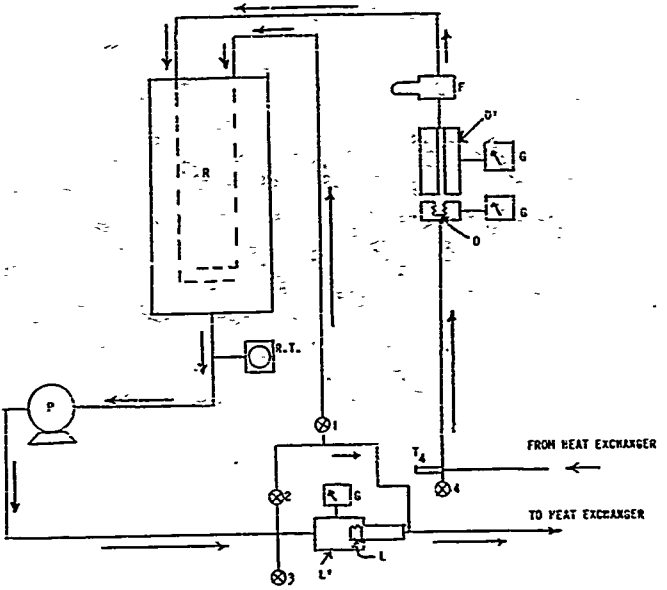
3. Pump Test Results. A total of 29 tests have been conducted with the Vickers vane pump in the high temperature pump test stand. Tests 1 through 14 are essentially exploratory tests using high quality di-2-ethylhexyl sebacate and mineral oil compositions. A summary of these exploratory tests is shown on Table 19. The schedule followed in pump part replacement is shown in Table 20. The test data on Table 19 represent a total test time of 72.5 hours at 500°F., 81 hours above 400°F. and 115 hours above 300°F. These pump test data have been obtained with both mineral oil and ester compositions. The property changes in the fluids during the pump tests are shown on Table 21.

Tests 1 through 7 evaluate the operational characteristics of the pump under high temperature conditions. In addition, this series of tests has been used to show the effect of pressure, temperature, and fluid viscosity on volumetric efficiency. This series of preliminary tests indicates that this Vickers vane pump will run satisfactorily at temperatures up to 500°F. and pressures well in excess of the maximum rated pressure (700 p.s.i.) with high quality ester and mineral oil compositions.

The effect of system temperature on the volumetric efficiency of the pump is shown on Figure 12. These data show essentially no change

Figure 46

FLOW DIAGRAM FOR HIGH TEMPERATURE PUMP TEST STAND




Flow Diagram

P = PUMP
R.T. = RECORDING THERMOMETER
G = PRESSURE GAUGE
F = FILTER
R = RESERVOIR
T = THERMOCOUPLE
OO' = ORIFICE AND ORIFICE HOLDER FOR MEASURING FLOW RATE
LL' = ORIFICE AND ORIFICE HOLDER FOR IMPOSING LOAD ON SYSTEM
⊗ = NEEDLE VALVE

Figure 7
CONSTRUCTION DETAILS OF FLUIDIZED SOLIDS BED HEAT EXCHANGER
CROSS SECTION OF SIDE VIEW
SCALE - 1 INCH = 5 INCHES

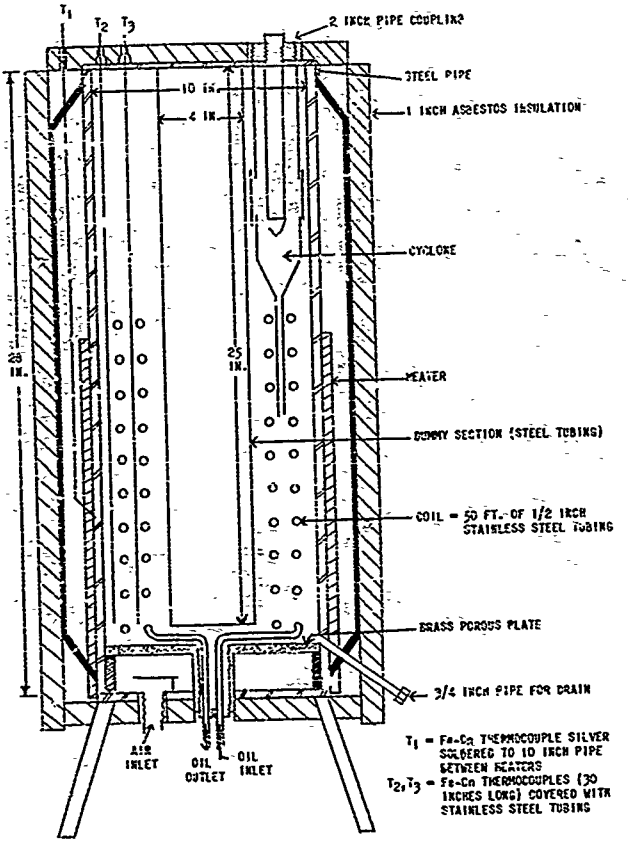
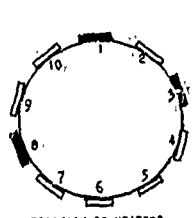


Figure 8

WIRING DIAGRAM OF HEATERS FOR FLUIDIZED SOLIDS BED HEAT EXCHANGER




POSITION OF HEATERS

16 INCH, 500 WATT HEATERS.
12 INCH, 500 WATT HEATERS

$V_1$ - VARIAC, TYPE V-5

A, B, C - THREE HEAT SWITCHES

A - HIGH 1000 WATTS
MED. 500 WATTS
LOW 250 WATTS

B - HIGH 1000 WATTS
MED. 500 WATTS
LOW 250 WATTS

C - HIGH 2000 WATTS
MED. 1000 WATTS
LOW 500 WATTS

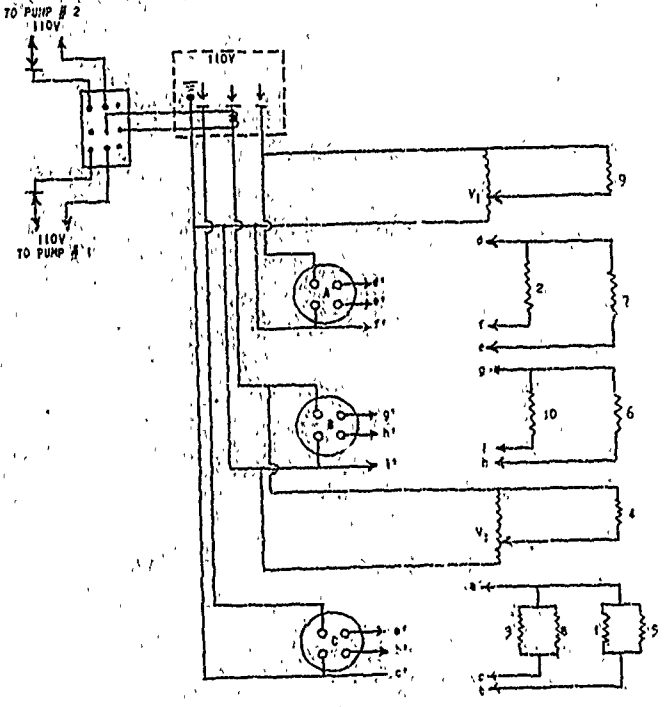


Table 17

HEAT INPUT FOR OPERATION OF THE HIGH TEMPERATURE PUMP TEST UNIT UNDER VARIOUS CONDITIONS

| TEST NO. | SYSTEM PRESSURE, P.S.I. | FLOW RATE, G.P.M. | <--- HEAT INPUT, WATTS ---> FROM PUMP EST.(1) | FROM HEATER | TOTAL | <-------- TEMPERATURES, °F. --------> PUMP INLET | <--------(2)--------> $T_1$ | $T_2$ | $T_3$ | $T_4$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 100 | 4.0 | 230 | 3000 | 3230 | 480 | 490 | 517 | 570 | 630 |
| 2 | 460 | 3.7 | 1060 | 0 | 1060 | 340 | - | - | - | - |
| 3 | 535 | 2.6 | 1235 | 2000 | 3235 | 490 | 507 | 513 | 582 | 668 |
| 6 | 1100 | 2.1 | 2540 | 0 | 2540 | 510 | 540 | 534 | 513 | 475 |
| 9 | 750 | 1.8 | 1730 | 1500 | 3230 | 500 | 520 | 536 | 544 | 556 |
| 10 | 1000 | 2.0 | 2305 | 0 | 2305 | 500 | 530 | 532 | 496 | 496 |
| 11 | 700 | 2.0 | 1610 | 1500 | 3100 | 505 | 535 | 536 | 558 | 575 |
| 12 | 700 | 1.9 | 1610 | 1500 | 3110 | 500 | 514 | 517 | 540 | 552 |

(1) HEAT INPUT FROM PUMP CALCULATED AS FOLLOWS:

H (WATTS) = 0.435 (CONVERSION FACTOR) X PRESSURE (P.S.I.) X FLOW RATE (G.P.M.)

FOR THESE CALCULATIONS THE HEAT GENERATED DUE TO FRICTION IN THE PUMP HAS BEEN NEGLECTED. A VALUE OF 5.3 G.P.M. WAS USED FOR THE FLOW RATE IN THESE CALCULATIONS; THIS VALUE IS THE MAXIMUM FLOW RATE WHICH HAS BEEN OBTAINED WITH THE VICKERS VANE PUMP WHICH WAS USED. THE EFFECT OF PRESSURE ON THE VOLUMETRIC EFFICIENCY OF THE PUMP WAS NOT CONSIDERED.

(2) $T_4$ = TEMPERATURE MEASURED AT OUTLET FROM HEAT EXCHANGER.

$T_2$ = TEMPERATURE MEASURED IN HEAT EXCHANGER BETWEEN COILS.

$T_3$ = TEMPERATURE MEASURED IN HEAT EXCHANGER BETWEEN OUTER COIL AND HEAT EXCHANGER SHELL.

$T_1$ = TEMPERATURE MEASURED ON THE HEAT EXCHANGER SHELL.

(SEE FIGURES 6 AND 7 FOR THERMOCOUPLE LOCATIONS).

Figure 9

CALIBRATION OF SHARP-EDGED ORIFICES USED FOR FLOW RATE DETERMINATIONS

△ = a sharp-edged orifice with a diameter of 0.120 inches.

○ = a sharp-edged orifice with a diameter of 0.160 inches

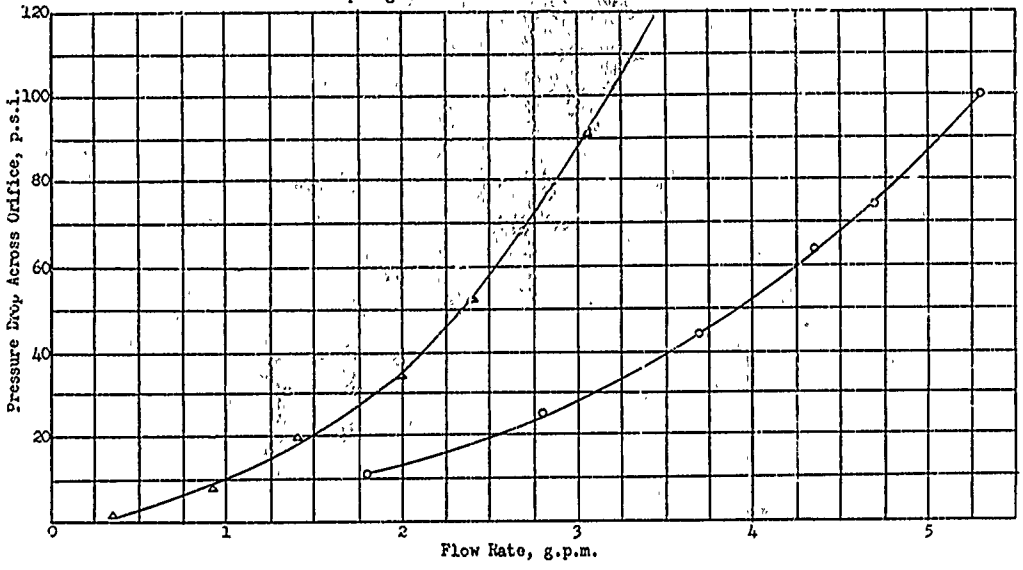


Figure 10
VICKERS MODEL VT4-200-40-75-10 VANE PUMP

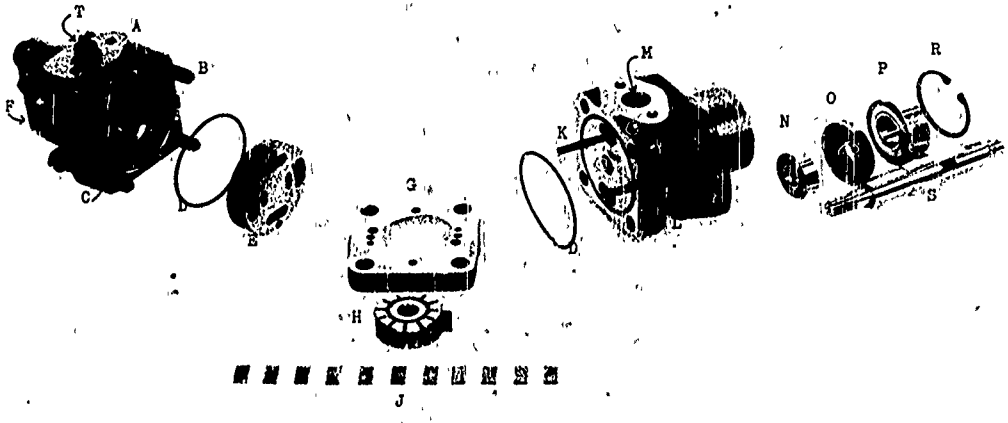


Figure 11
VICKERS MODEL VT4-100-40-75-10 VANE PUMP

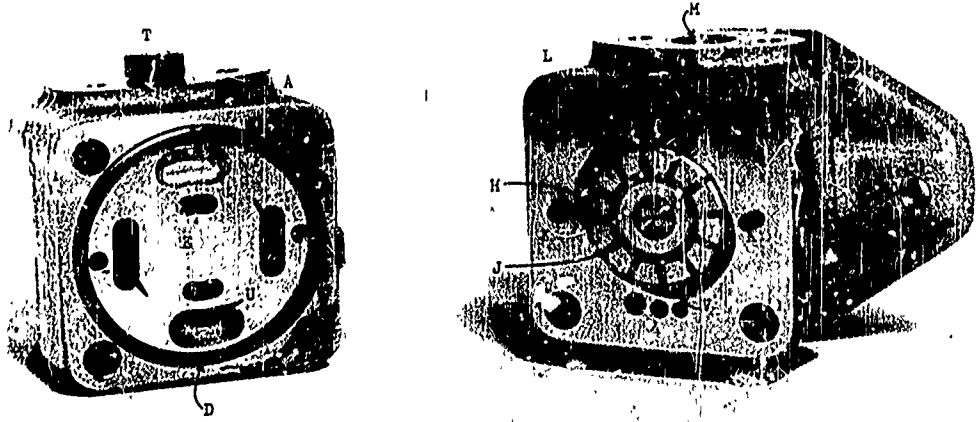


Table 18

NOMENCLATURE OF PARTS FOR THE VICKERS MODEL
VT4-100-40-75-10 VANE PUMP

| Symbol | Part Description |
|---|---|
| A | Cover |
| B | Body Bolt |
| C | Control Valve Assembly and Spring |
| D | Pump Body Seal |
| E | Valve Plate |
| F | Pump Discharge Port |
| G | Cam Ring |
| H | Rotor |
| J | Vanes |
| K | Pin |
| L | Body |
| M | Pump Inlet Port |
| N | Drive Shaft Bearing |
| O | Drive Shaft Seal Assembly |
| P | Drive Shaft Bearing |
| R | Snap Ring |
| S | Drive Shaft |
| T | Pump By-Pass Port |
| U | Area of Maximum Wear on the Valve Plate |
| V | Area of Maximum Wear on the Cam Ring |

in volumetric efficiency with increased temperature. The effect of pressure on volumetric efficiency is shown on Figure 13. This Vickers vane pump shows a relatively large change in volumetric efficiency with increasing pressure. The effect of fluid viscosity on volumetric efficiency is shown on Figure 14. These data indicate that the effect of viscosity change and pressure change on flow rate is much greater for this Vickers vane pump than for the Vickers aircraft type piston pump. The combined effect of pressure and viscosity is illustrated by the two curves on Figure 13. The extent to which the volumetric efficiency versus viscosity and pressure characteristics can be improved by design changes is not known to this Laboratory.

The lubricity characteristics of the fluids evaluated at 500°F. may be estimated from the average vane loss during the tests. This Laboratory has used previously a Vickers V105A type vane pump as a lubricity tester. The use of the Vickers V105A vane pump as a lubricity tester is discussed in detail in reports PRL 3.30-Feb47 and PRL 3.42-Jul48 issued by this Laboratory under Contract NOrd 7958 (Task B). These data show that lubrication of the vane-cam ring bearing surface is improved by increasing fluid viscosity or by the inclusion of tricresyl phosphate as an anti-wear additive. The basic vane-cam ring bearing area in the Vickers V105A and the Vickers vane type power steering pump are essentially the same.

Wear studies with the V105A pump indicate that inadequate lubricity results in vane and cam ring wear. In general, the major portion of the wear from a poor lubricant is noted as cam ring wear. When cam ring wear becomes excessive in the V105A vane pump colloidal metal particles are noted in the test fluid. This same behavior has been noted for the Vickers vane type power steering pump at 500°F. The V105A vane pump requires a mineral oil of about 25 centistokes at the test temperature to eliminate essentially all wear without the use of anti-wear additives. Thus, it would appear that good lubricity in the Vickers vane pump at elevated temperatures would come from the use of chemical anti-wear additives. The data in tests 1 through 6 indicate that excellent wear values result from the use of the di-2-ethylhexyl sebacate type fluid containing 1.0 weight per cent tricresyl phosphate. Moderate wear is noted from the 500°F. tests conducted with the PRL 3457 mineral oil composition containing 1.0 weight per cent tricresyl phosphate.

The same relative wear results between the ester and mineral oil fluid are shown by tests 11 and 12 in which the test times have been extended. These lubricity differences between the mineral oil and ester compositions, both containing 1.0 weight per cent tricresyl phosphate, appear to be due to the elevated operating temperature. Data are available to indicate that adequate lubricity is obtained from either the mineral oil or ester compositions with 1.0 weight per cent tricresyl phosphate to produce essentially no wear in the Vickers vane type pump in the temperature range of 100° to 200°F. The apparent difference in lubricity between mineral oil and ester compositions at 500°F. will be investigated further.

Tests 7, 8, 13 and 14 were conducted to determine the effect of chemical polishing type lubricity additives on the pump parts showing

moderate wear. These four tests are relatively low temperature tests in the range of 200° to 350°F. Test 7 was conducted with a highly refined naphthenic mineral oil (3.5 centistokes viscosity at 100°F.) containing 5.0 weight per cent tricresyl phosphate. The pressure was increased to 1200 p.s.i. to achieve the same severe conditions of vane on cam ring bearing load as those under which moderate wear was noted in test 6. Examination of the vanes and cam ring after test 7 indicated that the wearing surfaces were polished during the test. It is interesting to note that this marked change in wearing surface appearance occurred with essentially no weight loss of the vanes. This is the expected result of chemical polishing with certain types of organo-phosphorus compounds.

Test 8 comprises another attempt to evaluate a more active chemical polishing agent. Alkyl acid phosphites have the same anti-wear activity as tricresyl phosphate in the four-ball wear tester. The alkyl acid phosphites, however, can be used at a much lower concentration than tricresyl phosphate and the effect extends to higher loadings in the extreme-pressure range. Test 8 indicates that di-2-ethylhexyl sebacate containing 0.5 weight per cent of diethyl acid phosphite is also a good anti-wear additive and does not show signs of chemical erosion in the Vickers vane pump. The vanes after test 7 appeared to be highly polished. There was no change in this appearance after test 8.

In test 13, the ester blend containing 0.5 weight per cent diethyl acid phosphite was used with the worn vanes of test 12. Visual evaluation of the vanes and cam ring following test 13 indicates that the vanes are highly polished. Weight loss values indicate that the polishing was again accomplished without appreciable wear. That is, the effect of 0.5 weight per cent diethyl acid phosphite in di-2-ethylhexyl sebacate and 5.0 weight per cent tricresyl phosphate in a low viscosity mineral oil appears to be the same.

In tests 7 and 13, rate fluctuations were noted during the course of the test. In both cases, these rate changes resulted in a net rate increase at the conclusion of the test. These changes in rate are attributed to the chemical polishing action in better mating the vane-cam ring bearing areas.

4. Effect of Temperatures and Fluids on the Pump Parts. The replacement schedule of pump parts is shown on Table 20. It can be noted from these data that essentially no mechanical failures occurred during this series of tests. The major portion of replacement parts consists of the rubber seals. The rubber O-rings and shaft seals are standard Vickers replacement parts. The type of rubber used for these parts is not known to this Laboratory. There are two body seal O-rings, one on each side of the cam ring. These seals had to be replaced after each 500°F. test, only if the pump was disassembled at that point. That is, in the cases where only one seal was replaced, the pump was disassembled by breaking the cam ring pump body seal on only one side. In the tests requiring two body seals, the cam ring was completely removed from the pump for examination.

This same behavior was noted with all of the static rubber seals. That is, as long as these seals were left undisturbed, several

500°F. tests could be conducted without troublesome leakage. In several cases, it was noted that fixed seals which did not leak at 500°F. would allow some fluid seepage at room temperature but would again seal satisfactorily when the temperature was raised to 500°F. The rubber seals appeared to be in better shape after the 500°F. test with the ester type fluid than with the mineral oil. The seals taken from 500°F. tests with mineral oils show evidence of a severe compression set and increased brittleness. The seals from tests with the ester fluid still show some pliability and rubber-like properties.

The shaft seal in the Vickers vane pump comprises a steel shaft rotating in a rubber "lip" type seal. It can be noted that this seal has only been replaced 3 times in the 14 high temperature tests. Two of these replacements have occurred following tests with mineral oils and the third following a complete dismantling of the pump to replace the shaft bearings. No cases of severe shaft seal leakage occurred during this series of tests.

It can be seen that replacement of the metal pump parts has been quite limited. The only pump part failure noted in the entire series of tests was a shaft bearing failure in test 11. This failure was not complete, but incipient failure was indicated by an increase in noise level during pump operation. The increase in pump noise is responsible for the incremental decrease in pressure starting after 12 hours of test 11. The pressure of the system was reduced to lessen the abnormally high noise level and vibration. It is interesting to note that while half of test 11 was conducted under conditions of high noise and excessive vibration, the wear of the vanes is very low and pump leakage through the seals was not excessive.

Examination of the two shaft bearings following test 11 indicated that one of these bearings was becoming "rough". Both shaft bearings were replaced at this point. The bearing showing incipient failure was disassembled and examined. This bearing showed no clear cut reasons for incipient failure. It is believed that mechanical failure from high temperature fatigue may have been experienced here. The bearings are not designed for high temperature use.

The cam ring, valve plate, and vanes which were removed from the pump after test 10 were still in satisfactory operating condition. These parts were changed to conduct long time tests with new parts on an ester- and mineral oil-type fluid.

It has been noted that the differential expansion problem can be troublesome at 500°F. It is extremely difficult to obtain leak proof fittings on the pump housing. Even with the use of steel fittings in the steel pump housing on the high pressure side, it is difficult to eliminate leakage. This leakage was eventually eliminated by silver-soldering the fitting in the housing.

5. Fluid Behavior in Preliminary High Temperature Pump Tests. One of the primary purposes of a high temperature hydraulic pump test stand is the evaluation of fluid behavior under these mock-up conditions.

The property changes in the test fluids incurred under the high temperature test conditions are shown on Table 21. It should be emphasized that these tests were conducted in the presence of air. The more important temperature with respect to property changes during the test is probably the discharge temperature of the fluid from the fluidized solids bed heat exchanger. The property changes shown on Table 21 are indicative primarily of thermal changes. That is, the property changes noted, with few exceptions, would result from subjecting the oil to a thermal stability test at the indicated maximum test temperature for the total test time. Appreciable oxidative effects would be noted by sizeable increases in viscosity. The viscosity changes (decreases) noted for the blend containing Polybutene and Acryloid are of the same order of magnitude as those of thermal stability tests of equivalent severity in test conditions. These data indicate that permanent viscosity decrease due to shear is not accelerated by the elevated temperatures.

There is no visible indication of sludge in the used fluids from these high temperature pump tests. There is some evidence of dirtiness, or metal coating, from both the ester and mineral oil fluids on the interior parts of the hydraulic pump. Non-rubbing metal parts in the pump tend to become coated, or stained, with a light coating quite similar to that noted on the metal catalysts from high temperature oxidation tests. These coatings are believed to be attributable, at least in part, to the amine type oxidation inhibitors used in both the mineral oil and ester fluids. There is some evidence, in the case of the mineral oil, that small amounts of sludge-like deposits collect in the pump body and on the wire screen filter. In the most severe of the mineral oil tests (test 12), this deposit is not sufficient to cause malfunctioning of the pump or plugging of the wire screen filter. A very slight pressure drop increase was noted over the filter toward the end of the test.

6. Evaluation of Promising Hydraulic Fluid Compositions at 500°F. These preliminary tests in the Vickers vane power steering pump test stand at 500°F. were encouraging. In general, it appeared that the reliability of this test vehicle is such that fluids could be evaluated reproducibly without excessive extraneous mechanical difficulties. During the 14 preliminary tests, a total pump test time of 137 hours was logged. Of this total time, about 73 hours was at 500°F. These preliminary data indicated that the Vickers vane pump could be operated to give reproducible results at 500°F. and an operating pressure of 700 p.s.i. A naphthenic mineral oil and a di-2-ethylhexyl sebacate composition operated successfully under these conditions for 24 hours.

As a common test procedure for high temperature hydraulic fluids the following test conditions were chosen:

Test fluid temperature in the pump = 500°F.
Test time = 4 hours at 500°F.
Pressure generated = 700 p.s.i.
Time for pump warmup to 500°F. from room temperature = approx. 2 hours
Pressure during pump warmup = 400 p.s.i.

Figure 12

THE EFFECT OF TEMPERATURE ON THE VOLUMETRIC EFFICIENCY OF A VICKERS VTM-100-40-75-10 VANE PUMP

Tests conducted in PRL high temperature pump test stand. For the comparison made below, the viscosity of the fluids used was the same at the temperature indicated (1.6 cs.). The system pressure in both cases was 750 p.s.i.

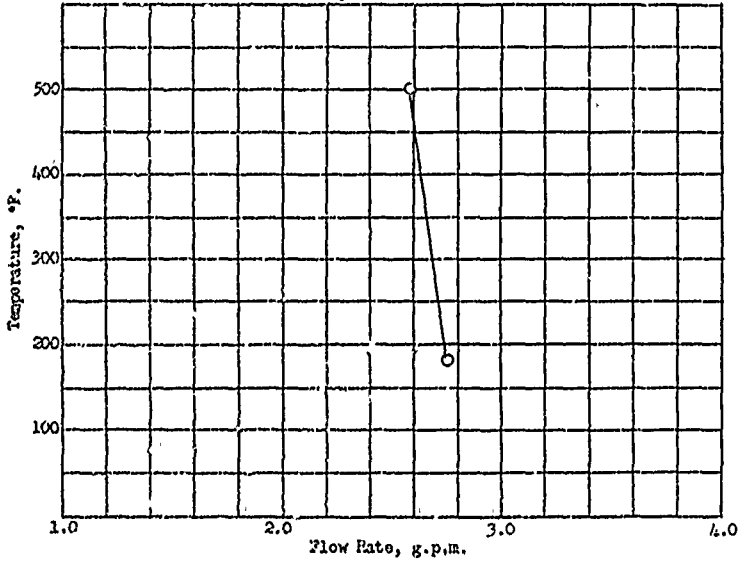


Figure 13

THE EFFECT OF PRESSURE ON THE VOLUMETRIC EFFICIENCY OF A VICKERS VT4-100-4C-75-10 VANE PUMP

Test Fluid = Di-2-Ethylhexyl Sebacate (PRL 3371) + 0.5 Wt.% Phenothiazine + 1.0 Wt.% Tricresyl Phosphate.

○ = Flow rates determined at 500° ± 20°F. (pump inlet temperature)

● = Flow rates determined at 100° ± 20°F. (pump inlet temperature)

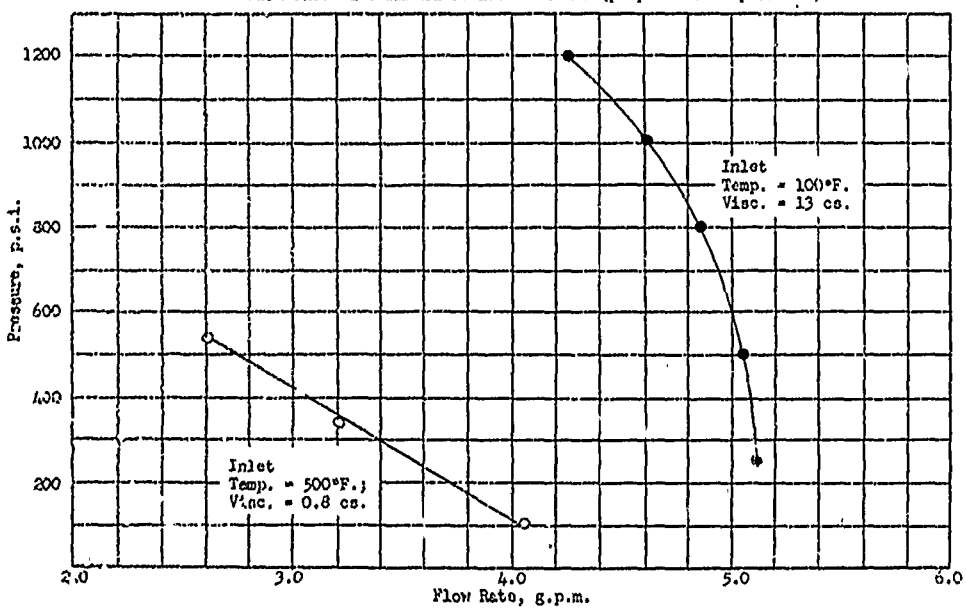


Figure 14

THE EFFECT OF VISCOSITY ON THE VOLUMETRIC EFFICIENCY OF A VICKERS VT4-100-40-75-1C VANE PUMP AT 500°F.

Tests Conducted in PRL High Temperature Pump Test Stand

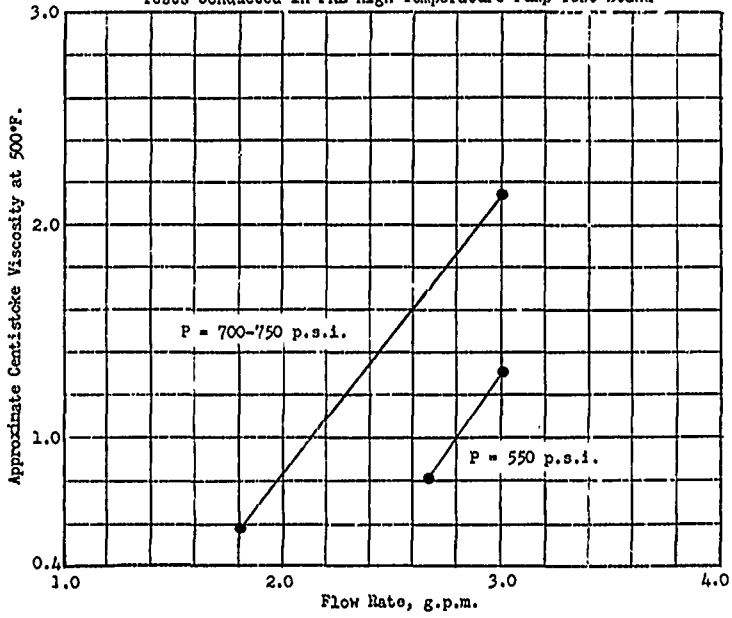


Table 19

SUMMARY OF TESTS MADE AT HIGH TEMPERATURES WITH A VICKERS VTA-100-40-75-10 VANE PUMP

TESTS MADE IN PRL HIGH TEMPERATURE PUMP TEST STAND. FLUID CHARGE = 1.5 GALLONS. TEMPERATURES RECORDED BELOW ARE MEASURED AT THE PUMP INLET.
PRL 3371 = DI-2-ETHYLHEXYL SEBACATE. PRL 2964 = XCT WHITE OIL (A WELL REFINED NAPHTHENIC GAS OIL).
PRL 3457 = ESSTIC 45 (A WELL REFINED NAPHTHENIC NEUTRAL OIL).

| TEST NO. | TEST FLUID (COMPOSITION IN WT.%) | <--TIME IN OPERATION, HOURS---> TOTAL | AT 500°F. | ABOVE 400°F. | ABOVE 500°F. | SYSTEM PRESS., P.S.I. AT MAX. TEMP. | FLOW RATE, G.P.M. AT INDICATED PRESS. AND MAX. TEMP. | FLUID VISC. AT MAX. TEMP., CS. | AVERAGE WT. LOSS PER VANE, MG. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | PRL 3371 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE | 7 | 2.5 | 5 | 6 | 100 | 4.1 | 0.8 | 0.2 |
| 2 | PRL 3371 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE | 28 | 4 | 5.5 | 24.5 | 350 | 3.2 | 0.8 | 0.1 |
| 3 | PRL 3371 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE | 7.5 | 5 | 6 | 7 | 550 | 2.7 | 0.8 | 0.2 |
| 4 | PRL 3371 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE + 9.0 ACRYLOID HF-25 | 3 | 1 | 1.5 | 2 | 550 | 3.0 | 1.3 | - |
| 5 | PRL 3457 + 0.2 PHENYL-α-NAPHTHYLAMINE + 1.0 TRICRESYL PHOSPHATE + 5.0 POLYBUTENE B-12 | 5.5 | 4 | 4.5 | 5 | 700 | 3.0 | 2.2 | 1.2 |
| 6 | PRL 3457 + 0.2 PHENYL-α-NAPHTHYLAMINE + 1.0 TRICRESYL PHOSPHATE + 5.0 POLYBUTENE B-12 | 3.5 | 2 | 2.5 | 3 | 1150 | 2.0 | 2.2 | 5.3 |
| 7 | PRL 2964 + 0.4 PARANOX 441 + 5.0 TRICRESYL PHOSPHATE | 5.5(1) | - | - | - | 100-1200 | 5.2-1.0(2) | 1.6 | 0.1 |
| 8 | PRL 3371 + 0.5 PHENOTHIAZINE + 0.5 DIETHYL HYDROGEN PHOSPHITE | 5.5(1) | - | - | 3.5 | 100-1200 | 5.0-2.0(2) | 1.1 | 0.2 |
| 9 | PRL 3457 + 0.2 PHENYL-α-NAPHTHYLAMINE | 6 | 4 | 4.5 | 5.5 | 7.5 | 1.8 | 0.6 | 0.0 |
| 10 | PRL 3457 + 0.2 PHENYL-α-NAPHTHYLAMINE + 1.0 TRICRESYL PHOSPHATE + 5.0 POLYBUTENE B-12 | 5.5 | 4 | 5.5 | 5 | 1000 | 2.0 | 2.3 | 0.3 |
| 11 | PRL 3371 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE + 9.0 ACRYLOID HF-25 | 24 | 22 | 22.5 | 23 | 700-400(4) | 2.0-2.7(4) | 1.3 | +0.2 |
| 12 | PRL 3457 + 1.0 PHENYL-α-NAPHTHYLAMINE + 1.0 TRICRESYL PHOSPHATE + 5.0 POLYBUTENE B-12 | 25.5 | 24 | 24.5 | 25 | 700 | 2.1-1.9(3) | 2.2 | 9.3 |
| 13 | PRL 3371 + 0.5 PHENOTHIAZINE + 0.5 DIETHYL HYDROGEN PHOSPHITE | 6.5(1) | - | - | 3 | 1000-1200 | 1.5-1.1(2) | 1.3 | +0.2 |
| 14 | PRL 3371 + 0.5 PHENOTHIAZINE + 0.5 DIETHYL HYDROGEN PHOSPHITE | 4(1) | - | - | 2.5 | 1000-1200 | 1.5-1.1(2) | 1.3 | 0.3 |
| | TOTAL HOURS ON PUMP | 137.0 | 72.5 | 81.0 | 115.0 | | | | |

(1) MAXIMUM TEST TEMPERATURE SHOWN ON TABLE 21.
(2) FLOW RATES SHOWN ARE FOR THE MINIMUM AND MAXIMUM PRESSURES SHOWN.
(3) THE FLOW RATES DECREASED FROM 2.1 TO 1.9 G.P.M. DURING OPERATION AT 500°F.
(4) THE SYSTEM WAS OPERATED FOR 12 HOURS AT 700 P.S.I. THE SYSTEM PRESSURE WAS THEN REDUCED TO 400 P.S.I. AND OPERATED FOR AN ADDITIONAL 10 HOURS AT THIS PRESSURE. THE FLOW RATE INCREASED FROM 2.0 TO 2.7 G.P.M. WHEN THE PRESSURE WAS REDUCED.

Table 20

PARTS REPLACEMENT IN THE HIGH TEMPERATURE PUMP TEST STAND

Parts Replaced Following the Test Indicated

| Test No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pump | | | | | | | | | | | | | | |
| Body Seal "O" Rings | 1 | 1 | 2 | - | 2 | 2 | - | 1 | 1 | 2 | 2 | 2 | - | - |
| Vanes | - | - | - | - | - | - | - | - | - | 1 | - | - | - | - |
| Cam Ring | - | - | - | - | - | - | - | - | - | 1 | - | - | - | - |
| Valve Plate | - | - | - | - | - | - | - | - | - | 1 | - | - | - | - |
| Drive Shaft Bearings | - | - | - | - | - | - | - | - | - | - | 2 | - | - | - |
| Drive Shaft Seal Assembly | - | - | - | - | 1 | - | - | - | - | 1 | 1 | - | - | - |
| System | | | | | | | | | | | | | | |
| Reservoir Gaskets | - | - | 1 | - | - | - | - | - | 1 | - | - | - | 1 | - |
| Filter Case "O" Ring | - | - | - | - | 1 | - | - | - | - | - | - | 1 | - | - |

Note:

It has been noted that the rubber gasket material and "O" rings deteriorate more rapidly when a mineral oil is used than when an ester is used. This is evident when the replacement list above is compared with the fluid used in the test immediately preceding replacement. For example, excessive leakage occurs in the filter case during mineral oil tests and in both cases where "O" rings were replaced this occurred immediately following a mineral oil test (#5 and #12).

In all cases, the "O" rings in the pump body are more pliable following a run using an ester than following a run in which a mineral oil is used. This had also been observed for the gasket material used in the reservoir.

Table 21

SUMMARY OF FLUID PROPERTIES FOLLOWING TESTS IN THE PRL HIGH TEMPERATURE PUMP TEST UNIT

PRL 3371 = DI-2-ETHYLHEXYL SEBACATE
PRL 3457 = ESSTIC 45 (A WELL REFINED NAPHTHENIC NEUTRAL OIL)
PRL 2964 = XCT WHITE OIL (A WELL REFINED NAPHTHENIC GAS OIL)

| TEST NO. | TEST FLUID (COMPOSITION IN WT.%) | TIME IN OPERATION, HOURS: TOTAL | AT 500°F. | ABOVE 400°F. | ABOVE 300°F. | TEST TEMP. °F. (1) | MAX. OIL TEMP. °F. (2) | FLUID PROPERTIES: NEUT. NO. MG. KOH/GM. OIL ORIGINAL | NEUT. NO. MG. KOH/GM. OIL FINAL | CENTISTOKE VISC. AT 100°F. ORIGINAL | CENTISTOKE VISC. AT 100°F. FINAL |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | PRL 3371 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE | 7 | 2.5 | 5 | 6 | 490 | 505 | 0.2 | 1.0 | 12.9 | 13.0 |
| 2 | PRL 3371 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE | 28 | 4 | 5.5 | 24.5 | 490 | 515 | 1.0 | 3.1 | 13.0 | 13.9 |
| 3 | PRL 3371 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE | 7.5 | 5 | 6 | 7 | 500 | 520 | 0.2 | 2.2 | 12.9 | 12.9 |
| 4 | PRL 3371 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE + 9.0 ACRYLOID HF-25 | 3 | 1 | 1.5 | 2 | 500 | 530 | 0.2 | 1.5 | 39.6 | 23.8 |
| 5 | PRL 3457 + 0.2 PHENYL-α-NAPHTHYLAMINE + 1.0 TRICRESYL PHOSPHATE + 5.0 POLYBUTENE B-12 | 5.5 | 6 | 4.5 | 5 | 510 | 530 | 0.3 | 0.5 | 189 | 171 |
| 6 | PRL 3457 + 0.2 PHENYL-α-NAPHTHYLAMINE + 1.0 TRICRESYL PHOSPHATE + 5.0 POLYBUTENE B-12 | 3.5 | 2 | 2.5 | 3 | 510 | 545 | 0.3 | 0.4 | 176 | 166 |
| 7 | PRL 2964 + 0.4 PARANOX 441 + 5.0 TRICRESYL PHOSPHATE | 5.5 | - | - | - | 180 | 180 | 0.1 | 0.1 | 3.40 | 3.43 |
| 8 | PRL 3371 + 0.5 PHENOTHIAZINE + 0.5 DIETHYL HYDROGEN PHOSPHITE | 5.5 | - | - | 3.5 | 390 | 430 | 1.9 | 2.1 | 12.9 | 13.0 |
| 9 | PRL 3457 + 0.2 PHENYL-α-NAPHTHYLAMINE | 6 | 4 | 4.5 | 5.5 | 510 | 535 | 0.2 | 0.3 | 43.0 | 42.0 |
| 10 | PRL 3457 + 0.2 PHENYL-α-NAPHTHYLAMINE + 1.0 TRICRESYL PHOSPHATE + 5.0 POLYBUTENE B-12 | 5.5 | 4 | 4.5 | 5 | 520 | 540 | 0.4 | 0.6 | 128 | 127 |
| 11 | PRL 3371 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE + 9.0 ACRYLOID HF-25 | 24 | 22 | 22.5 | 23 | 510 | 555 | 0.8 | 9.7 | 42.0 | 24.6 |
| 12 | PRL 3457 + 1.0 PHENYL-α-NAPHTHYLAMINE + 1.0 TRICRESYL PHOSPHATE + 5.0 POLYBUTENE B-12 | 25.5 | 24 | 24.5 | 25 | 510 | 535 | 0.4 | 9.4 | 190 | 163 |
| 13 | PRL 3371 + 0.5 PHENOTHIAZINE + 0.5 DIETHYL HYDROGEN PHOSPHITE | 6.5 | - | - | 3 | 360 | 360 | 0.5 | 2.2 | 12.8 | 13.[illegible] |
| 14 | PRL 3371 + 0.5 PHENOTHIAZINE + 0.5 DIETHYL HYDROGEN PHOSPHITE | 4 | - | - | 2.5 | 375 | 375 | 2.2 | 3.1 | 13.2 | 19.2 |

(1) TEST TEMPERATURE MEASURED AT PUMP INLET.
(2) MAX. OIL TEMPERATURE MEASURED AT OUTLET FROM FLUIDIZED SOLIDS BED HEAT EXCHANGER.

The test results for the various high temperature hydraulic fluids under the above test conditions are shown on Tables 22, 23 and 24.

The data on Table 22 show the effect of the fluid on pump operation. The parts replacement schedule is shown on Table 23. In addition to weight loss of the vanes, the change in surface roughness has been determined following several of these tests to illustrate further the type of wear observed. Surface roughness was measured with a Brush Development Company surface analyzer. The two surfaces investigated are the valve plate which is hydraulically loaded against the sides of the vanes and the cam ring against which the vanes are loaded by centrifugal force. The maximum surface changes due to wear on the valve plate appeared to occur between the inlet port and the exit port in the direction of rotation of the vanes. This portion of the valve plate is indicated in Figure 11 (U).

The portion of the cam ring surface showing maximum surface roughness is the portion which communicates directly with the inlet port as indicated on Figure 11 (V). Only one of the two critical wear areas is marked for the cam ring and valve plate. The second area in each case is 180 degrees from the first since the pump completes two pumping cycles in one revolution. Traces of surface roughness for the cam ring and valve plate at the indicated areas for several lubricants in 500°F. pump tests are shown on Figures 15 through 23. A trace of surface roughness for the new parts is shown as Figure 15.

As indicated previously, both mineral oil and ester compositions gave satisfactory operation for 4 to 24 hours under the standard test conditions chosen for further hydraulic fluid evaluation. Pump tests 1 through 14 and 16 through 29 were conducted with different batches of pump parts. Therefore, a standard test with the di-2-ethylhexyl sebacate fluid is included in the current series of tests as a reference point.

Test No. 29 is the reference test with di-2-ethylhexyl sebacate containing 1.0 weight per cent tricresyl phosphate and 0.5 weight per cent phenothiazine. As indicated in Table 23, this test was conducted with essentially all new parts. The results of this test are in good agreement with the preliminary tests using the same test fluid, with the previous batch of pump parts. The volumetric efficiency of the pump shows a drop of approximately 14 per cent during the four hour test period at 500°F. pump temperature and 550°F. maximum fluid temperature. It can be seen from the surface profile data on Figure 16 that there is a noticeable increase in surface roughness of the cam ring and valve plate surfaces even though the vane wear gives indication of very little wear. The vane edges bear against the cam ring and valve plate where the surface roughness is measured. An attempt has been made to use the surface analyzer on the vane edges to determine surface roughness. The vane edge roughness cannot accurately be measured with the surface analyzer used for this work, because of the narrow curved surface of the worn vane edge. It has been determined by trial measurements that the vane edge and the mating wear surface on the cam ring do have similar roughness profiles.

In previous studies with the Vickers V105A vane pump and in this current study with the Vickers power steering pump, test data have indicated that severe overall pump wear can occur with only moderate vane wear. Severe pump wear in the Vickers V105A vane pump, evaluated at 100°F., generally followed a pattern of severe abrasive wear of the cam ring with moderate to severe vane wear. This severe pump wear was accompanied by the appearance of colloidal metal (steel) particles in the test fluid. In low temperature pump runs, it is possible to weigh the cam ring and valve plate on an analytical balance with good results. In the high temperature runs with the power steering pump, weight changes of the cam ring and valve plate are confused by the extraneous effects of paint charring on the outside surface of the cam ring and/or the deposition of sludge or tenacious charred deposits on the outside of the cam ring due to body seal leakage. The valve plate is also subject to sludge deposits or coatings during the test. Thus, moderate to high vane wear (>1 mg. wear per vane) accompanied by the formation of colloidal metal in the test fluid is considered severe or excessive wear. Moderate vane wear (1 to 5 mg. wear per vane) without colloidal metal formation in the test fluid is considered a tolerable wear level. Wear is considered to be low if the average vane wear is less than 1 mg. in this standard test, and if no colloidal metal is noted in the test fluid.

Test 19 was conducted to determine the effect of tricresyl phosphate as an anti-wear additive on a phenothiazine-inhibited di-2-ethylhexyl sebacate fluid. The test fluid for test 19 is the same as that for test 29 except that no tricresyl phosphate anti-wear additive was used in the former. Test 19, as indicated in Table 23, was conducted with new vanes, cam ring, and rotor. The test proceeded satisfactorily for the four hour test period at 500°F. pump temperature and 525°F. maximum fluid temperature. The initial volumetric efficiency was superior to that of the similar test (29) with tricresyl phosphate. The drop in volumetric efficiency of about 20 per cent during the test is about the same as that noted for test 29. Moderate vane wear but no evidence of colloidal metal in the test fluid was noted. On the basis of wear, it is apparent that tricresyl phosphate at 1.0 weight per cent concentration is an effective anti-wear additive in di-2-ethylhexyl sebacate at 500°F.

Test 21 has been conducted with Hercoflex 600 as the test fluid containing 1.0 weight per cent tricresyl phosphate and 0.5 weight per cent phenothiazine. As pointed out previously in this section, interest in Hercoflex 600 (pentaerythritol type ester) stems from its improved thermal stability compared with the dibasic acid esters evaluated. For test 21, the major wearing parts of the pump were renewed as indicated in Table 23. The viscosity of the Hercoflex 600 fluid at 500°F. is the same as that of the two di-2-ethylhexyl sebacate fluids. The standard test was conducted for four hours at 500°F. pump temperature and 540°F. maximum fluid temperature without difficulty. The volumetric efficiency is the same as for test 29 with the di-2-ethylhexyl sebacate test fluid containing tricresyl phosphate. It is interesting to note that a moderate amount of wear (2.3 mg. average wear per vane) was noted in test 21. This amount of wear resembles that obtained in test 19 with di-2-ethylhexyl sebacate without tricresyl phosphate. It has been pointed out in previous reports that

Hercoflex 600 shows relatively poor tricresyl phosphate susceptibility as measured by the Shell four-ball wear tester. Hercoflex 600 containing 1.0 weight per cent tricresyl phosphate gives essentially the same lubricity values in the Shell four-ball wear tester as di-2-ethylhexyl sebacate without an anti-wear additive. In general, the cam ring surface exhibits more surface roughness in the case of the Hercoflex 600 fluid (test 21) than for the equivalent di-2-ethylhexyl sebacate fluid (test 29). These surface roughness data are shown in Figure 17.

Test 20 is a 600°F. maximum fluid temperature, 570°F. pump temperature test with a mineral oil composition. This composition consists of 92.8 weight per cent Necton 45 (a highly refined naphthenic mineral oil), 5.0 weight per cent Polybutene B-12, 1.0 weight per cent tricresyl phosphate, and 0.2 weight per cent phenyl alpha naphthylamine. The Polybutene B-12 thickener has been used in an attempt to maintain a reasonable level of viscosity at the 570°F. pump temperature. The initial extrapolated viscosity at the 570°F. test temperature is 1.7 centistokes. Approximately 30 per cent viscosity decrease in the 100°F. viscosity value was noted during the course of the pump test due to thermal and shear effects. The magnitude of the viscosity decrease at 570°F. is estimated to be about the same as that at 100°F. That is, the estimated final viscosity in this pump test is 1.2 centistokes at 570°F. Test 20 ran without difficulty for four hours at 570°F. pump temperature and 600°F. maximum fluid temperature. The parts for this test had previously been used in the four hour test 19 at 500°F. pump temperature with di-2-ethylhexyl sebacate test fluid. The volumetric efficiency decreases about 30 per cent during this test. This value is somewhat larger than previously noted for the ester fluids. The loss in volumetric efficiency does not appear to be unusually high in view of the 30 per cent loss in viscosity of the test fluid in this run. Moderate vane wear was noted.

The overall behavior of the mineral oil and pump at 570°F. pump temperature compares favorably with the behavior of this same composition in the standard four hour test at 500°F. pump temperature discussed previously.

It has been noted previously that tricresyl phosphate is not as effective in reducing wear in a mineral oil fluid at 500°F. as it is in di-2-ethylhexyl sebacate. There was no indication of colloidal metal formation in the test fluid. Surface roughness of the cam ring and valve plate, as shown on Figure 18, appears to be of the same order of magnitude in tests 20 and 29. In the case of the di-2-ethylhexyl sebacate fluid containing tricresyl phosphate (test 29), the increase in surface roughness occurs without indication of significant wear. The same increase in surface roughness with the mineral oil fluid in test 20 shows indication of moderate vane wear.

Test 26 has been conducted with Ucon LB-170X under the standard test conditions. New pump parts installed prior to test 26 include: body seal "O" rings, shaft seal, cam ring, vanes, rotor, valve plate, and pump body. Vane wear in this test is very low. In addition, the surface roughness of the cam ring and valve plate following the test are essentially the same as that of the new parts

(compare Figures 15 and 19). This lack of wear or surface roughening is also indicated by the good initial volumetric efficiency and small change in volumetric efficiency throughout the test. The 500°F. pump temperature and 550°F. maximum fluid temperature are in the range at which incipient thermal deterioration of Ucon LB-170X to volatile products is noted. Ucon LB-170X has about the same effect on the rubber seals in the pump as the mineral oils evaluated. In both cases, the rubber becomes very hard and brittle during the test. The ester fluids on the other hand leave the rubber seals in a pliable and flexible, but not particularly elastic, condition after the standard 500°F. pump test.

A fluid prepared in accordance with the NACA SD-17 formulation has been evaluated in test 16. This fluid has been formulated to contain 66.5 weight per cent Dow Corning Silicone Type 510 (100 cs. viscosity level at 77°F.), 33 weight per cent di-2-ethylhexyl sebacate and 0.5 weight per cent phenothiazine. The standard warmup procedure was being followed in this test. That is, a pressure of 400 p.s.i. was used during the warmup. At a pump temperature of 450°F. the pressure was increased to 700 p.s.i. In less than 15 minutes of operation under the 700 p.s.i. pressure, colloidal metal appeared in the test fluid. During the 1.5 hour test at 500°F. pump temperature, the flow rate fell from 2.8 to 1.0 g.p.m. The test was terminated at this point. The pump was disassembled and examined. The vanes show an excessive weight loss of 20.4 mg. per vane. The cam ring and valve plate were badly scored and eroded. The critical wear areas on the cam ring showed evidence of erosion to the extent of 1/32-inch increase in cam ring radius. The valve plate showed deep gouges into the bearing surface between the inlet and outlet parts. In general, the severe valve plate wear might be considered secondary damage. This damage would result from the rubbing of the sides of the vane against the valve plate or the presence of an abrasive such as colloidal metal particles, which in turn would act as a grinding compound between the edge of the vanes and the valve plate. It should be noted that the SD-17 composition has an extrapolated viscosity at 500°F. of 3.4 centistokes. This is higher by a factor of 4 than the viscosity of the esters which gave satisfactory pump behavior.

An attempt was made to rule out the quality of the pump parts in this pump failure. The same parts from test 16 were reassembled and tested (test 17) at 500°F. for four hours at a pressure of 350 p.s.i. with di-2-ethylhexyl sebacate containing 1.0 weight per cent tricresyl phosphate and 0.5 weight per cent phenothiazine. Unfortunately, 350 p.s.i. was the maximum pressure that could be generated with the orifice loading device and the relatively low flow rate. Under these conditions, the pump ran satisfactorily without the formation of colloidal metal in the ester test fluid. Following test 17 the pump parts were again examined. The average vane weight loss was 1.0 mg. and the vane edges and cam ring surface appeared to have a polish on the high spots of the gouges incurred in test 16. The valve plate appeared essentially unchanged. It was apparent that the major cause of the poor volumetric efficiency was due to the excessive gouging of the valve plate in test 16.

The vanes and cam ring from tests 16 and 17 were reassembled with a new valve plate. Test 18 was conducted with these parts and the

same ester composition used in test 17. This test was conducted to show the effect of these vanes and cam ring with the ester at a higher pressure. At 500°F. with these parts, a steady state could be maintained at a pressure of 650 p.s.i. Operation for 0.5 hours under these conditions gave no signs of reduced volumetric efficiency or colloidal metal formation. The test was terminated at this point and the parts re-examined. The cam ring and vanes gave evidence of further polishing. The average vane wear of 1.3 mg. is considered low for the very rough mating surfaces involved. The new valve plate installed for test 18 showed no signs of wear or cutting. Tests 17 and 18 have been interpreted to show that the pump parts for test 16 were of satisfactory quality. The evidence of lubrication failure is believed to be attributable to the lubricity properties of the D-17 formulation.

The surface roughness of the cam ring from tests 16, 17 and 18 and the valve plate from tests 16 and 17 are shown on Figures 20 and 21, respectively. It should be emphasized that for the cam ring, the surface roughness shown on Figure 20 is somewhat improved over the surface roughness obtained from test 16 alone. The surface as shown is considerably rougher than the surfaces formed from mineral oil and ester tests. It can be seen that the gouges are not only deeper but much wider. In the case of the valve plate, the major wear resulted in a trough 3/8 inches wide and 1500 micro inches deep as shown on Figure 21.

Test 22 shows the results of a 500°F. pump test with silicate composition O.S. 45 obtained from Monsanto Chemical Company. The warm up period at 400 p.s.i. was satisfactory. When the temperature reached 400°F., the pressure was increased to 700 p.s.i. but steady operation at 700 p.s.i. could not be maintained. The warm up period was then continued at 500 p.s.i. At 500°F. the pressure was again increased to 700 p.s.i. Colloidal metal in the reservoir was noted almost immediately. The flow rate began to decrease from 1.8 to 1.2 g.p.m. and the pressure could no longer be maintained at 700 p.s.i. due to the reduced flow rate. The test was terminated after 0.5 hours at 500°F. The parts were disassembled and examined. An average vane wear of 1.3 mg. was measured. The cam ring and valve plate, however, showed signs of relatively severe gouging.

Again as a check on the quality of the parts, test 23 was made with the parts from test 22 and a phenothiazine-inhibited di-2-ethylhexyl sebacate fluid containing 1.0 weight per cent tricresyl phosphate. Between tests 22 and 23 the pump system was flushed with di-2-ethylhexyl sebacate at a low pressure. The colloidal metal was collected in a 5 micron porosity micronic line type Purolator filter. Test 23, with the worn parts from test 22, gave a flow rate at 700 p.s.i. of 2.0 g.p.m. This value compares with a flow rate of 1.2 g.p.m. at a pressure of less than 700 p.s.i. in test 22. It is interesting to note that both of these test fluids exhibit about the same viscosity level at 500°F.

As noted in previous runs, the discrepancy in volumetric efficiency may be attributable to the character of the wear or surface mating with the various fluids. In test 23, the run was continued at 500°F. for 1.5 hours without difficulty. The test was terminated and the

parts examined. There were signs of polishing on the high spots of the gouged surfaces from test 22. The vane weight loss of 0.2 mg. is very low. The same wearing parts were reassembled and O.S. 45 silicate fluid recharged to the system. At a temperature of 500°F., steady conditions could not be maintained at a pressure above 600 p.s.i. After 1 hour running at 500°F., the pressure had fallen to 400 p.s.i. and the flow rate dropped to 1.0 g.p.m. Pump operation became rough and the test was terminated because of excessive shaft seal leakage. The pump was disassembled and examined. Both ball bearings failed in this test. The cam ring and valve plate showed signs of scoring. The vane weight loss was 1.3 mg. The surface roughness of the cam ring and valve plate from tests 22, 23 and 24 are shown on Figure 22. It is apparent from this figure that the scoring is much deeper and wider than that in corresponding mineral oil and ester runs where the same order of magnitude of vane wear is noted.

A second silicate formulation (MLO 8200) prepared by the Oronite Chemical Company was evaluated in test 25. As indicated in Table 23, an entirely new pump was used for test 25. The pump test stand was completely flushed with mineral oil using a 5 micron Purolator filter to remove all solid foreign matter. The warm up of test 25 was conducted at 400 p.s.i. as usual. In this case, however, 400 p.s.i. was severe enough to cause the formation of colloidal metal particles in the oil by the time the test temperature reached 450°F. At this point, the pressure was increased to 700 p.s.i. Steady operation could not be maintained under these conditions and the pressure dropped steadily to 500 p.s.i. in a 15 minute interval. The flow rate fell from 1.6 to 1.0 g.p.m. during this time. The test was terminated at this point without reaching 500°F. The cam ring and valve plate showed severe scoring. The average vane wear was 4.0 mg. The surface roughness measurements, as shown on Figure 23, indicate scoring of the same degree of severity as on test 22 with O.S. 45 silicate fluid.

It should be noted that MLO 8200 has an extrapolated viscosity at 500°F. of 2.6 centistokes which is about 3 times the viscosity of O.S. 45 silicate fluid, the dibasic acid ester, and Hercoflex 600 evaluated.

Aroclor 1248 was used as the test fluid for test 27. The warm up run proceeded without difficulty. The pressure was increased to 700 p.s.i. at a temperature of 500°F. Operation under these conditions appeared to be satisfactory. After about 15 minutes operation at 500°F. and 700 p.s.i., shaft seal leakage became excessive and the unit was shut down. The rubber seals from this test were all badly swollen and softened during the test. It is apparent from the seal conditions that satisfactory operation with Aroclor will require seals with better resistance to swell and deterioration with this type of fluid.

It is interesting to note that the flow rate at 500°F. and 700 p.s.i. was higher for the Aroclor 1248 than for any of the other fluids evaluated. Aroclor exhibits a viscosity of only 0.6 centistoke at 500°F. The centistoke viscosity comparison may be somewhat misleading in this case because of the relatively high density of the

Aroclor 1248 (1.4 at 100°F.) compared with the ester fluid (0.92 at 100°F.). Flow behavior in a pump system such as this is related to the centipoise viscosity rather than the centistoke viscosity. The centipoise viscosity of Aroclor 1248 at 500°F. is about 0.85 compared with a value of about 0.75 for the two ester fluids. Thus, it appears that the flow rate can not be satisfactorily explained on the basis of viscosity difference. The differences in flow rate may be explained by the differences in lubricity. Aroclor 1248, under some test conditions in the four-ball wear and E.P. testers, shows evidence of extreme-pressure activity. Chemical erosion of the type noted with E.P. additives may keep the pump parts well mated and result in improved flow rate for a given viscosity. The vane loss of 1.5 mg. is indicative of moderate wear. Moderate wear is normally indicated by extreme-pressure additives in the four-ball wear tester.

The flow rate is measured as a pressure drop across the orifice in the high temperature pump test stand. As a further check on the validity of the flow rate measurement in test 27, test 28 was conducted with the same pump parts using a phenothiazine-inhibited di-2-ethylhexyl sebacate fluid containing 1.0 weight per cent tricresyl phosphate. The system was flushed with an ester fluid between tests 27 and 28. Test 28 was conducted as a standard test. The initial flow rate of 2.7 g.p.m. is typical for this test fluid under the indicated conditions. A vane loss of 4.0 mg. is noted in test 28 accompanied by a 50 per cent loss in volumetric efficiency during the test. These values are unusually high for the di-2-ethylhexyl sebacate test fluid. It is believed that this high wear may have been influenced by the conditioning of the wearing parts by the Aroclor 1248 test fluid in the previous test.

7. Effect of High Temperature Pump Test on Fluid Properties. As indicated previously, the high temperature pump test stand utilized in these studies is not a sealed unit. The reservoir is vented to the atmosphere. Thus, fluid deterioration may be more severe in this test system than in a sealed hydraulic system of the type used in actual aircraft under the same temperature conditions. The fluid deterioration data for the series of tests discussed in Table 22 are shown in Table 24. These data indicate, in all cases, relatively minor fluid property changes. The large viscosity decrease noted in test 20 at 600°F. is due to thermal effects on the Polybutene B-12 polymer. In general, all of the fluids evaluated show adequate stability properties in this series of pump tests.

F. REPORT PRL 6.3-Dec53 ENTITLED SOME PROPERTIES OF SPEC. MIL-O-5606 HYDRAULIC FLUID AT ELEVATED TEMPERATURES. The Wright Air Development Center requested that this Laboratory evaluate the properties of Spec. MIL-O-5606 hydraulic fluid at elevated temperatures. Spec. MIL-O-5606 hydraulic fluid has been used over the past 10 years as the aircraft hydraulic fluid by the U.S. Air Force and the British and Canadian Air Forces. Indications are that Spec. MIL-O-5606 hydrocarbon-base hydraulic fluids have performed satisfactorily in a wide variety of uses over this period. The bulk of the data on the behavior of this hydraulic fluid has been obtained from use in conventional World War II piston engine aircraft.

Table 22

SUMMARY OF TESTS CONDUCTED AT HIGH TEMPERATURES WITH A VICKERS MODEL VT4-100-40-75-10 VANE PUMP

TESTS MADE IN PRL HIGH TEMPERATURE PUMP TEST STAND. FLUID CHARGED = 1.5 GALLONS. TEST TEMPERATURE MEASURED AT THE PUMP INLET. MAXIMUM OIL TEMPERATURE MEASURED AT OUTLET FROM FLUIDIZED SOLIDS BED HEAT EXCHANGER.

TEST FLUIDS:

PRL 3371 = DI-2-ETHYLHEXYL SEBACATE
PRL 3483 = DI-2-ETHYLHEXYL SEBACATE
PRL 3497 = SILICONE TYPE 510 (D.C.)
PRL 3457 = ESSTIC 45 (MINERAL OIL)
PRL 3498 = HERCOFLEX 600
PRL 3505 = SILICATE FLUID OS-45
PRL 3506 = SILICATE FLUID MLO-8200
PRL 3507 = UCON LUBRICANT LB-170X
PRL 3508 = ANDOCOR 1048
PRL 3529 = 66.5 WT.% SILICONE 510 + 33.0 WT.% DI-2-ETHYLHEXYL SEBACATE + 0.5 WT.% PHENOTHIAZINE

| TEST NO. | TEST FLUID (COMPOSITION IN WT.%) | TIME IN OPERATION, HRS. TOTAL | TIME IN OPERATION, HRS. AT OR ABOVE 500°F. | TEST TEMP., °F. | MAX. OIL TEMP., °F. | SYSTEM PRESS., P.S.I. AT MAX. TEMP. | FLOW RATE, G.P.M. AT INDICATED PRESS. AND MAX. TEMP. | FLUID VISC. AT MAX. TEMP., CS. | AVE. WT. LOSS PER VANE, MG. |
|---|---|---|---|---|---|---|---|---|---|
| 16 | PRL 3529 | 4 | 1.5 | 500 | 550 | 700 | 2.0-1.0(1) | 3.4 | 20.4 |
| 17 | PRL 3371 + 0.5 PHENOTHIAZINE + 5.0 TRICRESYL PHOSPHATE | 7 | 4 | 500 | 580 | 350(2) | 0.9-0.7 | 0.8 | 1.0 |
| 18 | PRL 3483 + 0.5 PHENOTHIAZINE + 5.0 TRICRESYL PHOSPHATE | 2 | 0.5 | 500 | 585 | 650(2) | 0.8 | 0.8 | 1.2 |
| 19 | PRL 3483 + 0.5 PHENOTHIAZINE | 6 | 4 | 500 | 575 | 700 | 3.4-2.7(1) | 0.8 | 2.3 |
| 20 | PRL 3457 + 5.0 POLYBUTENE 8-12 + 1.0 TRICRESYL PHOSPHATE + 0.2 PHENYL-α-NAPHTHYLAMINE | 5.5 | 4 | 570 | 600 | 700 | 3.3 2.3 | 2.2 | 1.3 |
| 21 | PRL 3498 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE | 6 | 4 | 500 | 540 | 700 | 2.8-2.4(1) | 0.8 | 2.3 |
| 22 | PRL 3505 | 2.5 | 0.5 | 500 | 540 | 700(3) | 1.8-1.2(3) | 0.9 | 1.3 |
| 23 | PRL 3483 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE | 3.5 | 1.5 | 500 | 560 | 700 | 2.0-1.8( ) | 0.8 | 0.2 |
| 24 | PRL 3505(4) | 3 | 1 | 500 | 550 | 600(5) | 1.4-1.0(5) | 0.9 | 1.3 |
| 25 | PRL 3506 | 3 | -(6) | 475 | 550 | 700(3) | 1.6-1.0(3) | 2.5 | 4.0 |
| 26 | PRL 3507 | 6.5 | 4 | 500 | 540 | 700 | 3.5-3.3(1) | 1.4 | 0.1 |
| 27 | PRL 3508 | 2 | -(7) | 500 | 540 | 700 | 4.0 | 0.6 | 1.5 |
| 28 | PRL 3483 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE | 6 | 4 | 500 | 525 | 700 | 2.7-1.4(1) | 0.8 | 4.0 |
| 29 | PRL 3483 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE | 6 | 4 | 500 | 550 | 700 | 2.8-2.4(1) | 0.8 | 0.2 |

(1) DURING OPERATION AT INDICATED MAX. SYSTEM TEMPERATURE AND PRESSURE THE FLOW RATE DECREASED STEADILY FROM MAXIMUM TO MINIMUM VALUE INDICATED.
(2) THIS WAS THE MAXIMUM PRESSURE OBTAINABLE AT 500°F.
(3) PRESSURE INDICATED COULD NOT BE MAINTAINED; THE PRESSURE DROPPED FROM 700 P.S.I. TO 600 P.S.I. OVER A TEN MINUTE PERIOD. A CORRESPONDING DECREASE IN FLOW RATE WAS ALSO NOTED.
(4) THE FLUID FROM TEST 22 WAS USED FOR THIS TEST. SIX HUNDRED MILLILITERS OF NEW FLUID WERE ADDED AS MAKE UP.
(5) A STEADY SYSTEM PRESSURE INDICATED COULD NOT BE MAINTAINED; THE MAX. SYSTEM PRESSURE OBTAINABLE WAS 600 P.S.I. THE SYSTEM PRESSURE DROPPED STEADILY FROM 600 P.S.I. TO 400 P.S.I. OVER A 30 MINUTE PERIOD. AS THE SYSTEM PRESSURE DECREASED THE FLOW RATE DECREASED ALSO.
(6) THE TEST WAS TERMINATED WHEN THE SYSTEM TEMPERATURE WAS 490°F.
(7) THE SYSTEM TEMPERATURE HAD JUST REACHED 500°F. WHEN THE DRIVE SHAFT SEAL BEGAN TO LEAK AND THE TEST WAS TERMINATED.

Table 23

PARTS REPLACEMENT IN THE HIGH TEMPERATURE PUMP TEST STAND

PARTS REPLACED FOLLOWING THE TEST INDICATED

| TEST NO. | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PUMP | | | | | | | | | | | | | |
| BODY SEAL "O" RINGS(3) | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| VANES | - | - | 1(2) | - | 1(4) | 1(4) | - | - | 1(2) | 1(2) | 1(4) | - | 1(4) |
| CAM RING | - | - | 1(2) | - | 1(4) | 1(4) | - | - | 1(2) | 1(2) | 1(4) | - | 1(4) |
| VALVE PLATE | - | 1 | 1(2) | - | 1(4) | - | - | - | 1 | 1(2) | 1(4) | - | 1(4) |
| DRIVE SHAFT BEARINGS(2) | 1 | - | 2 | - | - | 2 | - | - | 2 | - | 2 | - | 2 |
| DRIVE SHAFT SEAL ASSEMBLY(3) | 1 | - | 1 | - | 1 | 1 | 1 | - | 1 | 1 | 1 | 1 | 1 |
| PUMP BODY(2) | - | - | - | - | - | - | - | - | 1 | 1 | - | - | 1 |
| DRIVE SHAFT(2) | - | - | - | - | - | - | - | - | 1 | - | - | - | - |
| SYSTEM | | | | | | | | | | | | | |
| RESERVOIR GASKETS(1) | - | - | 2 | - | - | - | - | 2 | - | - | - | - | - |
| FILTER CASE "O" RING(1) | 1 | - | 1 | - | - | - | 1 | - | 1 | 1 | - | 1 | 1 |

(1) THESE PARTS ARE REPLACED AT FREQUENT INTERVALS DUE TO CUMULATIVE DETERIORATION WHICH OCCURS DURING THE COURSE OF TESTING.
(2) PARTS WERE REPLACED BECAUSE THEY WERE NO LONGER SERVICEABLE, I.E., THEY HAD BECOME WORN AND WOULD NOT FUNCTION PROPERLY.
(3) THESE PARTS WERE USUALLY REPLACED AFTER EACH RUN. PREVIOUS EXPERIENCE INDICATED THAT THE MAXIMUM LIFE OF THE BODY SEAL "O" RINGS AND THE "O" RING SEAL IN THE DRIVE SHAFT SEAL ASSEMBLY IS TWO OR THREE RUNS AT 500°F.
(4) PARTS WERE REPLACED BECAUSE IT WAS DESIRED THAT THE SUBSEQUENT TEST BE MADE WITH NEW PARTS. THE PARTS REPLACED WERE IN GOOD CONDITION AND COULD HAVE BEEN REUSED.

Figure 15

SURFACE ROUGHNESS CHARACTERISTICS OF UNUSED VICKERS VANE PUMP PARTS

SURFACE ROUGHNESS DETERMINED WITH A BRUSH DEVELOPMENT CO. SURFACE ANALYZER, MODEL NO. BL-103

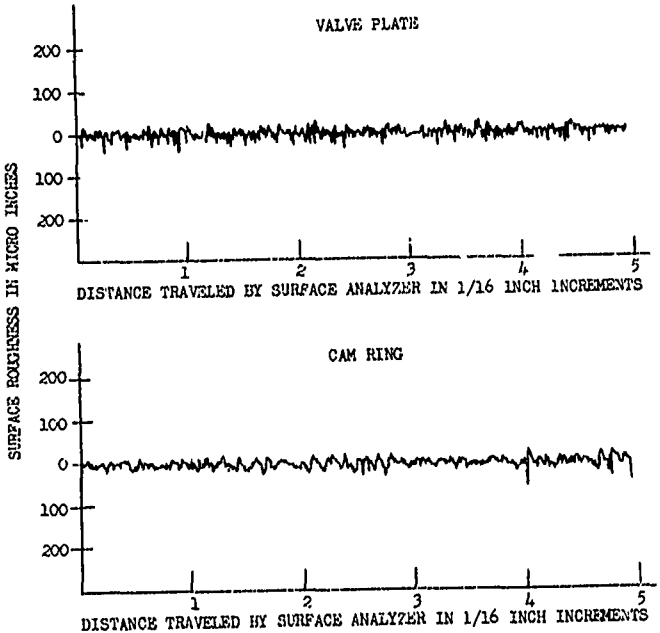


Figure 16

SURFACE ROUGHNESS CHARACTERISTICS OF VICKERS VANE PUMP PARTS AFTER 500°F. PUMP TEST WITH DI-2-ETHYLHEXYL SEBACATE CONTAINING TRICRESYL PHOSPHATE

SURFACE ROUGHNESS DETERMINED WITH A BRUSH DEVELOPMENT CO. SURFACE ANALYZER, MODEL NO. BL-103.
CAM RING AND VALVE PLATE TAKEN FROM HIGH TEMPERATURE PUMP TEST NO. 29.
DATA FOR TEST NO. 29 ARE SHOWN ON TABLE 22.

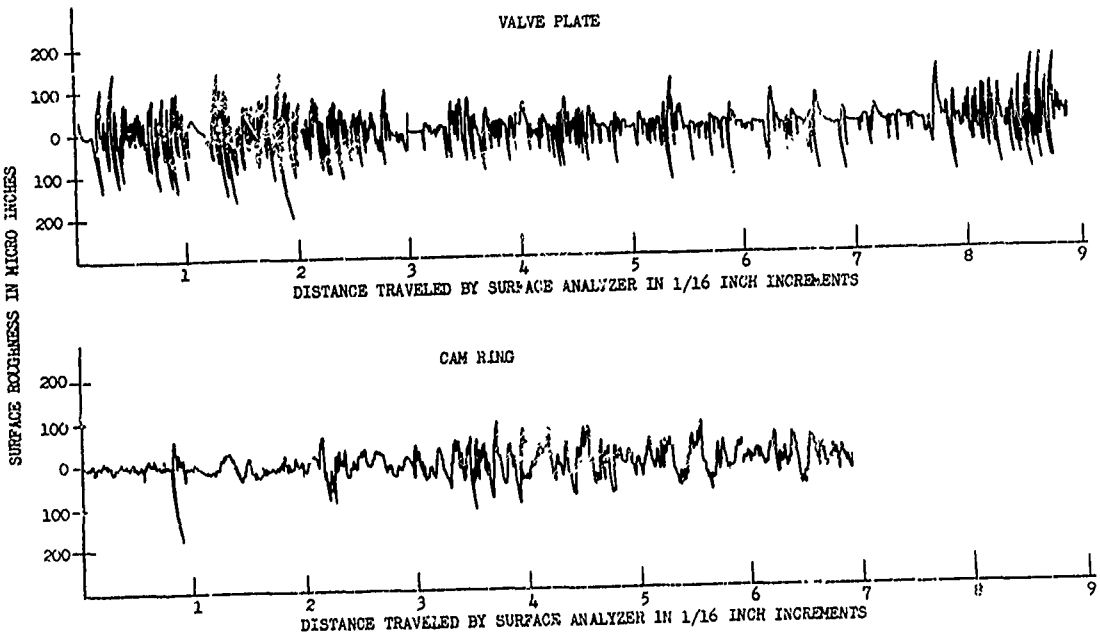


Figure 17

SURFACE ROUGHNESS CHARACTERISTICS OF VICKERS VANE PUMP PARTS AFTER 600°F. PUMP TEST WITH A MINERAL OIL BLEND

SURFACE ROUGHNESS DETERMINED WITH A BRUSH DEVELOPMENT CO. SURFACE ANALYZER, MODEL NO. SL-103. CAM RING AND VALVE PLATE TAKEN FROM HIGH TEMPERATURE PUMP TESTS NOS. 18, 19 AND 20. DATA FOR TESTS NOS. 18, 19 AND 20 ARE SHOWN ON TABLE 22.

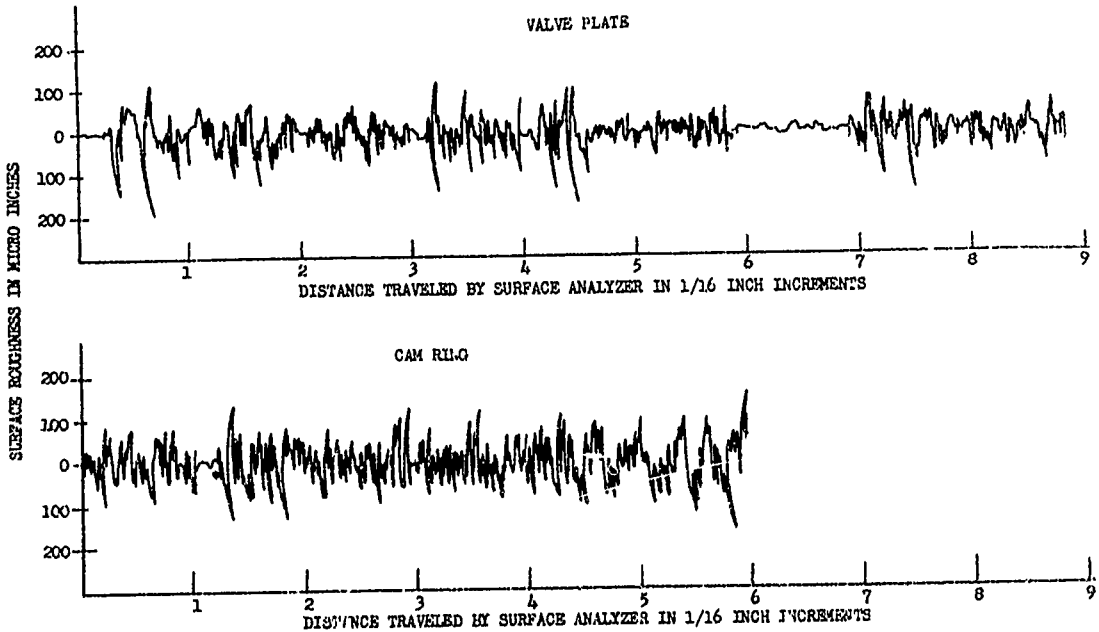


Figure 18

SURFACE ROUGHNESS CHARACTERISTICS OF CAM RING FROM VICKERS VANE PUMP AFTER 500°F. PUMP TEST WITH HERCOFLEX 600

SURFACE ROUGHNESS DETERMINED WITH A BRUSH DEVELOPMENT CO. SURFACE ANALYZER, MODEL NO. BL-103.
CAM RING TAKEN FROM HIGH TEMPERATURE PUMP TEST NO. 21.
DATA FOR TEST NO. 21 ARE SHOWN ON TABLE 22.

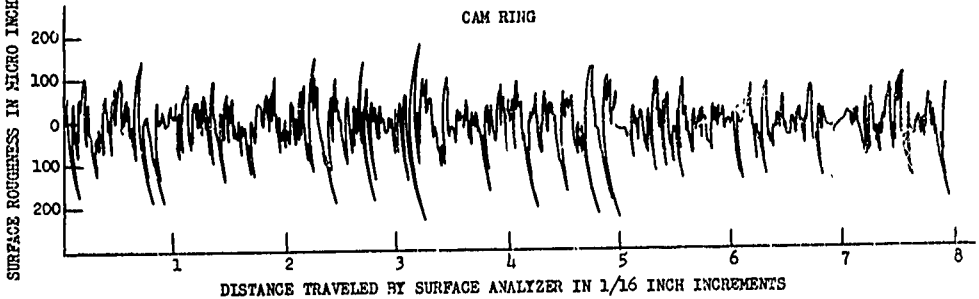


Figure 19
SURFACE ROUGHNESS CHARACTERISTICS OF VICKERS VANE PUMP PARTS AFTER 500°F.
PUMP TEST WITH UCON LUBRICANT LB-170X

SURFACE ROUGHNESS DETERMINED WITH A BRUSH DEVELOPMENT CO. SURFACE ANALYZER, MODEL NO. SL-103.
CAM RING AND VALVE PLATE TAKEN FROM HIGH TEMPERATURE PUMP TEST NO. 26.
DATA FOR TEST NO. 26 ARE SHOWN ON TABLE 22.

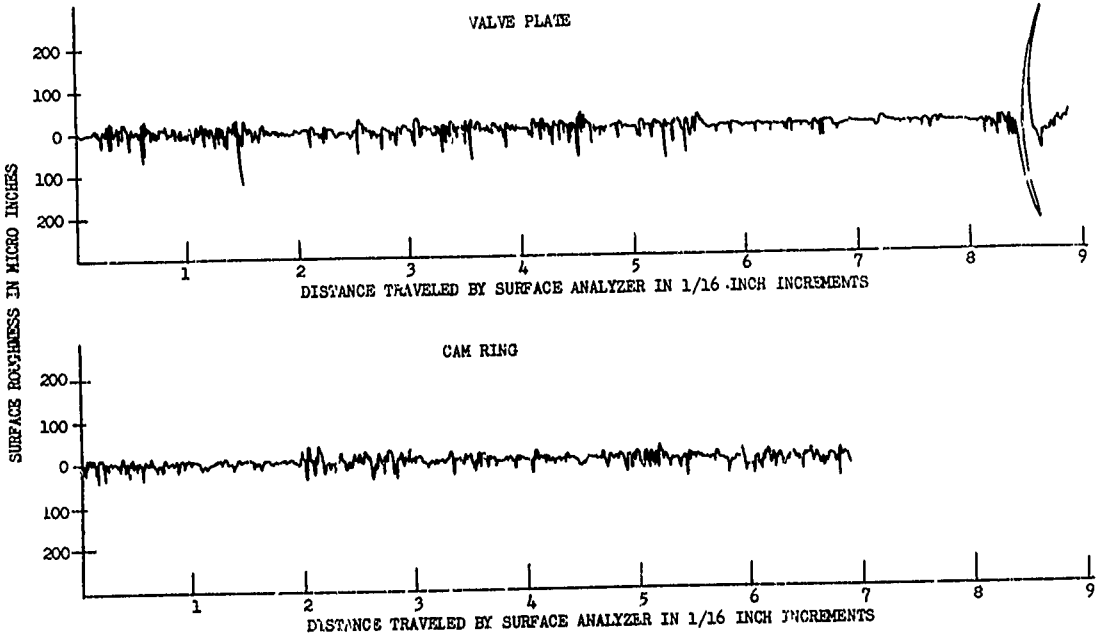


Figure 20

SURFACE ROUGHNESS CHARACTERISTICS OF CAM RING FROM VICKERS VANE PUMP AFTER 500°F. PUMP TEST WITH A SILICONE-ESTER BLEND (SD-17)

SURFACE ROUGHNESS DETERMINED WITH A BRUSH DEVELOPMENT CO. SURFACE ANALYZER, MODEL NO. BL-103.
CAM RING TAKEN FROM HIGH TEMPERATURE PUMP TESTS NOS. 16, 17 AND 18.
DATA FOR TESTS NOS. 16, 17 AND 18 ARE SHOWN ON TABLE 22.

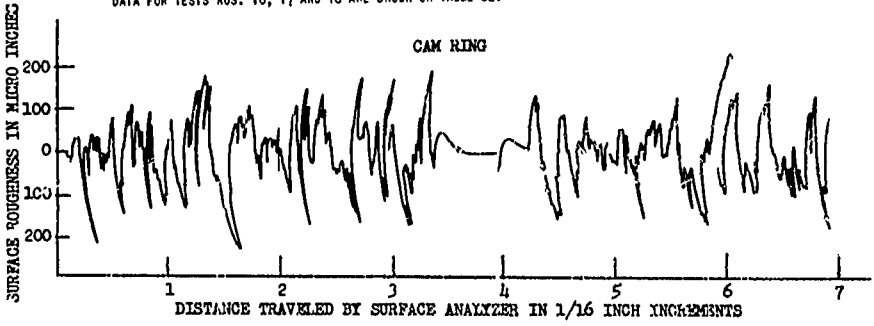


Figure 21.
SURFACE ROUGHNESS CHARACTERISTICS OF VALVE PLATE FROM VICKERS VANE PUMP
AFTER 500°F. PUMP TEST WITH A SILICONE-ESTER BLEND (SD-17)

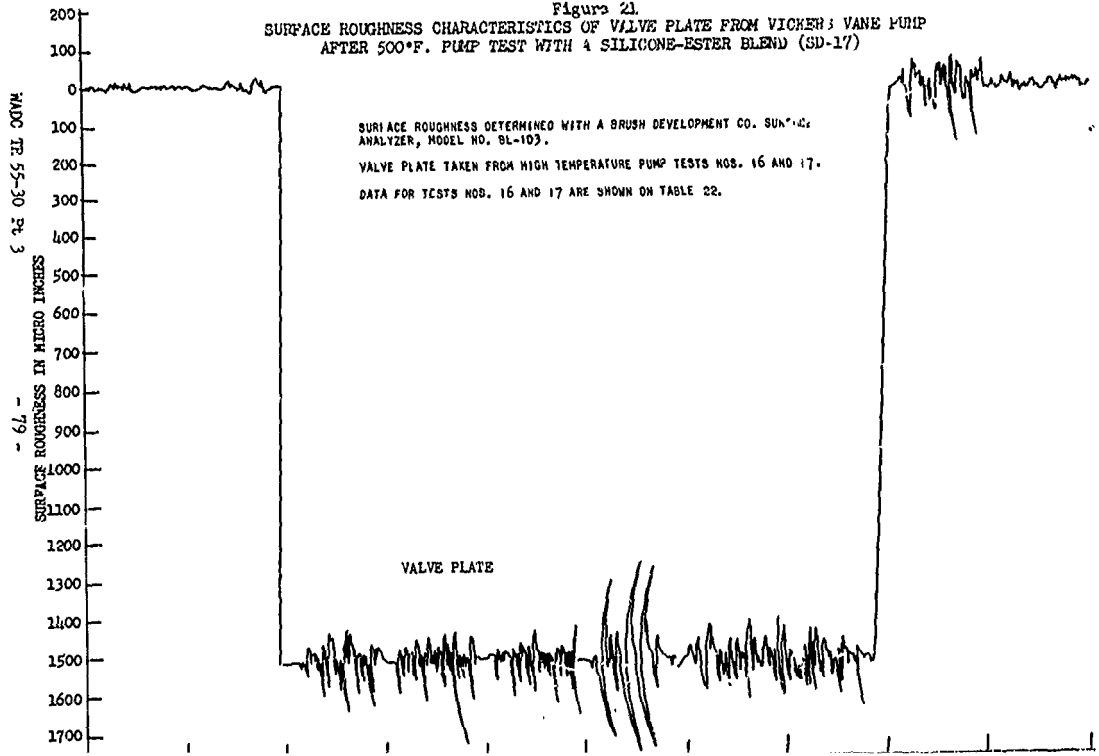


Figure 22
SURFACE ROUGHNESS CHARACTERISTICS OF VICKERS VANE PUMP PARTS AFTER 500°F. PUMP TEST
WITH SILICATE FLUID OS-45

SURFACE ROUGHNESS DETERMINED WITH A BRUSH DEVELOPMENT CO. SURFACE ANALYZER, MODEL NO. BL-103
CAM RING AND VALVE PLATE TAKEN FROM HIGH TEMPERATURE PUMP TESTS NOS. 22, 23 AND 24.
DATA FOR TESTS NOS. 22, 23 AND 24 ARE SHOWN ON TABLE 22.

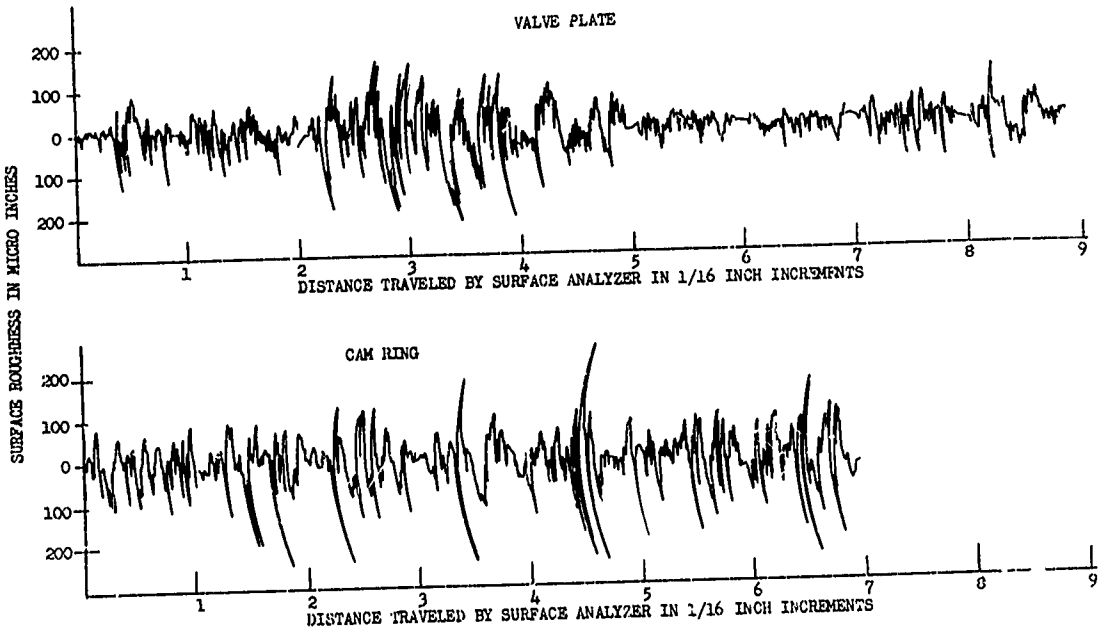


Figure 23
SURFACE ROUGHNESS CHARACTERISTICS OF VICKERS VANE PUMP PARTS AFTER 500°F. PUMP TEST WITH SILICATE FLUID MLO 8200

SURFACE ROUGHNESS DETERMINED WITH A BRUSH DEVELOPMENT CO. SURFACE ANALYZER, MODEL NO. BL-103
CAM RING AND VALVE PLATE TAKEN FROM HIGH TEMPERATURE PUMP TEST NO. 25.
DATA FOR TEST NO. 25 ARE SHOWN ON TABLE 22.

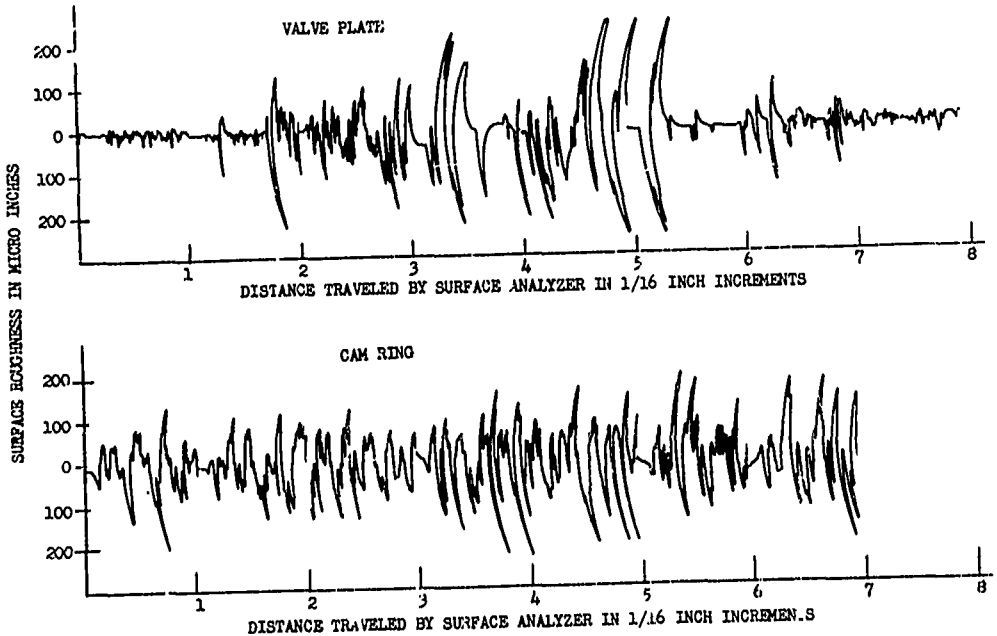


Table 24

SUMMARY OF TESTS CONDUCTED AT HIGH TEMPERATURES WITH A VICKERS MODEL VT4-100-10-75-10 VANE PUMP

TESTS MADE IN PRL HIGH TEMPERATURE PUMP TEST STAND. FLUID CHARGED = 1.5 GALLONS. TEST TEMPERATURE MEASURED AT THE PUMP INLET. MAXIMUM OIL TEMPERATURE MEASURED AT OUTLET FROM FLUIDIZED SOLIDS BED HEAT EXCHANGER.

TEST FLUIDS:

PRL 3371 = DI-2-ETHYLHEXYL SEBACATE
PRL 3483 = DI-2-ETHYLHEXYL SEBACATE
PRL 3497 = SILICONE TYPE 510 (D.C.)
PRL 3457 = ESSTIC 45 (MINERAL OIL)
PRL 3498 = HERCOFLEX 600
PRL 3505 = SILICATE FLUID OS-45
PRL 3506 = SILICATE FLUID MLO-8200
PRL 3507 = UCON LUBRICANT LB-170X
PRL 350 = AROCLOR 1248
PRL 3529 = 66.5 WT. % SILICONE 510 + 33.0 WT. % DI-2-ETHYLHEXYL SEBACATE + 0.5 WT. % PHENOTHIAZINE

| TEST NO. | TEST FLUID (COMPOSITION IN WT.%) | TIME IN OPERATION, HRS. TOTAL | AT 500°F. | ABOVE 400°F. | ABOVE 300°F. | TEST TEMP., °F. | MAX. OIL TEMP., °F. | FLUID PROPERTIES NEUT. NO. (MG. KOH/GM. OIL) ORIGINAL | FINAL | CENTISTOKE VISC. AT 100°F. ORIGINAL | FINAL |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 16 | PRL 3529 | 4 | 1.5 | 2.5 | 3.5 | 500 | 550 | 0.1 | 0.7 | 37.0 | 37.6 |
| 17 | PRL 3371 + 0.5 PHENOTHIAZINE + 5.0 TRICRESYL PHOSPHATE | 7 | 4 | 4.5 | 5 | 500 | 580 | 0.1 | 5.2 | 12.9 | 12.7 |
| 18 | PRL 3483 + 0.5 PHENOTHIAZINE + 5.0 TRICRESYL PHOSPHATE | 2 | 0.5 | 1 | 1.5 | 500 | 585 | 0.1 | 2.1 | 12.9 | 12.9 |
| 19 | PRL 3483 + 0.5 PHENOTHIAZINE | 6 | 4 | 4.5 | 5 | 500 | 525 | 0.0 | 2.0 | 12.7 | 12.7 |
| 20 | PRL 3457 + 5.0 POLYBUTENE B-12 + 1.0 TRICRESYL PHOSPHATE + 0.2 PHENYL- -NAPHTHYLAMINE | 5.5 | 4 | 4.5 | 5 | 570 | 600 | 0.3 | 1.5 | 168 | 119 |
| 21 | PRL 3498 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE | 6 | 4 | 4.5 | 5 | 500 | 540 | 0.1 | 4.0 | 24.6 | 24.7 |
| 22 | PRL 3505 | 2.5 | 0.5 | 1.0 | 1.5 | 500 | 540 | 0.3 | 0.9 | 12.3 | 10.7 |
| 23 | PRL 3483 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE | 3.5 | 1.5 | 2.0 | 2.5 | 500 | 560 | 0.0 | 1.5 | 12.7 | 12.7 |
| 24 | PRL 3505(1) | 3 | 1 | 1.5 | 2 | 500 | 550 | 0.9 | 0.9 | 11.0 | 10.8 |
| 25 | PRL 3506 | 3 | -(2) | 1 | 1.5 | 475 | 550 | 0.8 | 0.6 | 32.1 | 30.3 |
| 26 | PRL 3507 | 6.5 | 4 | 5 | 5.5 | 500 | 540 | 0.1 | 0.2 | 39.1 | 36.5 |
| 27 | PRL 3508 | 2 | -(3) | 0.5 | 1 | 500 | 540 | 0.1 | 0.1 | 40.3 | 40.4 |
| 28 | PRL 3483 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE | 6 | 4 | 4.5 | 5 | 500 | 525 | 0.0 | 3.5 | 12.7 | 12.9 |
| 29 | PRL 3483 + 0.5 PHENOTHIAZINE + 1.0 TRICRESYL PHOSPHATE | 6 | 4 | 4.5 | 5 | 500 | 550 | 0.0 | 3.8 | 12.7 | 13.0 |

(1) THE FLUID FROM TEST 22 WAS USED FOR THIS TEST. SIX HUNDRED MILLILITERS OF NEW FLUID WERE ADDED AS MAKE-UP.
(2) THE TEST WAS TERMINATED WHEN THE SYSTEM TEMPERATURE WAS 490°F.
(3) THE SYSTEM TEMPERATURE HAD JUST REACHED 500°F. WHEN THE DRIVE SHAFT SEAL BEGAN TO LEAK AND THE TEST WAS TERMINATED.

Current developments in aircraft place emphasis on higher speeds and, therefore, higher ambient temperatures which result in higher hydraulic system temperatures. The hydraulic system temperature problem is intensified in some cases by the proximity of hydraulic lines to the combustion chamber and to the exhaust of turbine engines. With current emphasis on higher hydraulic system temperatures, a study of some of the practical limitations, temperature-wise, of Spec. MIL-O-5606 hydraulic fluid is of particular interest. Many of the data pertinent to a high temperature study of Spec. MIL-O-5606 hydraulic fluid had been obtained and discussed in reports on contracts prior to Contract AF33(038)18193. These data along with current data are presented in this report.

Report PRL 6.3-Dec53 is included as Appendix A of this report. Copies of PRL 6.3-Dec53 were distributed to the Air Frame Manufacturers, Navy Bureau of Aeronautics, and Army Air Force at a Navy-Air Force-Industry Conference on High Temperature Hydraulic Systems and Fluids held in the Navy Building, Washington 25, D. C. on January 26 and 27.

G. CONCLUSIONS. A group of finished compositions and base stocks have been obtained for evaluation as high temperature hydraulic fluids. This group of materials were chosen as good current commercial examples of ten chemical classes. Evaluation of these materials will be placed on a quantitative basis wherever possible.

A suitable apparatus and test procedure has been employed for the measurement of viscosities in the 300° to 700°F. range. Most of the measured viscosities at 500°F. and essentially all the 700°F. viscosity values fall below the predicted viscosity based on the ASTM viscosity-temperature chart. Maximum deviations from the chart are shown by the silicones. This means that the effective ASTM slope or V.I. is poorer than predicted, thus requiring higher viscosities at low temperatures than predicted to give the desired viscosity level at 700°F. Very few of the materials evaluated give constant viscosity values at 700°F. The general trend of these viscosity values with time is a decrease over the 30 minute test interval. These changes are believed to be indicative of incipient thermal instability. Changes of a similar nature can be observed in the thermal stability tests.

Thermal stability tests have been conducted in glass and stainless steel equipment over the temperature range of 500° to 750°F. The temperature limitations of thermal stability can be summarized as follows:

1. Good thermal stability at 700° to 750°F., Aroclor 1248.
2. Good thermal stability at 700°F., methylphenyl silicone, G. E. Silicone No. 81406, and naphthenic mineral oils.
3. Good thermal stability at 600° to 700°F., Hercoflex 600 and silicate esters (mixed $C_6$-$C_8$ silicate and tetra-2-ethylhexyl silicate).
4. Good thermal stability at 500° to 600°F., di-2-ethylhexyl sebacate, tricresyl phosphate, Ucon Lubricant LB-170X, O.S. 45 (silicate-base fluid), MLO 8200 (silicate-

base fluid), Indopol (a low molecular weight Polybutene), SD-17 (a silicone-di-2-ethylhexyl sebacate blend), Alkazene 42 (ethyldibromobenzene), and Fluorolube-FS (a trifluoromonochloroethylene polymer).

Thermal stability data at 500° and 700°F. indicate that volatile decomposition products are formed to some extent by essentially all of the fluids evaluated in this temperature range. These data indicate that precautions for inflammability in hydraulic system design may have to be based on the volatile decomposition products rather than the initial inflammability properties of the fluid.

Preliminary thermal stability studies with a polyester containing all primary alcohol type ester linkages indicate a viscosity and chemical stability equivalent to di-2-ethylhexyl sebacate. The viscosity stability of this polyester is superior to that of Acryloid-HF or Polybutene polymeric thickeners. The thermal stability of viscous resins obtained from Pennsylvania crude oil appears to be good at 500°F.

The presence of tricresyl phosphate as an additive in esters appears to have some adverse effect on thermal stability properties. A similar trend toward decreased thermal stability is noted for esters in the presence of steel.

The oxidation and corrosion characteristics of the fluids evaluated at 500°F. with a low air rate (0.6 liters per hour) are satisfactory, in general. Dirtiness or sludge formation is probably the most critical item. The SD-17 composition shows excessive sludge formation. Tricresyl phosphate also shows a large amount of sludge formation. Methylphenyl silicone and Aroclor 1248 show no sludge formation. All of the remaining fluids show a trace ( 0.1 weight per cent) of sludge or dirt. A trace of dirtiness may, however, cause some difficulty in filter plugging and deposits in close fitting parts. These parts may have to be designed to function in the presence of trace dirtiness.

Trace dirtiness in ester oxidation may be caused by phenothiazine oxidation inhibitor. Increasing concentrations of phenothiazine improve the stable life of esters in 347°F. oxidation and corrosion tests and reduce oxidation rate in 500°F. tests. In all cases evaluated in the range of incipient oxidation at 347°F. or 500°F., uninhibited di-2-ethylhexyl sebacate appears to be cleaner on oxidation than a phenothiazine-inhibited di-2-ethylhexyl sebacate. The area of incipient oxidation appears to be the significant oxidation range for fluids used in sealed hydraulic systems.

All of the ester fluids containing tricresyl phosphate show increased sludging tendencies when evaluated in 500°F. accelerated oxidation and corrosion tests. The magnitude of sludge formation of an ester fluid due to the presence of one weight per cent tricresyl phosphate is considerably larger than the dirtiness tendencies from 0.5 weight per cent phenothiazine.

No appreciable increase in slide valve friction is noted when the slide valve is operated in a phenothiazine-inhibited di-2-ethylhexyl sebacate fluid under:

1. Thermal stability test conditions using a nitrogen blanket at 500°F.
2. Spec. MIL-L-7808 oxidation and corrosion test conditions within the stable life of the fluid.

Relatively severe oxidation of a phenothiazine-inhibited blend at 500°F. causes a large increase in slide valve friction. The increased friction appears to be due to a hard lacquer formation on the moving parts. It should be emphasized that for this study the slide valve was exercised in a static bath of fluid. No tests were conducted with actual fluid flow through the slide valve.

Copper-beryllium alloy does effect a reduction in the stable life of a well inhibited ester-base fluid. In this respect, copper-beryllium is similar to pure copper but slightly less severe. Copper-beryllium alloy is somewhat more stable to corrosion than pure copper in mineral oil and ester compositions with or without phosphorus-containing extreme-pressure lubricant additives. It is believed, therefore, that fluids which are satisfactory for use with copper at a given set of conditions will also be satisfactory with copper-beryllium.

The Vickers Model VT4-100-40-75-10 vane type pump gives satisfactory operation with mineral oils, esters, and polyglycol ethers at temperatures of at least 500°F. A successful mineral oil test at 600°F. has also been made. This pump has been operated satisfactorily at temperature levels of 500° and 600°F. with lubricants exhibiting viscosities in the range of 0.6 to 3.5 centistokes viscosity at the test temperature. The volumetric efficiency of the pump at elevated temperatures appears to be affected more by the lubricity than the viscosity level of the fluid over the range of viscosities evaluated thus far. Temperature per se has little effect on the volumetric efficiency of this pump. It should be emphasized that this Vickers vane type pump is essentially all steel with no fixed clearance parts involved in the pump mechanism to be adversely affected by differential expansion problems.

The fluidized solids bed type of heat exchanger affords efficient heating of the oil in the test cycle with a minimum of local overheating. Satisfactory operation of the fluidized solids bed heat exchanger is indicated by the equivalent of thermal effects for tests conducted at the same measured bulk oil temperature with static thermal stability tests under a nitrogen atmosphere in a glass test tube and in the PRL high temperature pump test stand.

The standard rubber seals used in the pump afford adequate sealing for the majority of the fluids for one complete test. In several cases, the running seal functioned satisfactorily for several tests. The mineral oil and Ucon LB-170X cause the rubber to become hard and very brittle. The rubber seals from the esters and silicate tests are considerably more pliable and flexible. The rubber seals from the

Aroclor 1248 test are soft and badly swollen. It is apparent from the rubber deterioration encountered that further Aroclor evaluations cannot be conducted in this test system unless rubber seals of adequate resistance to Aroclor are obtained.

The standard ball bearings used on the pump shaft give satisfactory performance. The failures noted are probably due to the elevated temperature rather than any lubricity deficiencies.

The wearing parts in the pumping mechanism, i.e. the cam ring, vanes, rotor, and valve plates appear to be sensitive to the lubricity level of the fluid. Tricresyl phosphate appears to be an effective lubricity additive in reducing wear in the Vickers vane pump parts at 500°F. The tricresyl phosphate susceptibility appears to vary at 500°F depending upon the nature of the fluid. The same phenomenon of varying tricresyl phosphate susceptibility has been noted at lower temperatures in the Shell four-ball wear tester. For example, tricresyl phosphate at 1.0 weight per cent concentration appears to be more effective in the di-2-ethylhexyl sebacate than in the mineral oil or Hercoflex 600 at 500°F. in the vane pump. These differences in lubricity between the mineral oil and ester fluids are not readily apparent at low (100° to 200°F.) temperatures in the Shell four-ball wear tester.

The lubricity level at 500°F. of SD-17 silicone-ester blend, O.S. 45 silicate composition, and silicate fluid MLO 8200 appears to be inadequate for satisfactory operation of the Vickers vane pumps. Di-2-ethylhexyl sebacate, Ucon LB-170X, Aroclor 1248 and blends of 1.0 weight per cent tricresyl phosphate in Hercoflex 600, a well refined mineral oil, and di-2-ethylhexyl sebacate appear to provide adequate lubricity for 500°F. pump operation. Ucon LB-170X and a phenothiazine-inhibited blend of di-2-ethylhexyl sebacate containing 1.0 weight per cent tricresyl phosphate appear to be the most effective as anti-wear lubricants. Tricresyl phosphate in a mineral oil or ester and diethyl acid phosphite in an ester function as chemical polishing agents to smooth up the vane-cam ring bearing area of a badly worn pump.

The property changes noted with the test fluids are encouraging. The maximum test fluid temperature is 540°F. in most cases. These tests are conducted in a system free to breath to the atmosphere through a 3/4 inch vent line in the reservoir. There is no evidence of excessive property changes indicative of severe oxidation from the test fluids even after 24 hours operation at the maximum temperature. Oxidative effects are of the same order of magnitude as the 20 hour oxidation and corrosion test at 500°F. using a 0.6 liter per hour air rate. The thermal effects in this series of tests were no greater than those obtained in static tests at the same bulk oil temperature in an all glass system under a nitrogen atmosphere. Visual inspection of the pump parts and the fluids following the high temperature tests indicate adequate fluid cleanliness. The ester shows somewhat less dirtiness than does the mineral oil in comparable tests.

In view of the increasing temperatures of hydraulic systems, the high temperature properties of Spec. MIL-O-5606 have been evaluated.

Perhaps the most severe limitation to the high temperature applications of this fluid is fluid volatility. The base stock component exhibits a normal boiling point of approximately 500°F. It is estimated that Spec. MIL-O-5606 fluid has sufficient viscosity and lubricity to lubricate hydraulic pumps at 400°F. Thermal stability and corrosion stability are good up to 500°F. Oxidation stability is typical of the mineral oils evaluated in this report. In general, these studies show that temperatures up to 500°F. can be tolerated by Spec. MIL-O-5606 under a variety of conditions. The formulation of specific limitations will require testing in actual hydraulic systems with the individual hydraulic system components.

H. FUTURE WORK. Thermal stability tests will be continued with particular emphasis on the effect of metals and additives on the stability of various classes of materials. The development of polymeric thickeners (V.I. improvers) with improved thermal stability will be continued. These thermal stability tests will be primarily in the range of 600° to 700°F.

Oxidation and corrosion tests at high temperatures will be continued. Preliminary oxidation and corrosion studies will be made at 600°F. The effect of additives and metals of construction on property changes noted for a small amount of oxygen assimilated will continue to be the main point of emphasis in this work.

Work with the high temperature pump stand will be continued. Tests will be conducted in the Vickers vane power steering pump at lower temperatures with silicate and silicone type compositions in an attempt to determine if there is a significant change in lubricity with temperature. Wear studies with the Shell four-ball wear tester will be conducted with the products of high temperature pump, oxidation, and thermal tests in an attempt to determine whether these high temperature tests result in lubricity changes which are also apparent in conventional low temperature tests.

Tests in the Vickers vane pump at temperatures of 600°F. and higher will be attempted. Studies will also be made with some of the effective anti-wear and E.P. additives studied by this laboratory in high temperature jet engine lubricant compositions.

## II. HIGH TEMPERATURE JET ENGINE OIL STUDIES

A. GENERAL. The desire for a jet engine oil suitable for use at bulk oil temperatures of 500° to 600°F. has been expressed by the personnel of the Wright Air Development Center in recent discussion with members of this Laboratory. The problems in jet engine oil development are somewhat more severe in several property requirements than in the case of high temperature hydraulic fluid requirements. In the jet engine oil requirements, the -65°F. tactical requirement of Spec. MIL-L-7808 is maintained. In addition, oxidation and corrosion requirements are more severe since current jet lubricant systems are not readily sealed, and the engine and bearing components contain more active metals than those currently proposed for hydraulic systems. Lubricity requirements of a jet engine oil are also more severe than for a hydraulic fluid. The use of engine oil to lubricate accessory drives in a turbo-jet and to lubricate the reduction gear box in a turbo-prop is responsible for the increased lubricity requirements.

Oxidation and corrosion stability and fluid lubricity will receive major emphasis in this study. Again, as in the case of the hydraulic fluid studies, all of the promising classes of high temperature lubricants will be carefully surveyed. It should be emphasized that high temperature stability will be studied for fluids and chemical compositions which do not now meet the low temperature fluidity and lubricity requirements proposed for these 500° to 600°F. jet engine oils. Emphasis will be placed on the quantitative evaluation of stability, i.e., the margin by which the test fluids pass or fail the various laboratory stability tests. Fundamental studies in high temperature fluid stability during the past two years at this laboratory have indicated that the quality margin enjoyed by synthetic lubricants over mineral oils decreases rapidly with temperature. For example, it has been possible to show an improvement of 10 to 20 fold in oxidation stability for dibasic acid esters over high quality mineral oils at a temperature of 350°F. The same dibasic acid ester fluid is less than twice as stable as high quality mineral oils under the same test conditions at 500°F. These data point to the need for mechanical and design changes of lubrication systems to go hand-in-hand with high temperature lubricant developments.

B. LUBRICITY STUDIES. Organo-phosphorus compounds have been evaluated as lubricity additives for synthetic jet engine lubricants. This evaluation has been discussed in reports PRL 5.4-Sep52 and PRL 5.8-Sep53. These data show that the presence of an acid hydrogen in an organo-phosphorus compound increases its effectiveness as a lubrication additive. That is, reduced concentrations of the acid phosphates or phosphites retain good anti-wear properties as well as improved lubricity characteristics in the extreme-pressure range.

Recently, a series of compounds containing an acid hydrogen along with other elements, such as chlorine or sulfur which are present in some conventional extreme-pressure additives, have been evaluated as lubricity additives in an ester-base and a mineral oil fluid. A list of

the compounds evaluated, along with wear and extreme-pressure values obtained for the additives in the synthetic fluid, are shown in Table 25. The wear values at 1, 10 and 40 kilograms load were obtained with the Shell four-ball wear tester at 75°C. (167°F.) with a test time of one hour. The seizure and weld values were determined with the Shell four-ball extreme-pressure lubricant tester at room temperature (70°-80°F.) with a test time of one minute. The bearing surfaces were steel-on-steel.

Table 25

WEAR AND LUBRICATION VALUES FOR SOME EXPERIMENTAL GEAR LUBRICANTS

TEST FLUID PRL 3379 - 9.0 WT.% ACRYLOID AF-25 + 0.5 WT.% PHENOTHIAZINE
1% DI-2-ETHYLHEXYL SEBACATE.

| ADDITIVE IN PRL 3379 TEST FLUID | CONC., WT.% | AVERAGE WEAR SCAR DIAMETER, MM. 1 KG. | 10 KG. | 40 KG. | APPROX. LOAD FOR INCIPIENT SEIZURE, KG. | PERMANENT WELDING, KG. |
|---|---|---|---|---|---|---|
| NONE | - | 0.37 | 0.64 | 0.91 | 50 | 120 |
| MERCAPTOACETIC ACID | 1.0 | 0.20 | 0.39 | 0.62 | 160 | 240 |
| | 0.5 | 0.19 | 0.26 | 0.54 | 140 | 220 |
| MERCAPTOBENZOIC ACID | 1.0 | 0.22 | 0.33 | 0.44 | 100 | 180 |
| | 0.5 | 0.20 | 0.40 | 0.44 | 80 | 180 |
| MERCAPTOSUCCINIC ACID(1) | 1.0 | 0.14 | 0.26 | 0.38 | 100 | 220 |
| | 0.1 | 0.15 | 0.23 | 0.43 | 80 | 200 |
| THIOLACETIC ACID | 1.0 | 0.34 | 0.35 | 0.41 | 80 | 180 |
| | 2.0 | 0.38 | 0.45 | 0.53 | 70 | 200 |
| TRICHLOROACETIC ACID | 1.0 | 0.56 | 0.71 | 0.66 | 100 | 240 |
| | 0.5 | 0.50 | 0.77 | 1.06 | 80 | 220 |
| TRICHLOROPHENOXYACETIC ACID | 1.0 | 0.43 | 0.67 | 1.04 | 80 | 120 |
| HEPTAFLUOROBUTYRIC ACID | 1.0 | 0.44 | 0.56 | 0.84 | 80 | 120 |
| DICHLOROBENZOIC ACID | 1.0 | 0.43 | 0.79 | 1.04 | 60 | 140 |
| DICHLOROPHENOL | 1.0 | 0.36 | 0.66 | 0.84 | 50 | 120 |
| TRICHLOROPHENOL | 1.0 | 0.31 | 0.57 | 0.91 | 50 | 120 |
| THIOCRESOL | 1.0 | 0.42 | 0.52 | 0.81 | 70 | 140 |

(1) SOLUBILITY OF THIS MATERIAL IN PRL 3379 IS LESS THAN 0.1 WEIGHT PER CENT.

The mercapto acids (mercaptoacetic, mercaptobenzoic and mercaptosuccinic acids) are the only compounds in Table 25 which are effective anti-wear additives under the conditions of evaluation in the wear tester. These compounds also show activity in the anti-seize and anti-weld regions in the extreme-pressure range. As might be expected, the chlorine-containing acid (trichloroacetic acid) is active in the extreme-pressure range and shows increased wear (chemical erosion) in the range of the wear tester.

It is interesting to note the difference in anti-wear activity shown by the thiolacetic acid and the mercaptoacetic acid. In the first acid, the sulfur is in the carboxyl group and is ineffective as an anti-wear agent in concentrations up to 2.0 weight per cent. In the latter case, the sulfur is in the alkyl portion of the molecule and is effective as an anti-wear additive in concentrations at least as low as 0.5 weight per cent.

This same series of compounds have been evaluated in a mineral oil-base hydraulic fluid. The test fluid (PRL 2574) is a Spec. 51-F-21 (Ord) hydraulic fluid prepared to contain no anti-wear additive. The values obtained are shown in Table 26.

Table 26

WEAR AND LUBRICATION VALUES FOR SOME EXPERIMENTAL GEAR LUBRICANTS

TEST FLUID PRL 2574 - A SPEC. 51-F-21 (ORD) HYDRAULIC FLUID PREPARED TO CONTAIN NO ANTI-WEAR ADDITIVE.

| ADDITIVE IN PRL 2574 TEST FLUID | CONC., WT.% | AVERAGE WEAR SCAR DIAMETER, MM. 1 KG. | 10 KG. | 40 KG. | APPROX. LOAD FOR INCIPIENT SEIZURE, KG. | INCIPIENT SCUFFING WELDING, KG. |
|---|---|---|---|---|---|---|
| NONE | - | 0.35 | 0.56 | 0.66 | 40 | 120 |
| MERCAPTOACETIC ACID(1) | 1.0 | 0.38 | 0.69 | 1.17 | 180 | 220 |
| | 0.5 | 0.33 | 0.67 | 1.17 | 100 | 220 |
| MERCAPTOBENZOIC ACID(2) | 1.0 | 0.24 | 0.30 | 0.48 | 70 | 160 |
| MERCAPTOSUCCINIC ACID(2) | 1.0 | 0.23 | 0.34 | 0.48 | 50 | 120 |
| THIOLACETIC ACID | 1.0 | 0.37 | 0.43 | 0.62 | 50 | 160 |
| TRICHLOROACETIC ACID | 1.0 | 0.53 | 0.76 | 0.82 | 160 | 360 |
| | 0.5 | 0.47 | 0.72 | 0.80 | 120 | 360 |
| TRICHLOROPHENOXYACETIC ACID(2) | 1.0 | 0.46 | 0.55 | 0.57 | 80 | 140 |
| HEPTAFLUOROBUTYRIC ACID | 1.0 | 0.42 | 0.51 | 0.66 | 60 | 120 |
| DICHLOROBENZOIC ACID(2) | 1.0 | 0.49 | 0.63 | 0.67 | 80 | 120 |
| DICHLOROPHENOL | 1.0 | 0.44 | 0.67 | 0.69 | 70 | 120 |
| TRICHLOROPHENOL | 1.0 | 0.49 | 0.66 | 0.71 | 70 | 120 |
| THIOCRESOL | 1.0 | 0.49 | 0.57 | 0.63 | 50 | 120 |

(1) SOLUBILITY OF THIS MATERIAL IN PRL 2574 IS BETWEEN 0.5 AND 1.0 WEIGHT PER CENT.
(2) SOLUBILITY OF THIS MATERIAL IN PRL 2574 IS LESS THAN 1.0 WEIGHT PER CENT.

The same general trends of wear behavior are noted with the mineral oil fluid as those previously noted for the synthetic fluid. That is, the mercapto acids are the only materials offering wear improvement in the wear tester and the trichloroacetic acid is active in the extreme-pressure range. There are several differences between the synthetic and the mineral oil fluids. The mercapto acids are less soluble in the mineral oil fluid. The mercaptoacetic acid, while it is active in the extreme-pressure range, shows no improvement in the wear range. Mercaptobenzoic and mercaptosuccinic acids show improvement in the wear range but no appreciable activity in the extreme-pressure range. In the synthetic fluid, the three mercapto acids show activity in both the wear and the extreme-pressure ranges.

It has been pointed out previously that some materials, such as sulfonate rust inhibitors, have a tendency to nullify the anti-wear improvement imparted to various fluids by tricresyl phosphate. One of the compounds in the current evaluation has been tested in conjunction with tricresyl phosphate in a synthetic fluid (di-2-ethylhexyl sebacate) and in a mineral oil (Voltesso 36). The values determined for these fluids are shown in Table 27.

Table 27

EFFECT OF TRICHLOROACETIC ACID ON TRICRESYL PHOSPHATE SUSCEPTIBILITY

| Test Fluid (Composition in Wt.%) | Ave. Wear Scar Diam., mm. Steel-on-Steel Surfaces 1 Kg. | 10 Kg. | 40 Kg. |
|---|---|---|---|
| Di-2-Ethylhexyl Sebacate | 0.34 | 0.56 | 0.69 |
| + 1.0 Tricresyl Phosphate | 0.15 | 0.26 | 0.40 |
| + 1.0 Trichloroacetic Acid | 0.66 | 0.91 | 0.84 |
| + 1.0 Tricresyl Phosphate + 1.0 Trichloroacetic Acid | 0.63 | 0.84 | 0.97 |
| Voltesso 36 (Naphthenic Mineral Oil) | 0.29 | 0.64 | 0.72 |
| + 1.0 Tricresyl Phosphate | 0.14 | 0.22 | 0.47 |
| + 1.0 Trichloroacetic Acid | 0.37 | 0.70 | 0.93 |
| + 1.0 Tricresyl Phosphate + 1.0 Trichloroacetic Acid | 0.45 | 0.61 | 0.75 |

Trichloroacetic acid is one of the more active of the compounds tested, as evidenced by the increased wear values in the wear tester. That is, this material probably gains its load carrying ability in the extreme-pressure range by means of chemical erosion at the bearing surfaces. The data in the above table indicate that when both tricresyl phosphate and trichloroacetic acid are present in either the ester or the mineral oil, the wear characteristics of the trichloroacetic acid completely dominate. The effect of the tricresyl phosphate is lost entirely.

Oxidation and corrosion tests at 347°F. for 72 hours have been conducted with 0.5 weight per cent concentrations of mercaptoacetic, mercaptobenzoic, and trichloroacetic acids in the mineral oil fluid. The results of these tests are shown on Table 28. Values for a similar test with 0.5 weight per cent dimethyl acid phosphite in the synthetic fluid are included for comparison.

These tests indicate that all of these materials are corrosive to copper under the test conditions. The trichloroacetic acid is corrosive to magnesium in both the synthetic and the mineral oil fluids. The mercaptobenzoic acid is corrosive to steel. Only the test with trichloroacetic acid in the mineral oil blend (PRL 2574) appears to have exceeded the stable life of the test fluid.

1. Effect of Storage Stability on Lubricity. Data have been presented in reports PRL 5.4-Sep52 and PRL 5.8-Sep53 to indicate that measurable changes occur in neutralization number, lubricity, and oxidation and corrosion stability of synthetic ester-base lubricants containing alkyl acid phosphites and phosphates as lubricity additives under normal storage in stoppered glass bottles at room temperature (70° to 80°F.). These synthetic lubricant compositions show an increase in neutralization number with storage time. Wear data for a synthetic lubricant containing an alkyl acid phosphate (Ortholeum 162) shows a decrease in lubricity

Table 28

OXIDATION ON CORROSION PROPERTIES OF SEVERAL EXPERIMENTAL GEAR LUBRICANTS

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 = 10 ± 1 LITERS PER HOUR;
CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.
TEST FLUID: PRL 3379 = 9.0 WT.% ACRYLOID HF-25 + 0.5 WT.% PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE
PRL 2574 = A SPEC. 51-F-21 MINERAL OIL FLUID WITHOUT AN ANTI-WEAR ADDITIVE.

| LUBRICITY ADDITIVE, WT.% | 0.5 MERCAPTOACETIC ACID | | 0.5 TRICHLOROACETIC ACID | | 0.5 MERCAPTO-BENZOIC ACID | 0.5 DIMETHYL ACID PHOSPHITE |
|---|---|---|---|---|---|---|
| TEST FLUID | PRL 3379 | PRL 2574 | PRL 3379 | PRL 2574 | PRL 3379 | PRL 3379 |
| FLUID LOSS, WT.% | 6 | 4 | 5 | 4 | 3 | 3 |
| % CHANGE IN CENTISTOKE VISCOSITY | | | | | | |
| AT 130°F. | +33 | +2 | +45 | +334 | +33 | +13 |
| AT 0°F. | +17 | +25 | +27 | +1840 | +12 | +17 |
| NEUT NO. (MG. KOH/GM. OIL) | | | | | | |
| ORIGINAL | 2.8 | 2.4 | 2.4 | 1.9 | 2.5 | 0.6 |
| FINAL | 3.9 | 2.6 | 3.5 | 13.0 | 3.0 | 6.6 |
| A.S.T.M. UNION COLOR | | | | | | |
| ORIGINAL | 2 | 2 | 2 | 2 | 2 | 2 |
| FINAL | >8 | >8 | >8 | >8 | >8 | >8 |
| WT.% INSOLUBLE MATERIAL | 0.1 | 0.1 | 0.1 | 0.8 | 0.2 | 0.3 |
| FINAL CATALYST CONDITION | | | | | | |
| APPEARANCE | | | | | | |
| COPPER | CORRODED | CORRODED | CORRODED | CORRODED | CORRODED | COATED |
| STEEL | DULL | DULL | DULL | CORRODED | CORRODED | COATED |
| ALUMINUM | DULL | DULL | DULL | DULL | DULL | COATED |
| MAGNESIUM | DULL | DULL | CORRODED | CORRODED | DULL | COATED |
| WT. LOSS (MG./SQ. CM.) | | | | | | |
| COPPER | 11.20 | 7.50 | 3.76 | 0.32 | 3.02 | +0.[illegible] |
| STEEL | +0.03 | +0.05 | 0.11 | 0.24 | 8.27 | +0.77 |
| ALUMINUM | +0.02 | +0.02 | 0.05 | 0.00 | 0.00 | +0.37 |
| MAGNESIUM | +0.02 | +0.02 | 1.98 | 32.60 | +0.04 | +0.61 |

with storage. Under the same storage conditions all of the compositions containing alkyl acid phosphites show increases in lubricity with storage The effect of storage on oxidation and corrosion will be discussed in a subsequent section of this report.

This study of storage stability has been broadened to include the effect of room temperature storage of the alkyl acid phosphite additives alone and in Spec. MIL-L-7808 type lubricants which contain tricresyl phosphate as a lubricity additive. Neutralization number measurements as a function of storage time on the synthetic lubricant compositions reported in PRL 5.8-Sep53 have been continued. These data for gear lubes containing acid phosphates are shown on Table 29. Data for gear lubes containing alkyl acid phosphites are shown on Table 30. Similar data for two commercial Spec. MIL-L-7808 type fluids are shown in Table 31. The ester-base fluids containing an alkyl acid phosphate, alkyl acid phosphite, or a trialkyl phosphite, all show a tendency toward an increase in neutralization number with continued storage.

Some of the ester-base lubricants containing tricresyl phosphat show an increase in neutralization number with storage while others show good storage stability. The samples showing relatively poor storage stability are both Spec. MIL-L-7808 type lubricants supplied by different commercial suppliers. The three samples which show good storage stabilit in the presence of 5.0 weight per cent tricresyl phosphate are Spec. MIL-L-7808 samples prepared by this Laboratory. The reasons for these differences in neutralization number change on storage are not readily apparent.

As indicated previously this trend toward increased neutralization number is believed to be due to hydrolysis of the organo-phosphorus lubricity additive and the fact that many alkyl and aryl acid phosphates and phosphites appear to exert a catalytic effect on the splitting of the ester linkage in the dibasic acid ester. It can be noted from these data that the storage stability of mineral oils containing alkyl acid phosphates and phosphites is superior to that of a dibasic acid ester containing the same phosphorus type additive.

Some additional lubricity tests have been conducted on storage samples containing tricresyl phosphate and tri-2-ethylhexyl phosphite, and on new samples of ester blends prepared from alkyl acid phosphites which have been stored neat. These data are shown on Table 32. In the case of the alkyl acid phosphites, original and storage samples of the completed formulations are shown as a basis of comparison. These lubricity data have been obtained with the Shell four-ball E.P. lubricant tester.

The Spec. MIL-L-7808 type formulations which show an increase neutralization number on storage also show a substantial increase in the point of incipient seizure which is evidence of improved lubricity. The Spec. MIL-L-7808 type formulations which exhibit no neutralization number increase on storage show essentially no change in lubricity. The formulation containing tri-2-ethylhexyl phosphite shows an increase in lubricity after storage. In the lubricity tests conducted after storage, all

of the ester-base compositions containing phosphorus additives showing increased neutralization number also show increased lubricity in the four-ball E.P. lubricant tester with the exception of those blends containing alkyl acid phosphates. These latter blends show a decrease in lubricity and increasing neutralization number with storage (see report PRL 5.8-Sep53).

Several alkyl acid phosphite additives have been stored in glass bottles neat. These stored additives have been used to prepare fresh ester-base formulations. The lubricity values of these fresh formulations, using the additives stored neat, show substantial lubricity improvements over the original blends and smaller improvements over the stored blends. These data would tend to indicate that the improvement in lubricity with storage is due to chemical changes in the additive, itself. That is, the presence of the ester base stock during storage is not necessary for the improved lubricity. It appears that the presence of the ester in the complete formulation may limit somewhat the lubricity improvement during storage. This seems reasonable on the basis of previous data. The increase in neutralization number in the finished composition is believed to be a result of the combined hydrolysis of the phosphorus additive and a splitting of the ester to an organic acid due to the catalytic effect of the phosphorus additive. The competition of the polar organic acid with the acid phosphate or phosphite for surface adsorption is believed to be at least partially responsible for the fact that the storage of the additive neat gives better lubricity than the storage of the additive in a finished ester-base composition.

Of the alkyl acid phosphite additives evaluated, those prepared from secondary alcohols show the best storage stability, i.e. the least property change with storage. Secondary alkyl acid phosphites will continue to be of interest in compounding gear lubricants for this reason. The change in neutralization number with storage stability for some Spec. MIL-L-7808 type fluids and not for others of the same type deserves further study.

2. Wear Tester Studies With M-10 Tool Steel and Heat Stabilized 52-100 Steel Balls. Samples of two different types of steel ball bearings have been obtained from the SKF Industries. These bearings are prepared from (1) M-10 tool steel and (2) heat stabilized 52-100 steel. These steels are typical of bearing surfaces found in various high temperature applications involving hydraulic fluids and lubricants.

The wear behavior of these bearing materials in the Shell four-ball wear tester has been investigated. The test temperature is 75°C. (167°F.) and test time is one hour. Both mineral oil and ester type test fluids have been used. The behavior of tricresyl phosphate as an anti-wear additive has been determined. The test fluids used are shown in Table 33.

Table 29

EFFECT OF STORAGE TIME ON THE NEUTRALIZATION NUMBER OF SOME BLENDS CONTAINING VARIOUS ACID PHOSPHATES

ALL FLUIDS EXCEPT THOSE NOTED STORED IN STOPPERED GLASS BOTTLES AT ROOM TEMPERATURE.

| PRL NO. | TEST FLUID (COMPOSITIONS IN WT.%) | NEUTRALIZATION NUMBER, MG. KOH/GM. FLUID | | | | | | | | | THEORETICAL VALUE IF PHOSPHORUS-CONTAINING ADDITIVE IS COMPLETELY HYDROLYZED(4) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | ORIG. | AFTER INDICATED STORAGE TIME, MONTHS | | | | | | | | |
| | | | 1 | 3 | 5 | 9 | 13 | 15 | 17 | 27 | |
| 3313A | 9.0 ACRYLOID HF-25 + 5.0 TRICRESYL PHOSPHATE + 0.5 ORTHOLEUM 162(1) + 0.5 PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE | 1.6 | - | - | - | 4.7 | 4.9 | - | 5.1 | 5.8 | 26.6 |
| 3313 | COMMERCIAL BATCH 6931 | 4.2(3) | 5.0 | 5.2 | - | - | - | - | 6.9 | 7.7 | 26.6 |
| 3313(2) | COMMERCIAL BATCH 6931 | 4.2(3) | - | - | - | - | - | - | 7.2 | 7.4 | 26.6 |
| 3312 | COMMERCIAL BATCH 6980 (COMPOSITION SAME AS PRL 3313 EXCEPT PRL 3312 CONTAINS NO ACRYLOID POLYMER) | 3.0(3) | 4.1 | 3.1 | - | - | - | - | 3.6 | 3.4 | 26.6 |
| 3312(2) | COMMERCIAL BATCH 6980 | 3.0(3) | - | - | - | - | - | - | 5.1 | 5.5 | 26.6 |
| 3379 | 9.0 ACRYLOID HF-25 + 0.5 PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE | 0.1 | - | - | - | - | - | - | - | 0.1 | 0.0 |
| - | 0.5 MONO-DILAURYL ACID ORTHOPHOSPHATE IN PRL 3379 | 2.0 | 3.5 | - | - | 7.9 | - | 12.0 | - | 12.3 | 2.0 |
| - | 0.5 DI-2-ETHYLHEXYL ACID PYROPHOSPHATE IN PRL 3379 | 2.8 | 5.1 | - | - | - | - | 8.0 | - | 9.5 | 2.9 |
| - | 0.5 ETHYL ACID PHOSPHATE IN PRL 3379 | 3.1 | 4.8 | 6.1 | 6.7 | 7.2 | 7.0 | 7.5 | - | - | 7.2 |
| - | 0.5 AMYL ACID PHOSPHATE IN PRL 3379 | 3.4 | 5.7 | 7.7 | 8.6 | 8.9 | 10.0 | 12.3 | - | - | 5.8 |
| - | 0.5 DIETHYL ACID PHOSPHATE IN PRL 3379 | 1.6 | 4.2 | 6.1 | 6.9 | 7.3 | 8.1 | 10.1 | - | - | 6.1 |
| - | 0.5 DIETHYL ACID PHOSPHATE IN PRL 3405 | 1.7 | 3.7 | 5.5 | 6.4 | 7.2 | 7.8 | 11.0 | - | - | 6.1 |
| 3405 | 9.0 ACRYLOID HF 25 + 1.0 PARANOX 141 IN DI-2-ETHYLHEXYL SEBACATE | 0.1 | - | - | - | - | - | - | - | 0.1 | 0.0 |
| - | 0.5 MONOLAURYL ACID ORTHOPHOSPHATE IN PRL 3405 | 2.2 | - | - | 4.2 | 6.9 | - | - | 8.8 | - | 3.2 |
| 3057 | HERCOFLEX 600 | | | | | | | | | | |
| - | 0.5 ORTHOLEUM 162(1) + 0.5 PHENOTHIAZINE IN PRL 3057 | 2.2 | - | - | - | - | - | - | 1.7 | 5.9 | 2.6 |
| 3134 | VOLTESSO 36 | | | | | | | | | | |
| - | 0.5 MONO-DILAURYL ACID ORTHOPHOSPHATE IN PRL 3134 | 1.2 | - | - | - | 1.2 | 1.0 | - | - | - | 2.0 |

(1) COMMERCIAL ADDITIVE BELIEVED TO BE A MIXTURE OF MONO- AND DI-LAURYL ACID PHOSPHATES.
(2) THIS SAMPLE STORED IN A CLOSED METAL FIVE GALLON DRUM AT ROOM TEMPERATURE.
(3) THIS IS THE NEUTRALIZATION NUMBER SHOWN BY FLUID WHEN IT WAS RECEIVED BY THIS LABORATORY.
(4) THIS VALUE IS THE THEORETICAL NEUTRALIZATION NUMBER OF THE BLEND IF ONLY THE PHOSPHORUS-CONTAINING ADDITIVE WERE HYDROLYZED.

Table 30

EFFECT OF STORAGE TIME ON THE NEUTRALIZATION NUMBER OF SOME BLENDS CONTAINING VARIOUS ACID PHOSPHITES

ALL FLUIDS STORED IN STOPPERED GLASS BOTTLES AT ROOM TEMPERATURE.

| PRL NO. | TEST FLUID (COMPOSITIONS IN WT.%) | NEUTRALIZATION NUMBER, MG. KOH/GM. FLUID: ORIG. | AFTER INDICATED STORAGE TIME, MONTHS: 1 | 3 | 5 | 8 | 10 | 13 | 20 | 25 | THEORETICAL VALUE IF PHOSPHORUS-CONTAINING ADDITIVE IS COMPLETELY HYDROLYZED(3) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3393 | 9.0 ACRYLOID HF-25 IN DI-2-ETHYLHEXYL SEBACATE | 0.1 | - | - | - | - | - | - | - | 0.1 | |
| - | 0.5 DIMETHYL ACID PHOSPHITE IN PRL 3393 | 0.4 | 6.5 | - | - | 14.9 | - | 16.4 | - | 17.3 | 7.6 |
| - | 0.5 DIETHYL ACID PHOSPHITE IN PRL 3393 | 0.2 | 3.0 | - | - | 12.2 | - | 15.3 | - | 14.0 | 6.1 |
| - | 0.5 DIBUTYL ACID PHOSPHITE IN PRL 3393 | 0.2 | 2.0 | - | - | 9.9 | - | 14.[illegible] | - | 16.7 | 4.3 |
| - | 0.5 DI-2-ETHYLHEXYL ACID PHOSPHITE IN PRL 3393 | 0.2 | 1.2 | - | - | 6.7 | - | 7.1 | - | - | 2.8 |
| - | 0.5 TRI-2-ETHYLHEXYL PHOSPHITE IN PRL 3393 | 0.1 | - | - | 0.1 | - | 1.4 | - | 3.4 | - | 2.0 |
| 3379 | 9.0 ACRYLOID HF-25 + 0.5 PHENOTHIAZINE IN DI-2-ETHYL HEXYL SEBACATE | 0.1 | - | - | - | - | - | - | - | 0.1 | |
| - | 0.5 DIMETHYL ACID PHOSPHITE IN PRL 3379 | 0.4 | 3.7 | 4.3 | - | - | 13.6 | 10.1 | - | 20.0 | 7.6 |
| - | 0.5 DIETHYL ACID PHOSPHITE IN PRL 3379 | 0.2 | 2.3 | 4.3 | - | - | 6.7 | 8.2 | - | 10.0 | 6.1 |
| - | 0.5 DIBUTYL ACID PHOSPHITE(1) IN PRL 3379 | 0.1 | - | - | - | - | 10.6 | 12.9 | - | 13.9 | 4.3 |
| - | 0.5 DIBUTYL ACID PHOSPHITE(2) IN PRL 3379 | 0.1 | - | - | 1.4 | - | 1.6 | - | - | 2.0 | 4.3 |
| - | 0.5 DI-2-ETHYLHEXYL ACID PHOSPHITE IN PRL 3379 | 0.1 | 0.1 | - | - | - | 5.7 | 10.3 | - | 11.9 | 2.8 |
| - | 0.5 TRI-2-ETHYLHEXYL PHOSPHITE IN PRL 3379 | 0.1 | 0.1 | - | - | - | 0.6 | 3.1 | - | 7.2 | 2.0 |
| - | 0.5 DIISOPROPYL ACID PHOSPHITE IN PRL 3379 | 0.2 | - | 0.9 | 1.4 | 1.9 | 2.0 | - | 2.4 | - | 5.0 |
| - | 0.5 BIS (2-OCTYL) ACID PHOSPHITE IN PRL 3379 | 0.5 | - | 1.7 | 2.0 | 2.0 | 2.0 | - | 2.3 | - | 2.7 |
| 3405 | 9.0 ACRYLOID HF-25 + 1.0 PARANOX 441 IN DI-2-ETHYLHEXYL SEBACATE | 0.1 | - | - | - | - | - | - | - | 0.1 | |
| - | 0.5 DIMETHYL ACID PHOSPHITE IN PRL 3405 | 0.4 | 1.2 | - | 10.7 | 16.9 | - | - | 19.4 | - | 7.6 |
| - | 0.5 DIETHYL ACID PHOSPHITE IN PRL 3405 | 0.2 | - | - | 3.1 | - | 6.0 | - | 17.1 | - | 6.1 |
| - | 0.5 DIBUTYL ACID PHOSPHITE IN PRL 3405 | 0.2 | - | - | 1.8 | 2.5 | - | - | 4.1 | - | 4.3 |
| - | 0.5 DI-2-ETHYLHEXYL ACID PHOSPHITE IN PRL 3405 | 0.2 | 0.4 | - | 3.3 | - | 9.1 | - | 13.6 | - | 2.8 |
| - | 0.5 TRI-2-ETHYLHEXYL PHOSPHITE IN PRL 3405 | 0.1 | - | - | 0.1 | - | 1.2 | - | 3.6 | - | 2.0 |
| 2054. | NECTON 55 (A NAPHTHENIC MINERAL OIL; 98 CSTKS. AT 100°F.) | | | | | | | | | | |
| - | 0.5 DIMETHYL ACID PHOSPHITE + 1.0 PARANOX 441 IN PRL 2054 | 0.2 | - | 0.6 | - | 0.4 | - | - | 0.8 | - | 7.6 |
| - | 0.5 DIBUTYL ACID PHOSPHITE + 1.0 PARANOX 441 IN PRL 2054 | 0.2 | - | 1.1 | - | 0.3 | - | - | 0.6 | - | 4.3 |

(1) OBTAINED FROM THE VICTOR CHEMICAL COMPANY.
(2) OBTAINED FROM THE MONSANTO CHEMICAL COMPANY.
(3) THIS VALUE IS THE THEORETICAL NEUTRALIZATION NUMBER OF THE BLEND IF ONLY THE PHOSPHORUS-CONTAINING ADDITIVE WERE HYDROLYZED.

Table 31

EFFECT OF STORAGE TIME ON THE NEUTRALIZATION NUMBER OF SOME SPEC. MIL-L-7808 TYPE FLUIDS

ALL FLUIDS EXCEPT AS NOTED STORED IN STOPPERED GLASS BOTTLES AT ROOM TEMPERATURE

| PRL NO. | TEST FLUID (COMPOSITIONS IN WT.%) | STORAGE TIME, MONTHS | NEUT. NO., MG. KOH/GM. FLUID ORIG. | FINAL |
|---|---|---|---|---|
| 3539 | SPEC. MIL-L-7808 TYPE GEAR LUBRICANT (COMMERCIALLY PREPARED) | 42(1) | 0.2(2) | 1.3 |
| 3540(3) | SPEC. MIL-L-7808 TYPE GEAR LUBRICANT (COMMERCIALLY PREPARED) | 12(1) | 0.3(2) | 2.8 |
| 3076 | 3.9 ACRYLOID NF-25 + 0.5 PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE | 30 | 0.1 | 0.1 |
| - | 5.0 TRICRESYL PHOSPHATE (BATCH S-1018) IN PRL 3076 | 40 | 0.1 | 0.1 |
| - | 5.0 TRICRESYL PHOSPHATE IN PRL 3076 | 40 | 0.1 | 0.1 |
| - | 3.9 ACRYLOID NF-25 + 0.4 PARANOX 441 + 5.0 TRICRESYL PHOSPHATE IN DI-2-ETHYLHEXYL SEBACATE | 40 | 0.1 | 0.1 |

(1) STORAGE TIME IS THE TIME THESE COMMERCIAL SAMPLES HAVE BEEN STORED AT THIS LABORATORY.
(2) NEUTRALIZATION NUMBER IS THAT SHOWN BY FLUID WHEN RECEIVED AT THIS LABORATORY.
(3) THIS SAMPLE WAS STORED IN METAL CAN.

Table 32

EFFECT OF STORAGE TIME ON THE LUBRICITY BEHAVIOR OF SOME SPEC. MIL-L-7808 TYPE GEAR LUBRICANTS

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;
TEST SPEED = 1750 R.P.M.; AND BEARING SURFACES ARE STEEL-ON-STEEL.
TEST FLUID PRL 3379 = AN ACRYLOID-DIESTER-PHENOTHIAZINE BLEND.

| PRL NO. | TEST FLUID (COMPOSITIONS IN WT.%) | NEUT. NO. MG. KOH/GM. FLUID | APPROX. LOAD FOR INCIPIENT SEIZURE, KG. | APPROX. LOAD FOR PERMANENT WELDING, KG. | AVERAGE WEAR SCAR DIAMETER, MM. STEEL-ON-STEEL BEARING SURFACES 60 KG. | 80 KG. | 100 KG. | 120 KG. | 140 KG. | 160 KG. | 180 KG. | 200 KG. | 220 KG. | 240 KG. | 260 KG. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3515(1) | 0.5 DIISOPROPYL ACID PHOSPHITE IN PRL 3379 | 0.2 | 110 | 160 | 0.39 | 0.46 | 0.43 | 2.62 | 2.84 | WELDED | | | | | |
| | AFTER 8 MONTHS STORAGE | 1.9 | 170 | 180 | - | - | - | 0.47 | 0.52 | 0.53 | WELDED | | | | |
| 3514(2) | 3.5 ACRYLOID HF-25 + 1.0 PARANOX 441 + 0.5 DIISOPROPYL ACID PHOSPHITE IN DI-2-ETHYL-HEXYL SEBACATE | 0.2 | 190 | 200 | - | - | - | - | - | 0.52 | 0.55 | WELDED | | | |
| -(3) | 0.5 DIMETHYL ACID PHOSPHITE IN PRL 3379 | 0.4 | 130 | 180 | 0.39 | 0.42 | 0.45 | 0.47 | 2.86 | 2.73 | WELDED | | | | |
| | AFTER 10 MONTHS STORAGE | 13.6 | 190 | >260 | - | - | - | - | - | - | 0.71 | 1.02 | 1.23 | 1.35 | 1.56 |
| -(3) | 0.5 DIMETHYL ACID PHOSPHITE IN PRL 3379 | 0.7 | 260 | 280 | - | - | 0.46 | - | 0.51 | - | 0.56 | - | 0.61 | - | 0.65 |
| -(1) | 0.5 TRI-2-ETHYLHEXYL PHOSPHITE IN PRL 3379 | 0.1 | 60 | 120 | 0.65 | 3.03 | 2.68 | WELDED | | | | | | | |
| | AFTER 20 MONTHS STORAGE | 3.4 | 140 | 180 | - | 0.42 | 0.44 | 0.47 | 0.74 | 2.99 | WELDED | | | | |
| 3539(4) | COMMERCIALLY PREPARED SPEC. MIL-L-7808 TYPE LUBRICANT | 0.2 | 70 | 120 | 0.37 | 2.29 | 2.92 | WELDED | | | | | | | |
| | AFTER 25 MONTHS STORAGE | - | 90 | 120 | 0.31 | 0.32 | 2.64 | WELDED | | | | | | | |
| | AFTER 41 MONTHS STORAGE | 1.3 | 110 | 120 | - | 0.43 | 0.45 | WELDED | | | | | | | |
| 3540(4) | COMMERCIALLY PREPARED SPEC. MIL-L-7808 TYPE LUBRICANT | 0.3 | 70 | 140 | 0.39 | 2.23 | 2.40 | 2.68 | WELDED | | | | | | |
| | AFTER 19 MONTHS STORAGE | 2.8 | 110 | 140 | - | 0.41 | 0.47 | 2.85 | WELDED | | | | | | |
| - | SPEC. MIL-L-7808 TYPE LUBRICANT PREPARED FROM STOCKS AVAILABLE AT THIS LABORATORY | 0.1 | 70 | 120 | 0.35 | 2.29 | 2.98 | WELDED | | | | | | | |
| | AFTER 41 MONTHS STORAGE | 0.1 | 80 | 120 | 0.40 | 0.69 | 2.94 | WELDED | | | | | | | |

(1) THIS BLEND WAS PREPARED WHEN THE PHOSPHITE ADDITIVE WAS OBTAINED BY THIS LABORATORY.
(2) THIS WAS A FRESHLY PREPARED BLEND. THE PHOSPHITE ADDITIVE HAD BEEN STORED AT THIS LABORATORY FOR 18 MONTHS.
(3) THIS WAS A FRESHLY PREPARED BLEND. THE PHOSPHITE ADDITIVE HAD BEEN STORED AT THIS LABORATORY FOR 22 MONTHS.
(4) THESE VALUES WERE DETERMINED WHEN THE FLUID WAS RECEIVED BY THIS LABORATORY.

Table 33

TEST FLUIDS UTILIZED IN WEAR TESTS WITH SPECIAL STEELS

| Designation | Type Fluid | Wt.% Tricresyl Phosphate |
|---|---|---|
| PRL 2574 | Mineral Oil | None |
| PRL 3078 | Mineral Oil | 1.0 |
| PRL 3371 | Ester | None |
| PRL 3490 | Ester | 1.0 |

The values obtained for these two steels along with those obtained under the same test conditions for the 52-100 E.P. type steel balls conventionally used as wear tester specimens are shown in Table 34.

Table 34

WEAR CHARACTERISTICS OF SPECIAL HIGH TEMPERATURE STEEL BALLS IN THE FOUR-BALL WEAR TESTER

Wear Tester Conditions Include: Test Time = 1 Hour; Test Temperature = 75°C.; Test Speed = 850 r.p.m.

| | | - - - - - Test Fluid - - - - | | | |
|---|---|---|---|---|---|
| Type Bearings | Load, Kg. | PRL 2574 | PRL 3078 | PRL 3371 | PRL 3490 |
| E.P. Type 52-100 Steel | 1 | 0.35 | 0.15 | 0.29 | 0.19 |
| | 10 | 0.56 | 0.22 | 0.50 | 0.28 |
| | 40 | 0.66 | 0.44 | 0.71 | 0.75 |
| Heat Stabilized 52-100 Steel | 1 | 0.28 | 0.15 | 0.30 | 0.17 |
| | 10 | 0.55 | 0.30 | 0.47 | 0.27 |
| | 40 | 0.65 | 0.40 | 0.72 | 0.79 |
| M-10 Tool Steel | 1 | 0.31 | 0.19 | 0.35 | 0.19 |
| | 10 | 0.38 | 0.33 | 0.44 | 0.32 |
| | 40 | 0.42 | 0.46 | 0.62 | 0.45 |

The behavior of the E.P. type 52-100 steel and the heat stabilized 52-100 steel is essentially the same at corresponding loads and test fluids. Values for the M-10 tool steel tend to be somewhat lower at the high load (40 kg.) than those for the other two steels. The tricresyl phosphate appears to be effective in reducing the wear values for each type steel shown. This preliminary data would indicate that the four-ball wear tester can be used to evaluate the relative wear behavior of fluids and lubricants in relation to the bearing surfaces shown.

Further work will include the evaluation of various extreme-pressure and mild E.P. type additives relative to these bearing surfaces as well as the behavior of mixed bearing systems, that is, systems such

as E.P. type 52-100 steel-on-heat stabilized 52-100 steel.

3. Lubrication Studies With Titanium and Titanium Alloys. This laboratory is participating in a study of the lubrication characteristics of bearings of titanium and titanium alloys. This work is being done in cooperation with the Department of the Army, Chief of Ordnance. The Materials Laboratory of the Wright Air Development Center has also expressed an interest in this study.

Preliminary studies have been conducted in the Shell four-ball wear tester using titanium and titanium alloy ball bearing test specimens as well as special flat disc specimens. The flat disc specimens are used with a special test cup adapter designed for the four-ball wear tester. The flat specimens and the titanium balls were obtained through the Watertown Arsenal. The balls are 15/32-inch diameter instead of the standard 1/2-inch diameter for which the wear tester is designed. This size difference in the balls requires a special adapter in the rotating ball chuck and in the ball pot to accommodate the smaller 15/32-inch diameter titanium balls. The compositions of the titanium specimens are shown on Table 35.

Table 35

TITANIUM SPECIMENS FOR THE FOUR-BALL WEAR TESTER

| No. of Balls | No. of Discs | Alloy Designation | Nominal Composition, Wt.% |
|---|---|---|---|
| 12 | 12 | Ti 75A | Fe=0.10; N=0.02; C=<0.04; H=0.03; O=Trace; Balance=Ti |
| 12 | 6 | Ti 150A | Fe=1.3; N=0.02; Cr=2.7; C=0.02; H=0.03; O=0.25; Balance=Ti |
| 12 | 6 | RC 130A | Mn=8; C=0.10; Balance=Ti |
| 12 | 6 | RC 130B | Mn=4; Al=4; C=0.10; Balance=Ti |

The hardness of the test balls, or specimens, in the four-ball tester exerts considerable influence over the ball scars obtained and the load range over which the balls may be successfully evaluated for lubricity. The harder the specimens, the more satisfactory the results at higher bearing loads. As a preliminary measurement, therefore, the hardness of the titanium specimens was measured in order to establish the hardness relative to other test specimens successfully evaluated with a Shell four-ball wear tester. These hardness values are shown on Table 36.

Table 36

HARDNESS VALUES FOR TITANIUM AND TITANIUM ALLOYS

| Metal Specimen | Hardness |
|---|---|
| Sheet Stock from WADC | |
| L-53 | Rockwell C 28-31 |
| W7 (T-1) | Rockwell C 24-25 |
| Watertown Arsenal - Ti Balls | |
| Ti 75A | Rockwell C 20-21<br>B (99) |
| RC 150A | Rockwell C 43 |
| RC 130B | Rockwell C 33-39 |
| RC 130A | Rockwell C 42-43 |

The hardness increases with increasing hardness number. Values on the Rockwell C scale are indicative of harder specimens than the Rockwell B scale. A hardness of 20 on the Rockwell C scale is equivalent to a value of 98 on the Rockwell B scale. The titanium alloys are somewhat harder than the titanium 75A which is essentially pure titanium. The titanium alloys are not as hard as the 52-100 steel bearing specimens used for the bulk of the four-ball wear studies. However, softer specimens, namely Naval bronze and C-1019 soft steel, have been evaluated successfully with the four-ball wear tester in the low load range.

Wear characteristics with stainless steel balls may be of considerable interest in this discussion because of the similarity of corrosion resistance between titanium and stainless steel. Data are presented on Tables 37, 38 and 39 to illustrate the four-ball lubricity measurements with the various types of balls discussed as a basis of comparison for the titanium studies.

The data on Table 37 show the lubricity properties of bearing systems involving stainless steel and 52-100 steel. The test fluids comprise a typical ester and mineral oil composition with and without tricresyl phosphate as the anti-wear additive. It can be seen that stainless steel bearings are much more difficult to lubricate than the conventional 52-100 steel bearings. It is evident, however, that the same general trend exists in the lubrication of the stainless steel and 52-100 steel systems. This relative ease of lubrication correlates well with the relative ease of metal attack, or corrosion, of the stainless steel and 52-100 steel. It can be noted that the maximum differences in stainless steel and 52-100 steel show up at the higher loads (40 kilograms) where increased chemical activity is required to allow adequate lubrication via chemical erosion or polishing. These and subsequent data also point up the desirability of using the harder member of a dissimilar bearing system as the rotating member of the four-ball wear tester.

Table 38 shows the wear values for C-1019 soft steel and 52-100 steel bearings. The C-1019 soft steel balls exhibit a hardness typical of cold worked low carbon steel. These balls are considerably softer than those of titanium and the titanium alloys considered here. As in the case of stainless steel, however, the basic ingredient is still iron. This is important since it has been shown by several investigators that additives of the tricresyl phosphate type work by forming a low melting iron-phosphorus alloy. In general, the wear values for the systems involving C-1019 soft steel are high, but the effect of tricresyl phosphate is still evident. It is apparent from the scar sizes that loadings of 10 and 40 kilograms are excessive for these soft bearing systems. This suggests that the four-ball wear tester may be useful in evaluating chemical phenomena involved in lubrication even though the actual bearing loads used in practice cannot adequately be mirrored.

Table 39 shows some steel-on-bronze wear data from the four-ball wear tester. These data include the four fluids discussed in the two previous tables and, in addition, a mineral oil and ester containing S-106 which is a zinc neutralized di-thiophosphate additive. The softer metal, or the one incurring the most wear, is now a non-ferrous metal. The fluids containing the tricresyl phosphate do not produce decreased wear. The various classes of fluids do, however, produce reproducible scar values representing varying degrees of lubricity or wear. Again, as in the case of the C-1019 soft steel, the values are excessive for the higher loadings (10 kilograms and above) indicating that the wear values have been obtained at a loading above all practical bearing loadings involving bronze bearings. The relative degrees of wear do, however, line up roughly in accordance with ease of corrosion of the bronze in a high temperature oxidation process involving the lubricant, air, and bronze surface. That is, the mineral oil shows less bronze corrosion upon oxidation than the ester. The tricresyl phosphate and zinc di-thiophosphate show increasing rates of bronze corrosion on oxidation. It should be emphasized that all of the lubricant compositions discussed here are considered good lubricants for steel-on-bronze bearing systems.

Table 40 shows some bronze-on-bronze wear data for a typical Spec. MIL-L-7808 synthetic lubricant (PRL 3161) by itself and with quantities of chemically active extreme-pressure type additives. These extreme pressure additives all show excessive chemical activity with bronze. The bronze wear values for PRL 3161 increase with the addition of these relatively corrosive extreme-pressure additives.

In general, these results indicate that some significant wear and lubricity data can be obtained with metals other than 52-100 steel and with hardness values considerably below the optimum, which appears to be in the range of 60 to 65 Rockwell C.

Table 37

STAINLESS STEEL-52-100 BEARING STEEL WEAR CHARACTERISTICS
IN THE SKRIL FOUR-BALL WEAR TESTER

Test Conditions Include: Test Time = 1 hour; Test Speed = 850 r.p.m.; Test Temperature = 75°C.; Bearings = Stainless Steel Ball Bearings (0.5 inch diameter) SKF Industries Grade #1 and SKF Industries Grade #1 (0.5 inch diameter) Steel Ball Bearings, PRL Batch #9.

Test Fluids Include: PRL 2574 = Typical Hydrocarbon-base Hydraulic Fluid
PRL 3078 = 1.0 Wt.% Tricresyl Phosphate in PRL 2574
PRL 2429 = Di-2-Ethylhexyl Sebacate (Plasticizer Grade)
PRL 2860 = 1.0 Wt.% Tricresyl Phosphate in PRL 2429

| PRL Designation | Average Wear Scar Diameter, mm. at 1 Kg. | 10 Kg. | 40 Kg. |
|---|---|---|---|
| Steel-on-Steel Bearing Surfaces | | | |
| 2574 | 0.35 | 0.56 | 0.66 |
| 3078 | 0.15 | 0.22 | 0.44 |
| 2429 | 0.26 | 0.55 | 0.69 |
| 2860 | 0.14 | 0.26 | 0.37 |
| Stainless Steel-on-Stainless Steel Bearing Surfaces | | | |
| 2574 | 0.33 | 0.53 | 1.56 |
| 3078 | 0.21 | 0.30 | 1.43 |
| 2429 | 0.44 | 0.85 | 1.23 |
| 2860 | 0.21 | 0.63 | 1.12 |
| Rotating Steel Ball-on-3 Stationary Stainless Steel Balls | | | |
| 2574 | 0.33 | 0.46 | 0.54 |
| 3078 | 0.14 | 0.25 | 0.44 |
| 2429 | 0.20 | 0.42 | 0.50 |
| 2860 | 0.15 | 0.29 | 0.37 |
| Rotating Stainless Steel Ball-on-3-Stationary Steel Balls | | | |
| 2574 | 0.36 | 0.62 | 1.36 |
| 3078 | 0.15 | 0.25 | 0.44 |
| 2429 | 0.38 | 0.71 | 1.17 |
| 2860 | 0.19 | 0.29 | 1.10 |

Table 38

COMPARISON OF THE WEAR CHARACTERISTICS BETWEEN 52-100 BEARING STEEL AND C-1019 SOFT STEEL BEARINGS IN THE SHELL FOUR-BALL WEAR TESTER

Test Conditions Include: Test Time = 1 hour; Test Speed = 850 r.p.m.; Test Temperature = 75°C.; Bearings = Kilian Steel Ball corp. C-1019 Soft Steel Balls (0.5 inch diameter) and SKF Industries Grade #1 (0.5 inch diameter) Steel Ball Bearings, PRL Batch #9.

Test Fluids Include:
PRL 2574 = Typical Hydrocarbon-base Hydraulic Fluid
PRL 3078 = 1.0 Wt.% Tricresyl Phosphate in PRL 2574
PRL 2429 = Di-2-Ethylhexyl Sebacate (Plasticizer Grade)
PRL 2860 = 1.0 Wt.% Tricresyl Phosphate in PRL 2429

| PRL Designation | Average Wear Scar Diameter, mm. at 1 Kg. | 10 Kg. | 40 Kg. |
|---|---|---|---|
| 52-100 Steel-on-Steel Bearing Surfaces | | | |
| 2574 | 0.35 | 0.56 | 0.66 |
| 3078 | 0.15 | 0.22 | 0.44 |
| 2429 | 0.26 | 0.55 | 0.69 |
| 2860 | 0.14 | 0.26 | 0.37 |
| C-1019 Soft Steel-on-Steel Bearing Surfaces | | | |
| 2574 | 0.70 | 1.50 | 1.79 |
| 3078 | 0.65 | 1.23 | 1.69 |
| 2429 | 0.72 | 1.23 | 1.43 |
| 2860 | 0.65 | 1.36 | 1.56 |
| Rotating 52-100 Steel Ball-on-3 Soft Steel Stationary Balls | | | |
| 2574 | 0.56 | 0.63 | 0.80 |
| 3078 | 0.36 | 0.52 | 0.84 |
| 2429 | 0.56 | 0.66 | 0.78 |
| 2860 | 0.44 | 0.56 | 0.70 |

Table 39

STEEL-ON-BRONZE WEAR CHARACTERISTICS AS MEASURED ON THE SHELL FOUR-BALL WEAR TESTER

Test Conditions Include: Test Time = 1 hour; Test Speed = 850 r.p.m.; Test Temperature = 75°C.; Bearings = SKF Industries Grade #1 (0.5 inch diameter) Steel Ball Bearings, PRL Batch #9 and Hartford Steel Ball Co. Naval Bronze Grade #1 (0.5 inch diameter) Ball Bearings, PRL Batch #5.

Test Fluids Include:
PRL 2574 = Typical Hydrocarbon-base Hydraulic Fluid
PRL 3078 = 1.0 Wt.% Tricresyl Phosphate in PRL 2574
PRL 3302 = 1.0 Wt.% S-106(1) in PRL 2574
PRL 2429 = Di-2-Ethylhexyl Sebacate (Plasticizer Grade)
PRL 2860 = 1.0 Wt.% Tricresyl Phosphate in PRL 2429
PRL 3303 = 1.0 Wt.% S-106(1) in PRL 2429

| PRL Designation | Average Wear Scar Diameter, mm. at 0.4 Kg. Steel | 0.4 Kg. Bronze | 1.0 Kg. Steel | 1.0 Kg. Bronze | 10 Kg. Steel | 10 Kg. Bronze |
|---|---|---|---|---|---|---|
| **Steel-on-Steel Bearing System** | | | | | | |
| 2574 | - | - | 0.35 | - | 0.56 | - |
| 3078 | - | - | 0.15 | - | 0.22 | - |
| 3302 | - | - | 0.29 | - | 0.33 | - |
| 2429 | - | - | 0.26 | - | 0.55 | - |
| 2860 | - | - | 0.14 | - | 0.26 | - |
| 3303 | - | - | 0.19 | - | 0.28 | - |
| **Rotating Steel Ball-on-3 Stationary Bronze Balls** | | | | | | |
| 2574 | - | 0.34 | - | 0.44 | - | 1.04 |
| 3078 | - | 0.36 | - | 0.43 | - | 1.10 |
| 3302 | - | 0.61 | - | 0.74 | - | 1.17 |
| 2429 | - | 0.58 | - | 0.63 | - | 0.97 |
| 2860 | - | 0.69 | - | 0.78 | - | 1.43 |
| 3303 | - | 0.54 | - | 0.61 | - | 1.10 |
| **Rotating Bronze Ball-on-3 Stationary Steel Balls** | | | | | | |
| 2574 | 0.19 | 0.37 | 0.37 | 0.46 | 0.68 | 1.62 |
| 3078 | 0.19 | 0.30 | 0.26 | 0.46 | 0.38 | 1.25 |
| 3302 | 0.18 | 0.34 | 0.24 | 0.34 | 0.39 | 1.43 |
| 2429 | 0.36 | 0.40 | 0.33 | 0.56 | 0.50 | 0.91 |
| 2860 | 0.23 | 0.42 | 0.30 | 0.50 | 0.53 | 1.04 |
| 3303 | 0.21 | 0.38 | 0.30 | 0.48 | 0.41 | 0.93 |

(1) Reaction Product of Dodecyl Alcohol, Phosphorus Pentasulfide, and Zinc Oxide.

Table 40

WEAR CHARACTERISTICS OF SOME FLUIDS WITH BRONZE-ON-BRONZE BEARINGS

Tests Conducted with Shell Four-Ball Wear Tester for 1 Hour at 75°C. With Bronze-on-Bronze Bearing Surfaces.
Bronze Ballbearings = Hartford Steel Ball Company, Naval Bronze Grade #1 (0.5-Inch Diameter), PRL Batch #4.
Test Fluid PRL 3207 = 0.5 Wt.% Phenothiazine in Di-2-Ethylhexyl Sebacate.

| Wt % Additive in PRL 3207 | Ave. Wear Scar Diam., mm. 1 Kg. | 10 Kg. |
|---|---|---|
| 3.9 Acryloid HF-25 + 5.0 Tricresyl Phosphate (PRL 3161) | 0.46 | 0.91 |
| 10.0 Fluorolube FS | 0.64 | 1.03 |
| 10.0 Aroclor 1248 | 0.80 | 1.69 |
| 7.5 Santopoid S | 0.76 | 1.13 |
| 5.0 Ortholeum 202 | 1.12 | 1.19 |

In general, these results indicate that some significant wear and lubricity data can be obtained with metals other than 52-100 steel and with hardness values considerably below the optimum, which appears to be in the range of 60 to 65 Rockwell C.

Preliminary wear studies with titanium 75A are shown on Table 41. Steel (52-100 steel)-on-titanium as well as titanium-on-titanium data are presented. The bulk of the tests have been conducted at a load of one kilogram. A few exploratory tests have been attempted at 10 and 40 kilograms load in the four-ball wear tester. For the majority of the tests, di-2-ethylhexyl sebacate with various classes of additives has been used for the test fluid. Di-2-ethylhexyl sebacate shows good lubricity properties with steel as well as steel-on-bronze bearings.

The one kilogram test with the di-2-ethylhexyl sebacate type of fluid containing 5.0 weight per cent tricresyl phosphate (PRL 3161) had to be stopped after 1 minute test time because of the noise and vibration noted, which is generally indicative of failure of the lubricant. Fluorolube FS, which is a polymer of trifluoromonochloroethylene, shows only a slight improvement over PRL 3161 in lubricity for titanium-on titanium. Incipient breakdown of lubricity was evident when the test was terminated after 5 minutes. The supply of titanium test specimens is quite limited; therefore, no further titanium-on-titanium wear tests have been conducted. In the region of normal wear, it is possible to obtain as many as 10 to 15 tests with one set of 3 stationary balls and 4 to 6 tests with one rotating ball. Running under conditions of incipient failure is undesirable since it reduces greatly the number of tests that can be obtained with a given set of balls.

Table 41

WEAR CHARACTERISTICS OF TITANIUM (75-A)

TESTS CONDUCTED IN THE SHELL FOUR-BALL WEAR TESTER FOR 1 HOUR AT 75°C.
STEEL BALLS = SKF INDUSTRIES GRADE #1 (0.5 INCH DIAMETER) STEEL BALLBEARINGS, PRL BATCH #11.
TEST FLUID PRL 3207 = 0.5 WT.% PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE.

| WT.% ADDITIVE IN PRL 3207 | BEARING SYSTEM | TEST TIME, MINS. | AVE. WEAR SCAR DIAM., MM. 1 KG. | 10 KG. | 40 KG. |
|---|---|---|---|---|---|
| 3.9 ACRYLOID NF-25 + 5.0 TRICRESYL PHOSPHATE (PRL 3161) | TI-ON-TI | 1 | 1.17 | - | - |
| | STEEL-ON-TI | 10 | 1.38 | - | - |
| 100 FLUOROLUBE FS | TI-ON-TI | 5 | 1.62 | - | - |
| | STEEL-ON-TI | 60 | 0.47 | 0.47 | 3.12 |
| 10.0 FLUOROLUBE FS | STEEL-ON-TI | 60 | 0.42 | - | - |
| 10.0 HEXACHLOROBUTADIENE | STEEL-ON-TI | 60 | 3.42 | - | - |
| 1.0 PERFLUOROBUTYRIC ACID | STEEL-ON-TI | 60 | 3.44 | - | - |
| 10.0 AROCLOR 1248 | STEEL-ON-TI | 60 | 0.32 | 6.37(1) | - |
| 7.5 SANTOPOID S | STEEL-ON-TI | 60 | 0.52 | - | - |
| 5.0 ORTHOLEUM 202 | STEEL-ON-TI | 60 | 0.56 | - | - |

(1) 10 KG. LOAD RUN WITHOUT DISTURBING STATIONARY BALLS FOLLOWING 1 KG. RUN.

Lubricity tests with titanium have, therefore, been concentrated on steel-on-titanium systems. For these studies, a single 52-100 steel ball is used as the rotating member and three titanium balls are used as the stationary member of the bearing. These steel-on-titanium results indicate that phosphorus-containing additives are not particularly effective in steel-on-titanium lubrication. This applies equally to tricresyl phosphate and phosphoric acid. Both of these materials are effective lubricity additives for steel-on-steel systems. The phosphorus-containing additives work on the basis of iron-phosphorus alloy formation in the bearing area, which results in smoothing or chemically polishing the bearing surface. The use of an acidic phosphorus compound, in general, increases the effectiveness by virtue of physical adsorption on the metal surface, thereby reducing the concentration of additive required to produce a given lubricity level.

The use of extreme-pressure type lubricity additives containing fluorine and chlorine, chlorine and sulfur, chlorine, and sulfur appear to be effective in reducing steel-on-titanium wear. The composition of Fluorolube FS has already been discussed. Aroclor 1248 is believed to be a chlorinated biphenyl. Santopoid S is a chloronaphtha xanthate containing 10 to 15 weight per cent sulfur and 30 to 35 weight per cent chlorine. Ortholeum 202 is a sulfurized terpene containing about 35 weight per cent sulfur. These materials are conventional extreme-pressure agents for steel-on-steel. They appear to be effective because of a substantial rate of chemical erosion of an iron compound formed from the active ingredient of the extreme-pressure additive in the bearing area to prevent seizure and welding of the metal parts. This behavior suggests that the mechanism by which these extreme-pressure additives work is one of

sufficient chemical erosion of the steel bearing area to keep to a minimum the rate of titanium pick up on the rotating steel ball from the stationary titanium balls. It is believed that substantial titanium pick up by the rotating ball must be prevented to achieve low wear. This is based partially on the comparative effect of Fluorolube FS with steel-on-titanium versus titanium-on-titanium.

There is some difference between the extreme-pressure type additives in their effectiveness on steel-on-steel and steel-on-titanium. The ester containing 10.0 weight per cent hexachlorobutadiene and the ester containing 1.0 weight per cent perfluorobutyric acid are not effective steel-on-titanium lubricants at the one kilogram load in the four-ball wear tester. Of the extreme-pressure type additives evaluated in the two types of bearing systems, Aroclor 1248 and perfluorobutyric acid are not effective for steel-on-steel while hexachlorobutadiene and perfluorobutyric acid are not effective for steel-on-titanium. It has been suggested that the fluorine may be a critical constituent in a good titanium lubricant because of the ease of formation of titanium fluoride. There is no indication that perfluorobutyric acid is effective. Similarly, in steel-on-steel systems there is no indication that a compound containing fluorine without chlorine is effective. Compounds containing both fluorine and chlorine appear to be particularly effective in both steel-on-steel and steel-on-titanium.

A few tests have been conducted at loadings of 10 and 40 kilograms for steel-on-titanium in the four-ball wear tester. These tests, in general, emphasize the extreme difficulty in obtaining good steel-on-titanium lubrication. Results of lubrication tests in the four-ball wear tester using steel-on-titanium alloy discs or balls are shown on Table 42. Several comparative points are given for the discs and the balls on Table 42. In general, the titanium alloys are somewhat harder than the titanium 75A discussed previously. These data show that steel-on-titanium alloy systems appear to be more difficult to lubricate, in general, than steel-on-titanium 75A.

To summarize, titanium specimens in the form of discs and balls can be prepared to satisfactory properties for use as specimens for the Shell four-ball wear tester. No effective lubricants have been found in these preliminary tests for titanium-on-titanium bearing systems. In general, conventional extreme-pressure lubricant compositions show some degree of effectiveness for steel-on-titanium bearing systems. The mechanism by which steel-on-titanium lubrication is achieved appears to involve, primarily, chemical reaction with the steel. It would appear that steel-on-titanium bearing loads might be at least as restrictive and probably considerably more restrictive than steel-on-bronze bearing loads. Steel-on-titanium alloy bearing systems appear to be somewhat more difficult to lubricate than steel-on-titanium.

Table 42

WEAR CHARACTERISTICS OF SOME TITANIUM ALLOYS

Tests Conducted in Shell Four-Ball Wear Tester for 60 Minutes at 75°C.
Test Fluid PRL 3207 = 0.5 Wt.% Phenothiazine in Di-2-Ethylhexyl Sebacate.

| Wt.% Additive in PRL 3207 | Bearing System | Wear Scar Diam., mm. at 1 Kg. Load |
|---|---|---|
| | Alloy RC 130-A | |
| 100 Fluorolube FS | Steel-on-Ti Balls | 1.58 |
| | Alloy RC 130-B | |
| 100 Fluorolube FS | Steel-on-Ti Balls | 0.21 |
| | Steel-on-Ti Discs | 1.80 |
| 10 Fluorolube FS | Steel-on-Ti Balls | 2.58 |
| 7.5 Santopoid-S | Steel-on-Ti Balls | 2.60 |
| 5.0 Ortholeum 202 | Steel-on-Ti Balls | 0.28 |
| | Alloy RC 150-A | |
| 100 Fluorolube FS | Steel-on-Ti Balls | 0.80 |
| | Steel-on-Ti Discs | 1.17 |
| 100 Aroclor 1248 | Steel-on-Ti Balls | 1.80 |
| | Steel-on-Ti Discs | 2.08 |
| 5.0 Ortholeum 202 | Steel-on-Ti Balls | 2.32 |

C. OXIDATION AND CORROSION STUDIES. It has been pointed out previously that oxidation and corrosion properties are among the most critical for jet engine lubricants. The incorporation of additives, particularly extreme-pressure lubricity additives, generally affect adversely the oxidation and corrosion characteristics of esters and mineral oils. Oxidation and corrosion studies have been conducted in the moderate temperature range (347°F.) to determine the effect of various lubricity additives, oxidation inhibitors, and V.I. improvers (polymeric additives) on esters and mineral oils. Oxidation and corrosion tests at high temperatures (500°F.) have, for the most part, been conducted on essentially non-additive base stocks representing the various chemical classes of fluids that show promise as high temperature fluids and lubricants.

1. Phenothiazine Dirtiness. Phenothiazine is being used widely as an oxidation inhibitor for synthetic hydraulic fluids and lubricants of the ester type. Phenothiazine has been found, in this application, to be among the most effective high temperature oxidation inhibitors, in terms of stable life or induction period of the fluid. Phenothiazine does, however, have one characteristic which is typical of all of the amine type

oxidation inhibitors evaluated by this Laboratory. That is, phenothiazine or other amine type inhibitors have a tendency to cause a darkening of the fluid and to form a trace of solid material within the stable life or induction period of the fluid. This phenomenon is referred to as "trace dirtiness" in this discussion. There is evidence that trace dirtiness due to phenothiazine is encountered in essentially all of the relatively severe accelerated laboratory oxidation and corrosion tests. This is particularly true in the Spec. MIL-L-6387 and MIL-L-7808 oxidation tests conducted at 347°F. for 72 hours. Evaluation of esters inhibited with hindered phenol type oxidation inhibitors (Paranox 411 and Antioxidant 2246) shows essentially no trace dirtiness within the stable life or induction period at temperatures of 250° to 350°F. These data indicate that the trace dirtiness is a function of the phenothiazine rather than the ester base oil.

The Wright Air Development Center and several users of phenothiazine inhibited Spec. MIL-L-7808 type lubricants have indicated that trace dirtiness occurs in actual lubricant systems. The source of this dirtiness noted in service use is much more difficult to locate and characterize than in the laboratory accelerated oxidation and corrosion tests. This Laboratory has critically revaluated some of the oxidation and corrosion data for phenothiazine-inhibited esters to determine any "trace dirtiness" and its relationship to phenothiazine.

A series of stable life type oxidation and corrosion tests have been carried out with phenothiazine-inhibited di-2-ethylhexyl sebacate (PRL 3371). The concentration of phenothiazine was increased stepwise from 0.1 to 2.0 weight per cent in this series of tests. These data are shown on Table 43. It can be noted that the effect of increased concentration of phenothiazine on stable life is essentially linear. That is, doubling the phenothiazine concentration, within this concentration range, essentially doubles stable life. This trend has been noted and discussed in previous reports from this Laboratory. The interest in this discussion is in the sacrifice in properties, if any, that result from obtaining increased stable life by increased amounts of phenothiazine. For the most part, the fluids from the oxidation tests shown on Table 43 have exceeded the stable life, or induction period, and are in about the same state of incipient oxidation, as judged by overall property deterioration.

A 20-hour oxidation test with an uninhibited di-2-ethylhexyl sebacate sample is shown as a basis of comparison. This uninhibited sample shows essentially the same degree of oxidation on the basis of viscosity and neutralization number changes. The major difference, however, is in the oil insolubles formed and the condition of the metal catalysts. There are no oil insolubles in the uninhibited PRL 3371 sample and the metal catalysts show no signs of coating.

The samples containing phenothiazine all show some oil insolubles and metal coating trends. The amount of oil insolubles and the metal coating tendencies increase with increasing phenothiazine concentration. These data would indicate that steps in ester refining would be preferable to increasing the phenothiazine concentration in

order to achieve a given stable life or induction period. Previous reports, e.g. PRL 5.4-Sep52, indicate that overall fluid stability can be achieved by either increased oxidation inhibitor concentration, or by improved refining and purification procedures for the bulk ingredients of the fluid.

The discussion, thus far, has been concerned with stable life tests. A series of Spec. MIL-L-7808 oxidation and corrosion tests at 347°F. for 72 hours have been conducted with di-2-ethylhexyl sebacate containing varying percentages of phenothiazine. These data are shown on Table 44. The fluids from these tests are all well within the induction period. There is no appreciable difference in the trace dirtiness characteristics of these three test fluids containing from 0.5 to 2.0 weight per cent phenothiazine in the 72 hour Spec. MIL-L-7808 oxidation and corrosion test.

Trace dirtiness characteristics of phenothiazine-inhibited esters have also been evaluated at temperatures of 400° and 500°F. These tests have been conducted in accordance with the general procedures and techniques of Spec. MIL-L-7808. Tests at 500°F. were conducted without the magnesium metal catalyst. It has been found that magnesium corrosion becomes troublesome at 400°F. and above, particularly if an appreciable amount of oxidation occurs.

The data for 400°F. oxidation tests with PRL 3371 containing 0.5, 1.0 and 2.0 weight per cent phenothiazine, respectively, are shown on Table 45. These are stable life tests in which the stable life has been exceeded in each case. As in the case of the similar data at 347°F., the change in viscosity and neutralization number indicate about the same degree of oxidation. The oil insoluble material and metal coatings show an increase with increasing phenothiazine concentration.

More extensive oxidation and corrosion testing has been conducted at 500°F. on phenothiazine-inhibited esters. At 500°F. the phenothiazine-inhibited esters have essentially no stable life or induction period. The effect of the phenothiazine is to slow down the rate of oxidation rather than to prevent oxidation, as is the case in the conventional induction period at lower temperatures.

The effect of phenothiazine concentration has been evaluated at 500°F. in a 30 hour test. These data are shown on Table 46. The information obtained at 500°F. includes quantitative data on the amount of oxygen absorbed during the test. Typical oxygen absorption data given on Table 46 are shown in Figure 24. These rate data show that the amount of oxygen absorbed decreases with increasing phenothiazine concentration over the concentration range of 0.5 to 2.0 weight per cent. The data for the oxidation of PRL 3371 without an inhibitor for 30 hours at 500°F. are shown on Table 47. The oxidation rate for the blend containing 0.5 weight per cent phenothiazine is approximately 60 per cent of the oxidation rate of the uninhibited PRL 3371. These data again present a valid reason for the use of phenothiazine in esters as oxidation inhibitors at 500°F.

In comparing the results at 500°F., it can be noted that additional columns are added for the values of isopentane insolubles and the viscosity change after removal of isopentane insolubles. These properties are in effect an additional measure of dirtiness which could be called potential dirtiness. A study of the solubility of oxidized ester products indicates that ester materials which are highly oxidized are insoluble in the original ester and in isopentane. Ester materials undergoing only slight oxidation remain soluble in the original ester and in isopentane. During the course of the oxidation, however, the oxidized portion of the ester passes through a stage of intermediate oxidation in which the material is soluble in the original ester, but insoluble in isopentane. At this stage of oxidation the materials are approaching sludge, or ester insolubles, rapidly. In the isopentane insoluble stage, the material causes rather large viscosity increases.

The data shown on Table 46 indicate that while the amount of oxygen absorbed decreases with increasing phenothiazine concentration, The amounts of oil insolubles and isopentane insolubles increase. It can be seen that the oil soluble-isopentane insoluble portion of the oxidized fluid causes the majority of the viscosity increase in the oxidized fluid. These data show the effect of phenothiazine concentration under a given set of test conditions at 500°F. Report PRL 5.8-Sep53 contains a discussion of the comparison of oxidation of fluids at 500°F. as a function of oxygen absorbed and test time.

Oxidation and corrosion results at 500°F. as a function of oxygen absorbed and test time for di-2-ethylhexyl sebacate (PRL 3371) uninhibited, and with 0.5 weight per cent phenothiazine present, are shown on Table 47. A comparison of the rate of oxygen absorption indicates that the phenothiazine shows a big effect in reducing oxygen absorption. This effect is a maximum at the start of the test and tapers off as the test progresses. The comparison can only be carried successfully to the point at which the uninhibited ester is oxidized to essentially a solid sludge. The effect of the phenothiazine appears to persist to a measurable extent up to this point. The relative rates of oxygen absorption with and without phenothiazine are shown in Figure 25.

Comparison of dirtiness (Table 47) on a time basis indicates that the uninhibited and inhibited fluid exhibit about the same degree of dirtiness after 12 hours test time, but from 12 hours upward the rate of sludge formation is about twice as rapid for the uninhibited fluid. That is, the uninhibited fluid is oxidized to a solid at room temperature in 30 hours compared to 60 hours for the phenothiazine-inhibited fluid. At this point where the fluids become solid, about the same amount of oxygen has been absorbed by both the inhibited and uninhibited fluids.

A more interesting comparison for dirtiness can be made by comparing the inhibited and uninhibited fluids at the same values of oxygen absorbed. At a value of 1.3 moles of oxygen absorbed per mole of ester (426 grams), the uninhibited ester shows 0.1 weight per cent insolubles and 2.1 weight per cent isopentane insolubles compared with 0.8 weight per cent oil insolubles and 6.9 weight per cent

isopentane insolubles for the inhibited ester. The reproducibility of the 500°F. oxidation and corrosion tests is such that these may be considered significant differences. With increased oxygen absorbed, the differences between the inhibited and uninhibited become less until, as pointed out above, both fluids result in a solid at the same value of about 2.5 moles of oxygen absorbed per mole of ester.

The overall effect of increasing the phenothiazine concentration to at least 2.0 weight per cent is to improve the stable life or induction period. At temperatures of 500°F., where the induction period or stable life is too short to measure as a significant number, increased phenothiazine concentration is effective in reducing the rate of oxidation. The effect of the phenothiazine shows good persistence for periods of 30 to 60 hours at 500°F. All accelerated oxidation and corrosion conditions give indication of "trace dirtiness" within the stable life of the fluid. There are indications that this "trace dirtiness" increases with increasing amounts of phenothiazine.

In all cases evaluated in the region of incipient oxidation, uninhibited di-2-ethylhexyl sebacate appears to be cleaner on oxidation than a phenothiazine-inhibited di-2-ethylhexyl sebacate. Analysis of the oxidation products indicates that the presence of phenothiazine concentrates the effects of incipient oxidation on a relatively few ester molecules causing sludge, while in the uninhibited ester, the same amount of oxygen is spread out over a much larger portion of the molecules resulting in some viscosity increase but less sludge. These data would indicate, in general, that it is desirable to obtain as much inherent stability as possible by ester and bulk fluid refining so that the concentration of phenothiazine may be held to a minimum.

2. Effect of Phosphorus Type Lubricity Additives on 500°F. Oxidation and Corrosion Stability of Ester-Base Compositions. Oxidation and corrosion test data for phenothiazine-inhibited ester-base fluids are discussed in report PRL 5.8-Sep53. Additional tests have been conducted at 500°F. on complete lubricant formulations as a basis of comparison with the behavior of the inhibited base stock. The effect of phosphorus-containing lubricity additives on completed lubricant formulations has been emphasized in these tests. Data with a typical synthetic lubricant formulation (PRL 3161) at 500°F. are shown on Table 48 along with similar data for the phenothiazine-inhibited ester (PRL 3207). It can be seen that oxidative deterioration of PRL 3161 is more severe, under comparable test conditions, than that of the phenothiazine-inhibited di-2-ethylhexyl sebacate.

The additives present in PRL 3161, which are not components of the phenothiazine-inhibited ester, are the Acryloid polymeric additive and the tricresyl phosphate anti-wear additive. These two additives have, therefore, been added separately to the phenothiazine-inhibited di-2-ethylhexyl sebacate base stock (PRL 3207). Oxidation and corrosion data at 500°F. for these compositions are shown on Table 48.

Table 43

EFFECT OF PHENOTHIAZINE CONCENTRATION ON OXIDATION AND CORROSION PROPERTIES OF DI-2-ETHYLHEXYL SEBACATE AT 347°F.

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-6387.
TEST TEMPERATURE = 347 ± 3°F.; TEST TIME AS INDICATED; AIR RATE = 10 ± 1 LITERS PER HOUR; TEST FLUID = 100 ML.; CATALYST = A ONE INCH SQUARE EACH OF METALS INDICATED.

| TEST FLUID | DI-2-ETHYLHEXYL SEBACATE (PRL 3371) | | | | | |
|---|---|---|---|---|---|---|
| PHENOTHIAZINE CONCENTRATION, WT.% | NONE | 0.1 | 0.25 | 0.5 | 1.0 | 2.0 |
| TEST TIME, HOURS | 20 | 25 | 63 | 159 | 194 | 424 |
| APPROX. STABLE LIFE, HOURS | - | 21 | 46 | 152 | 180 | >424 |
| % CHANGE IN CENTISTOKE VISCOSITY | | | | | | |
| AT 130°F. | +30 | +7 | +24 | +15 | +12 | +7 |
| AT 0°F. | +71 | +16 | +57 | +36 | +27 | +13 |
| NEUT. NO. (MG. KOH/GM. OIL): | | | | | | |
| ORIGINAL | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| FINAL | 10.7 | 3.9 | 15.4 | 12.3 | 32.5 | 3.9 |
| A.S.T.M. UNION COLOR: | | | | | | |
| ORIGINAL | 2 | 2 | 2 | 2 | 2 | 2 |
| FINAL | 7 | 6 | 8 | 6 | >8 | >8 |
| WT.% INSOLUBLE MATERIAL | NONE | TRACE | 0.2 | 0.4 | 2.1 | 1.5 |
| FINAL CATALYST CONDITION | | | | | | |
| APPEARANCE | | | | | | |
| COPPER | BRIGHT | DULL | DULL | DULL | DULL | COATED |
| STEEL | BRIGHT | DULL | COATED | COATED | COATED | COATED |
| ALUMINUM | BRIGHT | DULL | COATED | COATED | COATED | COATED |
| MAGNESIUM | CORRODED | DULL | DULL | COATED | COATED | COATED |
| CADMIUM | CORRODED | DULL | CORRODED | CORRODED | CORRODED | COATED |
| WT. LOSS (MG./SQ. CM.) | | | | | | |
| COPPER | 0.02 | 0.05 | 0.08 | 0.02 | 0.23 | +0.77 |
| STEEL | 0.01 | 0.00 | +0.05 | +0.11 | +0.04 | +0.85 |
| ALUMINUM | 0.00 | 0.02 | +0.02 | +0.05 | +0.08 | +0.77 |
| MAGNESIUM | 4.54 | +0.02 | 0.12 | +0.11 | +0.69 | +0.72 |
| CADMIUM | 2.00 | +0.03 | 0.31 | 1.07 | 1.56 | +0.36 |

Table 44

EFFECT OF PHENOTHIAZINE CONCENTRATION ON OXIDATION AND CORROSION PROPERTIES OF DI-2-ETHYLHEXYL SEBACATE AT 347°F.

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-6387.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F.; AIR RATE = 10 ± 1 LITERS PER HOUR; TEST TIME = 72 HOURS; CATALYST = A 1 INCH SQUARE EACH OF METALS INDICATED.

| TEST FLUID | DI-2-ETHYLHEXYL SEBACATE (PRL 3371) | | |
|---|---|---|---|
| PHENOTHIAZINE CONCENTRATION, WT.% | 0.5 | 1.0 | 2.0 |
| LIQUID CHARGE, GRAMS | 91 | 92 | 93 |
| LIQUID LOSS, WT.% | 2 | 3 | 0 |
| % CHANGE IN CENTISTOKE VISCOSITY | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(1) | | | |
| AT 130°F. | +2 | +3 | +5 |
| AT 0°F. | +5 | +6 | +13 |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(2) | | | |
| AT 130°F. | 0 | +3 | +4 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | |
| ORIGINAL | 0.1 | 0.1 | 0.1 |
| FINAL | 1.2 | 1.3 | 0.6 |
| A.S.T.M. UNION COLOR | | | |
| ORIGINAL | 1 | 1 | 1 |
| FINAL | >8 | >8 | >8 |
| WT.% OIL INSOLUBLE MATERIAL | 0.5 | 0.6 | TRACE |
| WT.% ISOPENTANE INSOLUBLE MATERIAL | 1.2 | 1.6 | 0.2 |
| FINAL CATALYST CONDITION | | | |
| APPEARANCE | | | |
| COPPER | DULL | DULL | DULL |
| STEEL | DULL | DULL | DULL |
| ALUMINUM | DULL | DULL | BRIGHT |
| MAGNESIUM | BRIGHT | DULL | BRIGHT |
| WT. LOSS (MG./SQ. CM.) | | | |
| COPPER | 0.00 | +0.04 | 0.12 |
| STEEL | 0.00 | +0.08 | 0.02 |
| ALUMINUM | +0.02 | +0.08 | 0.00 |
| MAGNESIUM | 0.00 | +0.03 | 0.00 |

(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) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.

Table 45

EFFECT OF PHENOTHIAZINE CONCENTRATION ON OXIDATION AND CORROSION STABILITY OF DI-2-ETHYLHEXYL SEBACATE AT 400°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-6387.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 400 ± 4°F.; TEST TIME AS INDICATED; AIR RATE = 10 ± 1 LITERS PER HOUR; TEST FLUID = 100 ML.; AND CATALYST = A 1 INCH SQUARE EACH OF METALS INDICATED.
TEST FLUID PRL 3371 = DI-ETHYLHEXYL SEBACATE (PLASTICIZER GRADE).

| TEST FLUID | <---------- PRL 3371 | ----------> | |
|---|---|---|---|
| PHENOTHIAZINE, WT.% | 0.5 | 1.0 | 2.0 |
| TEST TIME, HOURS | 42 | 66 | 74 |
| APPROX. STABLE LIFE, HOURS | 27 | 48 | 64 |
| % CHANGE IN VISCOSITY | | | |
| AT 130°F. | +23 | +24 | +10 |
| AT 0°F. | +52 | +51 | +21 |
| NEUT. NO. (MG. KOH/GM. OIL): | | | |
| ORIGINAL | 0.3 | 0.1 | 0.1 |
| FINAL | 12.7 | 13.1 | 7.3 |
| A.S.T.M. UNION COLOR | | | |
| ORIGINAL | 1-1/2 | 1-1/2 | 1-1/2 |
| FINAL | >8 | >8 | >8 |
| WT.% INSOLUBLE MATERIAL | 1.7 | 2.5 | 4.1 |
| FINAL CATALYST CONDITION | | | |
| APPEARANCE | | | |
| COPPER | DULL | DULL | COATED |
| STEEL | DULL | COATED | DULL |
| ALUMINUM | DULL | COATED | COATED |
| MAGNESIUM | DULL | COATED | COATED |
| WT. LOSS (MG./SQ. CM.) | | | |
| COPPER | 0.16 | 0.11 | +0.26 |
| STEEL | 0.00 | +0.14 | +0.02 |
| ALUMINUM | +0.02 | +0.10 | +0.33 |
| MAGNESIUM | 0.00 | +0.24 | +0.36 |

Table 46

THE EFFECT OF PHENOTHIAZINE CONCENTRATION ON OXIDATION AND CORROSION CHARACTERISTICS OF DI-2-ETHYLHEXYL SEBACATE AT 500°F.

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-6387.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; AIR RATE = 5 ± 0.5 LITERS PER HOUR, TEST TIME = 30 HOURS; TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE OF EACH METAL INDICATED.

| TEST FLUID | DI-2-ETHYLHEXYL SEBACATE (PRL 3371) | | |
|---|---|---|---|
| PHENOTHIAZINE CONCENTRATION, WT.% | 0.5 | 1.0 | 2.0 |
| LIQUID CHARGED, GRAMS | 90 | 90 | 90 |
| LIQUID LOSS, WT.% | 9 | 7 | 1 |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 39.3 | 39.3 | 39.3 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | 5.7 | 8.1 | 6.7 |
| MOLS $O_2$ USED/MOL OF ESTER (426 GMS.) | 1.30 | 1.21 | 1.00 |
| % CHANGE IN VISCOSITY | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | | |
| AT 130°F. | +116 | +56 | +32 |
| AT 0°F. | +240 | - | - |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) | | | |
| AT 130°F. | +51 | +16 | +8 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | |
| ORIGINAL | 0.1 | 0.1 | 0.1 |
| FINAL | 16.8 | 13.3 | 7.6 |
| WT.% OIL INSOLUBLE MATERIAL(2) | 0.8 | 10.9 | 10.8 |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 6.9 | 13.7 | 14.2 |
| FINAL CATALYST CONDITION | | | |
| APPEARANCE | | | |
| COPPER | DULL | COATED | COATED |
| STEEL | COATED | DULL | DULL |
| ALUMINUM | BRIGHT | DULL | DULL |
| WT. LOSS (MG./SQ. CM.) | | | |
| COPPER | 0.07 | +0.17 | +0.18 |
| STEEL | +0.23 | 0.05 | +0.05 |
| ALUMINUM | 0.00 | 0.00 | 0.00 |

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

(3) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF THE OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.

Figure 24

EFFECT OF PHENOTHIAZINE CONCENTRATION ON OXYGEN ABSORPTION AT 500°F.

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME = 30 HOURS; AIR RATE = 5 ± 0.5 LITERS PER HOUR; AND CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.
OXYGEN ABSORPTION IS DETERMINED BY ANALYZING SAMPLES TAKEN FROM THE EXHAUST AIR STREAM FOR OXYGEN CONTENT.
PER CENT OXYGEN IS CALCULATED FROM THE DIFFERENCE IN THE OXYGEN CONTENT OF THE INLET AND EXHAUST AIR STREAMS.
TEST FLUID = DI-2-ETHYLHEXYL SEBACATE (PRL 3371) + THE INDICATED CONCENTRATION OF PHENOTHIAZINE

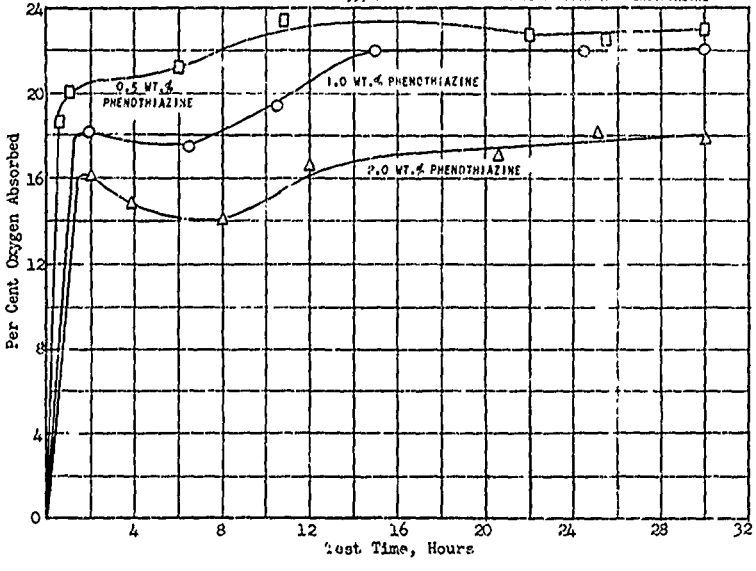


Table 47

EFFECT OF PHENOTHIAZINE ON OXIDATION AND CORROSION CHARACTERISTICS OF DI-2-ETHYLHEXYL SEBACATE AT 500°F.

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-6387.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST TIME AS INDICATED, CATALYST = A 1 INCH SQUARE EACH OF METALS INDICATED.

| TEST FLUID | DI-2-ETHYLHEXYL SEBACATE (PPL 3371) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| PHENOTHIAZINE CONCENTRATION, WT.% | NONE | 0.5 | NONE | 0.5 | NONE | 0.5 | 0.5 | 0.5 |
| TEST TIME, HOURS | 12 | 12 | 20 | 20 | 30 | 30 | 40 | 60 |
| LIQUID CHARGED, GRAMS | 90.0 | 90.0 | 90.0 | 91.0 | 90.0 | 90.0 | 90.0 | 91.0 |
| LIQUID LOSS, WT.% | 7 | 1 | 16 | 6 | 27 | 9 | 5 | 0 |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 15.7 | 15.7 | 26.2 | 26.2 | 39.3 | 39.3 | 52.4 | 78.6 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | 8.5 | 3.5 | 11.8 | 5.9 | 15.7 | 8.7 | 11.6 | 17.4 |
| APPROX. MOLS OF $O_2$ USED/MOL OF ESTER (426 GMS.) | 1.26 | 0.52 | 1.75 | 0.86 | 2.34 | 1.30 | 1.72 | 2.60 |
| % CHANGE IN VISCOSITY | | | | | | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | | | | | | | |
| AT 130°F. | +39 | +18 | +122 | +44 | SOLID(4) | +166 | +164 | SOLID(4) |
| AT 0°F. | +100 | +40 | +299 | +88 | SOLID(4) | +240 | +328 | SOLID(4) |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(3) | | | | | | | | |
| AT 130°F. | +38 | +12 | +58 | +4 | +62 | +51 | +45 | +50 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | | | | | |
| ORIGINAL | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| FINAL | 19.9 | 8.4 | 27.0 | 15.4 | 41.8 | 16.8 | 17.1 | 36.2 |
| WT.% OIL INSOLUBLE MATERIAL(2) | 0.1 | TRACE | 0.6 | 0.1 | -(4) | 0.8 | 0.9 | -(4) |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 2.1 | 1.4 | 7.0 | 4.8 | 22.2 | 6.9 | 8.7 | 25 |
| FINAL CATALYST CONDITION | | | | | | | | |
| APPEARANCE | | | | | | | | |
| COPPER | DULL | DULL | BRIGHT | DULL | DULL | DULL | CORRODED | CORRODED |
| STEEL | COATED | DULL | COATED | DULL | CORRODED | COATED | DULL | CORRODED |
| ALUMINUM | BRIGHT | BRIGHT | BRIGHT | BRIGHT | DULL | BRIGHT | BRIGHT | BRIGHT |
| WT. LOSS (MG./SQ. CM.) | | | | | | | | |
| COPPER | 0.04 | 0.08 | 0.02 | 0.10 | 0.07 | 0.07 | 0.75 | 0.52 |
| STEEL | +0.62 | 0.00 | +0.50 | 0.07 | 4.33 | +0.23 | 0.09 | 3.26 |
| ALUMINUM | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 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) 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.
(3) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.
(4) OXIDIZED FLUID WAS AN INTIMATE MIXTURE OF INSOLUBLE MATERIAL AND OXIDIZED LIQUID. OIL INSOLUBLES COULD NOT BE DETERMINED WITHOUT DILUTION.

Figure 25

EFFECT OF PHENOTHIAZINE ON OXYGEN ABSORPTION AT 500°F.

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME = 30 HOURS; AIR RATE = 5 ± 0.5 LITERS PER HOUR; AND CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.
OXYGEN ABSORPTION IS DETERMINED BY ANALYZING SAMPLES TAKEN FROM THE EXHAUST AIR STREAM FOR OXYGEN CONTENT.
PER CENT OXYGEN IS CALCULATED FROM THE DIFFERENCE IN THE OXYGEN CONTENT OF THE INLET AND EXHAUST AIR STREAMS.

| SYMBOL | TEST FLUID |
|---|---|
| ○ | DI-2-ETHYLHEXYL SEBACATE |
| □ | DI-2-ETHYLHEXYL SEBACATE + 0.5 WT.% PHENOTHIAZINE |

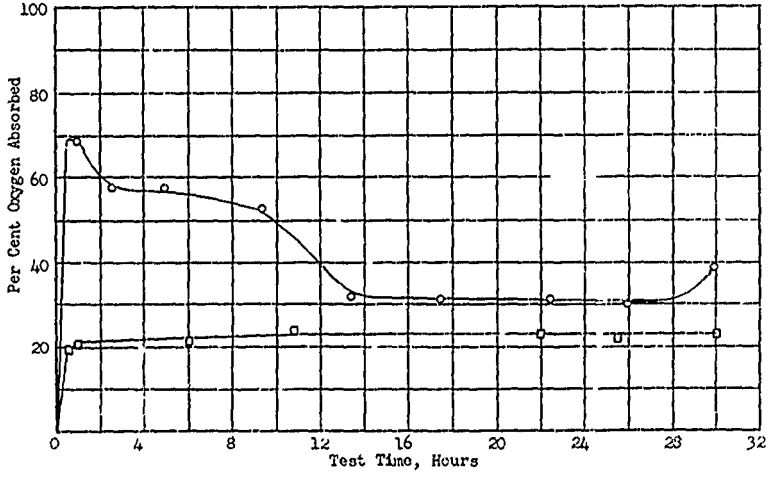


Table 48

EFFECT OF TRICRESYL PHOSPHATE ON OXIDATION AND CORROSION AT 500°F.

Test Conditions: Test Time - 20 Hrs.; Air Rate = 5 l./hr.; Test Fluid = 100 ml.; Catalyst = a 1 Inch Square of Each Metal.
Test Fluid = 0.5 Wt.% Phenothiazine in Di-2-Ethylhexyl Sebacate.

| | | | | |
|---|---|---|---|---|
| Tricresyl Phosphate, Wt.% | - | 5.0 | - | 5.0(1) |
| Acryloid HF-25, Wt.% | - | - | 3.9 | 3.9 |
| % Visc. Change at 130°F. | | | | |
| Oil Insol. Removed | +44 | +118 | -13 | +32 |
| Isopentane Insol. Removed | +4 | +79 | -22 | -23 |
| Neut. No. Increase | 15.3 | 15.2 | 13.6 | 13.3 |
| Wt.% Oil Insolubles | 0.1 | 3.6 | 0.2 | 3.3 |
| Wt.% Isopentane Insolubles | 4.8 | 8.3 | 3.5 | 8.6 |
| Catalyst Loss (Mg./Sq. Cm.) | | | | |
| Copper | 0.08 | 0.05 | 0.05 | 0.60 |
| Steel | 0.00 | +0.07 | +0.04 | +0.02 |
| Aluminum | 0.00 | +0.04 | 0.00 | 0.00 |

(1) This blend is equivalent to the finished fluid, PRL 3161.

These data indicate that the increased oxidative deterioration is due to the tricresyl phosphate anti-wear additive. The presence of the Acryloid has no deleterious effect on the oxidation stability of the fluid. The blend containing the Acryloid shows a viscosity loss, or less viscosity increase, on oxidation than does the phenothiazine-inhibited ester. It has previously been shown that these viscosity changes are due to the thermal properties of the Acryloid polymer and are not a direct function of oxidation.

The 500°F. oxidation and corrosion tests have been extended to include PRL 3161 type formulations containing alkyl acid phosphates and phosphites. These oxidation and corrosion results are shown on Tables 49, 50 and 51. A brief summary of test reproducibility may be helpful in understanding these data. Test results at 500°F. indicate that the deterioration noted in a given test is probably better expressed as a function of oxygen assimilated than as a function of test time.

Figure 26 shows a typical plot of deterioration properties for phenothiazine-inhibited di-2-ethylhexyl sebacate (PRL 3207) as a function of oxygen absorbed. These data have previously been presented in table form as Table 26 of report PRL 5.8-Sep53. These data indicate that property changes, such as sludge formation and neutralization number, are relatively gradual over the range of 0.5 to 1.5 moles of oxygen absorbed per mole of di-2-ethylhexyl sebacate. The molecular weight of di-2-ethylhexyl sebacate is 426 grams. The viscosity change over the same range of oxygen absorption is included on Figure 26. Since dirtiness is the primary point of comparison between the ester base



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stock and PRL 3161, a plot of isopentane insolubles versus oxygen assimilated is shown on Figure 27. Similar values for the ester (taken from Figure 26) are shown for comparison. These data indicate the striking difference in the rate of formation of isopentane insolubles.

The estimated overall reproducibility of measurement of the oxygen absorbed using the test techniques described in report PRL 5.8-Sep53 is shown on Figure 27. These limits are determined by the combined range in errors estimated for the measurement of air rate and the analysis of the exhaust gas for oxygen content in the range of test severity noted for the data on Tables 49, 50 and 51. It can be seen that for the same reproducibility of the test procedures, the PRL 3161 fluid shows a much wider range in the values of sludge formation than does the ester. In comparing the relative rates of oxygen assimilation on Table 49, it can be seen that much wide. limits of reproducibility are encountered if the comparative tests are based on time alone, without regard to the rate of oxygen assimilation.

The effect of varying the concentration of tricresyl phosphate and alkyl acid phosphites in a 20 hour, 500°F. oxidation and corrosion test is shown on Table 49. Two batches of di-2-ethylhexyl sebacate have been used for these studies. Both batches of ester show essentially identical physical properties and chemical stability. All of the blends shown on Table 49, which contain tricresyl phosphate or an alkyl acid phosphite, show an increased tendency to form sludge. The blends containing tricresyl phosphate do not show an increase in sludge forming tendencies with increasing tricresyl phosphate concentration in the range of 1 to 5 per cent. The differences in sludge values for blends containing tricresyl phosphate as noted for (1) the different grades of ester, (2) various concentrations of tricresyl phosphate, and (3) tests with or without metal catalysts are within the overall reproducibility limits indicated in the previous discussion of Figure 27.

Some trends are evident in the case of the blends containing alkyl acid phosphites as shown on Table 49. Increasing the concentration of alkyl acid phosphite from 0.1 to 1.0 weight per cent causes increased sludge formation. For a given acid phosphite concentration, the amount of sludge formed decreases with increasing size of the alkyl group. The effectiveness of the alkyl acid phosphite as a lubricity additive and as a synergist for oxidation inhibition also decreases with increasing size of the alkyl group. There appears to be no significant difference in sludging tendencies between 500°F. oxidation tests conducted with and without metal catalysts. Some minor differences can be seen between the blends with the same additive concentrations but different batches of di-2-ethylhexyl sebacate.

The data discussed above were obtained using phenothiazine as the oxidation inhibitor. Additional data for blends containing Paranox 441 in conjunction with an alkyl acid phosphite as the oxidation inhibitor are shown on Table 50. These data indicate about the same dirtiness level as the corresponding blend containing the phenothiazine instead of the Paranox 441. That is, a change of oxidation inhibitor does not change the basic dirtiness characteristics of the alkyl acid phosphites.

Data on the dirtiness characteristics of ester blends containing an alkyl acid phosphate are shown on Table 51. The composition evaluated in this study is PRL 3313, which contains 0.5 weight per cent of a commercial alkyl acid phosphate (Ortholeum 162). This is believed to be a lauryl acid phosphate composition. PRL 3313A is a fresh blend made up immediately prior to the oxidation test from raw materials available from the inventory of this Laboratory, while PRL 3313 is a commercial composition prepared by the Rohm and Haas Company and stored for a period of about 2 years before the evaluations shown on Table 51. These data show a very slight increased sludging tendency for the freshly prepared PRL 3313A over a fluid of similar composition without the acid phosphate (PRL 5.79). The PRL 3313 shows excessive sludge formation. The relatively poor storage stability of PRL 3313 is discussed in some detail in report PRL 5.8-Sep53.

All of the phosphorus-containing ester fluids evaluated at 500°F. in an accelerated oxidation test show increased sludging tendencies. The use of Paranox 441 instead of phenothiazine does not alter substantially these sludge forming tendencies. There is no appreciable difference in sludge forming tendencies between compositions of the PRL 3161 type prepared to the same lubricity level in the one case with 5.0 weight per cent tricresyl phosphate and in the second case with 0.1 weight per cent of an alkyl acid phosphite. More studies might profitably be made on the thermal and hydrolytic effects involved in sludge formation of ester blends containing alkyl acid phosphites.

3. Mineral Oil Oxidation Studies. The synergistic effect of alkyl acid phosphites on hindered phenols as oxidation inhibitors for ester type synthetic fluids has been discussed in report PRL 5.8-Sep53. Studies of the alkyl acid phosphite-hindered phenol inhibitors have been extended to mineral oils. These studies are a part of the revaluation program concerned with the oxidation stability of mineral oils in the high temperature range. A survey of mineral oil oxidation stability in the range of 350° to 500°F. has been undertaken primarily because of the current trend toward the use of closed hydraulic systems for high temperature applications.

The use of closed systems enables the amount of air or oxygen present in hydraulic systems to be greatly reduced. In such applications, oxidation stability may now be secondary to thermal stability in importance. On the basis of thermal stability, it has been shown in report PRL 5.8-Sep53 that some classes of mineral oils are equal or superior to many of the synthetic lubricants proposed as high temperature fluids. Oxidation studies at 500°F. for mineral oil fractions are discussed in report PRL 5.8-Sep53. This work indicates that under conditions of a limited supply of oxygen, the deterioration of mineral oils is not excessive and in many cases is tolerable. The tests presented here are oxidation and corrosion tests at 347°F. (175°C.). The relative measure of the stable life or induction period has been studied most frequently at 347°F. for ester type fluids.

Oxidation tests at 347°F. have been carried out with well refined naphthenic mineral oils. These naphthenic mineral oils represent

Figure 26

PROPERTIES OF DI-2-ETHYLHEXYL SEBACATE AT VARIOUS DEGREES OF OXIDATION AT 500°F.

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F., AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; AND CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.
TEST FLUID PRL 3207 = 0.5 WEIGHT PER CENT PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE.
NOTE: AFTER THE ABSORPTION OF APPROXIMATELY 2.6 MOLES OXYGEN/426 GRAMS OF FLUID, THE TEST FLUID WAS A INTIMATE MIXTURE OF LIQUID AND SOLIDS.

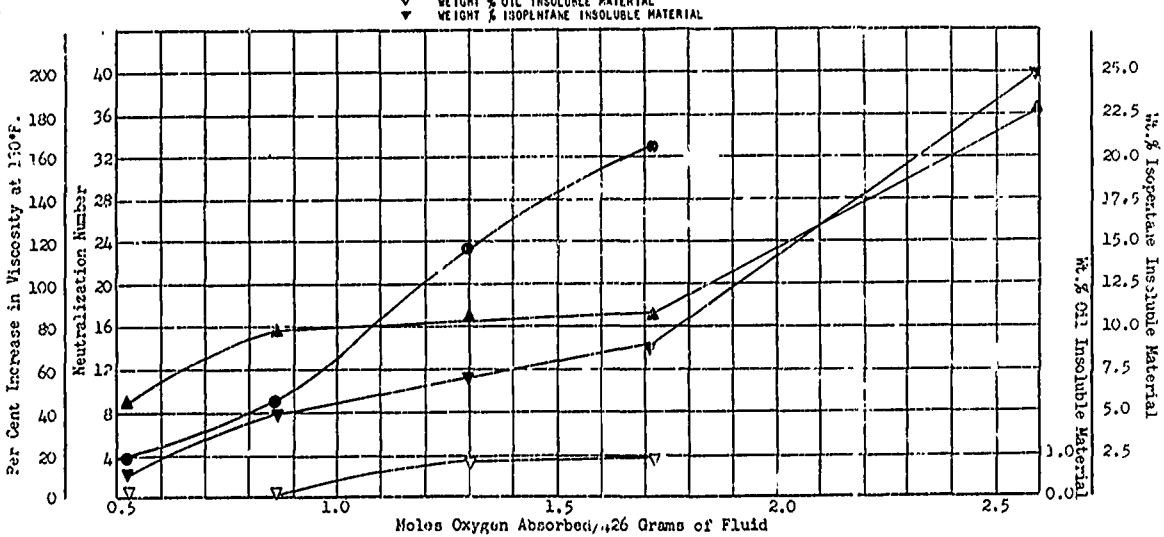


Figure 27

RATE OF FORMATION OF ISOPENTANE INSOLUBLES AT 500°F.

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; AND CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

TEST FLUIDS:

▼ = PRL 3161 (COMMERCIAL BATCH 5580), A SPEC. MIL-L-7808 TYPE SYNTHETIC GEAR LUBRICANT.
▽ = PRL 3207, 0.5 WT.% PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE.

NOTE: AFTER THE ABSORPTION OF APPROXIMATELY 1.3 MOLES OXYGEN/426 GRAMS OF FLUID, T . TEST FLUID WAS AN INTIMATE MIXTURE OF LIQUID AND SOLIDS.

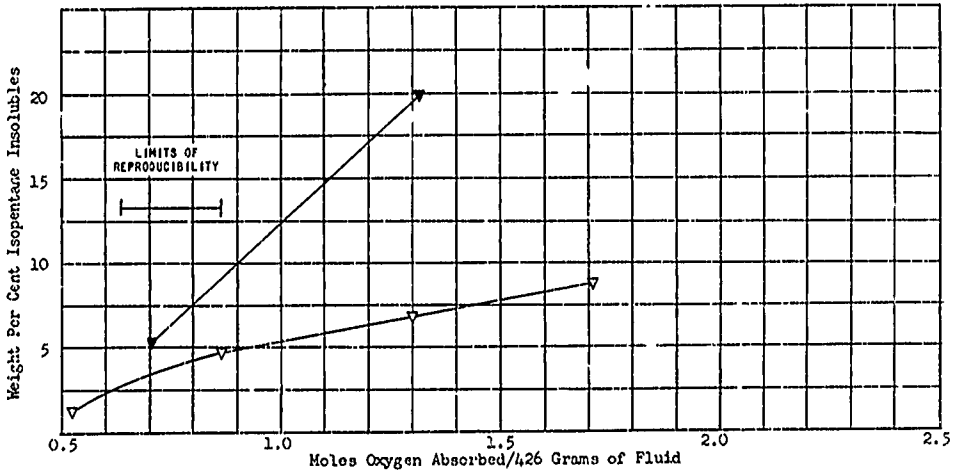


Table 49

THE EFFECT OF TRICRESYL PHOSPHATE AND DIALKYL ACID PHOSPHITES ON THE OXIDATION AND CORROSION STABILITY 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 = 20 HOURS; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL AND ALUMINUM WHERE INDICATED.
TEST FLUID: PRL 3207 = 0.5 WT.% PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE (PRL 3103).
PRL 3486 = 0.5 WT.% PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE (PRL 3371).

| TEST FLUID COMPOSITION | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| BASE STOCK | PRL 3207 | <---- PRL 3486 ----> | | PRL 3207 | PRL 3486 | PRL 3207 | <--PRL 3207--> | |
| ADDITIVE | <---------- | | TRICRESYL | PHOSPHATE | ---------- | ----------> | <----NONE----> | |
| WT.% OF ADDITIVE | 1.0 | 1.0 | 1.0 | 5.0 | 5.0 | 5.0 | - | - |
| LIQUID CHARGE, GRAMS | 90.0 | 90.5 | 90.0 | 90.0 | 90.0 | 90.0 | 90.5 | 90.0 |
| LIQUID LOSS, WT.% | 6 | 5 | 4 | 6 | 5 | 5 | 7 | 5 |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 26.2 | 26.2 | 26.2 | 26.2 | 26.2 | 26.2 | 26.2 | 26.2 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | 4.5 | 5.0 | 4.8 | 4.8 | 4.8 | 4.1 | 5.8 | 5.2 |
| APPROX. MOLES $O_2$ USED/426 GRAMS OF FLUID(4) | 0.66 | 0.72 | 0.69 | 0.69 | 0.69 | 0.59 | 0.83 | 0.75 |
| % CHANGE IN VISCOSITY | | | | | | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | | | | | | | |
| AT 130°F. | +71 | +52 | +37 | +118 | +44 | +32 | +44 | +58 |
| AT 0°F. | +158 | +83 | +76 | +146 | +77 | +54 | +88 | +159 |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) | | | | | | | | |
| AT 130°F. | +12 | +12 | +12 | +79 | +12 | +20 | +4 | +12 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | | | | | |
| ORIGINAL | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| FINAL | 15.7 | 12.9 | 14.3 | 15.3 | 12.7 | 15.7 | 15.4 | 15.6 |
| WT.% OIL INSOLUBLE MATERIAL(2) | 6.3 | 6.6 | 2.2 | 3.6 | 1.7 | 2.5 | 0.1 | 0.2 |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 9.2 | 10.3 | 5.1 | 8.3 | 4.7 | 4.4 | 4.8 | 3.9 |
| FINAL CATALYST CONDITION | | | | | | | | |
| APPEARANCE: | | | | | | | | |
| COPPER | CORRODED | CORRODED | CORRODED | CORRODED | CORRODED | - | DULL | - |
| STEEL | DULL | DULL | DULL | DULL | DULL | - | DULL | - |
| ALUMINUM | DULL | DULL | DULL | DULL | DULL | - | BRIGHT | - |
| WT. LOSS (MG./SQ. CM.) | | | | | | | | |
| COPPER | 0.81 | 0.74 | 0.36 | 0.50 | 0.40 | - | 0.10 | - |
| STEEL | 0.06 | +0.09 | 0.06 | +0.07 | 0.00 | - | 0.07 | - |
| ALUMINUM | 0.06 | +0.04 | 0.13 | +0.04 | 0.00 | - | 0.00 | - |

(CONCLUDED ON NEXT PAGE)

Table 49 (Concluded)

| TEST FLUID COMPOSITION | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| BASE STOCK | PRL 3207 | | PRL 3446 | | PRL 3207 | PRL 3486 | PRL 3207 | |
| ADDITIVE | DIBUTYL ACID PHOSPHITE | | | | | DIMETHYL ACID PHOSPHITE | | |
| WT.% OF ADDITIVE | 0.1 | 1.0 | 0.1 | 1.0 | 0.1 | 0.1 | 0.1 | 1.0 |
| LIQUID CHARGE, GRAMS | 90.0 | 90.5 | 91.0 | 90.5 | 90.0 | 90.5 | 90.0 | 90.0 |
| LIQUID LOSS, WT.% | 4 | 12 | 4 | 12 | 5 | 4 | 4 | 26 |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 26.2 | 26.2 | 26.2 | 26.2 | 26.2 | 26.2 | 26.2 | 26.2 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | 5.4 | 6.0 | 5.5 | 5.8 | [illegible] | 5.5 | 6.2 | 4.3 |
| APPROX. MOLES $O_2$ USED/426 GRAMS OF FLUID(4) | 0.78 | 0.86 | 0.79 | 0.83 | 0.70 | 0.79 | 0.89 | 0.62 |
| % CHANGE IN VISCOSITY | | | | | | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | | | | | | | |
| AT 130°F. | +30 | +116 | +32 | +82 | +23 | +78 | +25 | - |
| AT 0°F. | +53 | +277 | +55 | +156 | +53 | +170 | +47 | - |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) | | | | | | | | |
| AT 130°F. | +12 | +32 | | +34 | +15 | +13 | +15 | +97 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | | | | | |
| ORIGINAL | 0.[illegible] | 1.2 | 0.2 | 1.2 | 0.[illegible] | 0.2 | 0.2 | 0.6 |
| FINAL | 15.4 | 64.1 | 14.2 | 5.8 | 18.9 | 19.2 | 17.5 | 12.1 |
| WT.% OIL INSOLUBLE MATERIAL(2) | 2.9 | 6.6 | 3.3 | 22.9 | 2.1 | 3.7 | 1.7 | 22.6 |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 4.8 | 11.3 | 5.5 | 25.1 | 4.2 | 8.0 | 3.9 | 29.5 |
| FINAL CATALYST CONDITION | | | | | | | | |
| APPEARANCE | | | | | | | | |
| COPPER | CORRODED | CORRODED | CORRODED | CORRODED | - | CORRODED | - | - |
| STEEL | DULL | COATED | DULL | COATED | - | DULL | - | - |
| ALUMINUM | DULL | COATED | DULL | COATED | - | DULL | - | - |
| WT. LOSS (MG./SQ. CM.) | | | | | | | | |
| COPPER | 0.44 | 0.41 | 0.31 | 0.39 | - | 0.61 | - | - |
| STEEL | 0.05 | +0.07 | +0.08 | +0.39 | - | 0.00 | - | - |
| ALUMINUM | 0.06 | +0.12 | 0.00 | +0.14 | - | +0.02 | - | - |

(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) 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.

(3) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.

(4) THE MOLS OF $O_2$ FOR 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE $O_2$ ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYL-HEXYL SEBACATE IS 426.

Table 50

OXIDATION AND CORROSION CHARACTERISTICS OF DI-2-ETHYLHEXYL SEBACATE AT 500°F.

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST TIME = 20 HOURS; TEST FLUID CHARGED = 100 ML., CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL AND ALUMINUM.

| TEST FLUID | DI-2-ETHYLHEXYL SEBACATE (FEL 3371) | | | |
|---|---|---|---|---|
| OXIDATION INHIBITOR, WT.% | 1.0 PARANOX 441 | | | 0.5 PHENOTHIAZINE |
| LUBRICITY ADDITIVE, WT.% | 1.0 PHOSPHOROUS ACID | 1.0 DIMETHYL ACID PHOSPHITE | 1.0 DIBUTYL ACID PHOSPHITE | NONE |
| LIQUID CHARGED, GMS. | 90.5 | 89.5 | 91.0 | 90.0 |
| LIQUID LOSS, WT.% | 34 | 27 | 15 | 7 |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 26.2 | 26.2 | 26.2 | 26.2 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | 3.1 | 5.6 | 6.0 | 5.2 |
| MOLES $O_2$ USED/MOL OF FLUID (426 GMS.) | 0.47 | 0.83 | 0.90 | 0.86 |
| % CHANGE IN VISCOSITY | | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | | | |
| AT 130°F. | SOLID(4) | +119 | +93 | +44 |
| AT 0°F. | SOLID(4) | +372 | +290 | +48 |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) | | | | |
| AT 130°F. | +160 | - | +40 | +4 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | |
| ORIGINAL | 12.4 | 1.0 | 0.9 | 0.1 |
| FINAL | 215.9 | 99.4 | 51.9 | 15.4 |
| WT.% OIL INSOLUBLE MATERIAL(2) | -(4) | 14.6 | 7.2 | 0.1 |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 29.0 | 18.7 | 13.7 | 4.8 |
| FINAL CATALYST CONDITION | | | | |
| APPEARANCE | | | | |
| COPPER | DULL | COATED | CORRODED | DULL |
| STEEL | COATED | COATED | COATED | DULL |
| ALUMINUM | COATED | CORRODED | DULL | BRIGHT |
| WT. LOSS (MG./SQ. CM.) | | | | |
| COPPER | 0.02 | +0.44 | 0.49 | 0.10 |
| STEEL | +2.30 | +1.37 | +0.94 | 0.07 |
| ALUMINUM | +0.64 | 0.29 | 0.08 | 0.00 |

(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) 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.
(3) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.
(4) OXIDIZED FLUID WAS AN INTIMATE MIXTURE OF INSOLUBLE MATERIAL AND OXIDIZED LIQUID. OIL INSOLUBLES COULD NOT BE DETERMINED WITHOUT DILUTION

Table 51

THE EFFECT OF A COMMERCIAL ACID PHOSPHATE ON THE OXIDATION AND CORROSION STABILITY OF A SYNTHETIC GEAR LUBRICANT AT 500°F.

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME = 20 HOURS; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML., CATALYST = A 1 INCH SQUARE E[illegible] COPPER, STEEL, AND ALUMINUM.
TEST FLUID: PRL 3379 = 9.0 WT.% ACRYLOID HF-25 + 0.5 % [illegible]ENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE.
PRL 3313A = PRL 3379 + 0.5 WT.% ORTHOLEUM [illegible] A COMMERCIAL ACID PHOSPHATE) + 5.0 WT.% TRICRESYL PHOSPHATE (BLEND FRESHLY PREPARED AT PRL).
PRL 3313 = BATCH 6931 (COMMERCIALLY PREPARED BLEND CONTAINING ORTHOLEUM 162 AFTER APPROX. 2 YEARS STORAGE AT ROOM TEMPERATURE).

| TEST FLUID | PRL 3379 | PRL 3313A | PRL 3313 | PRL 3313 |
|---|---|---|---|---|
| LIQUID CHARGE, GRAMS | 90.5 | 90.0 | 93.5 | 95.5 |
| LIQUID LOSS, WT.% | 5 | [illegible] | 5 | 15 |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 26.2 | 26.2 | 26.2 | 26.2 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | - | 5.6 | | 4.6 |
| MOLES $O_2$ USED/426 GMS. OF FLUID(4) | - | 0.04 | - | 0.64 |
| % CHANGE IN VISCOSITY | | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | | | |
| AT 130°F. | -51 | -11 | +152 | +81 |
| AT [illegible]°F. | -38 | +30 | +418 | +312 |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) | | | | |
| AT 130°F. | -54 | -29 | -20 | -31 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | |
| ORIGINAL | 0.1 | 5.1 | 7.2 | 6.8 |
| FINAL | 15.1 | 32.8 | 64.5 | 43.6 |
| WT % OIL INSOLUBLE MATERIAL(2) | 0.1 | 0.6 | 23.6 | 26.0 |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 2.5 | 5.6 | 33.1 | 35.3 |
| FINAL CATALYST CONDITION | | | | |
| APPEARANCE | | | | |
| COPPER | DULL | CORRODED | CORRODED | CORRODED |
| STEEL | DULL | CORRODED | CORRODED | CORRODED |
| ALUMINUM | BRIGHT | DULL | DULL | DULL |
| WT. LOSS (MG./SQ. CM.) | | | | |
| COPPER | 0.14 | 0.47 | 0.55 | 1.02 |
| STEEL | 0.02 | 4.46 | 3.44 | 2.92 |
| ALUMINUM | 0.02 | +0.02 | 0.09 | 0.14 |

(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) 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.
(3) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.
(4) THE MOLES OF $O_2$ FOR 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE $O_2$ ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYLHEXYL SEBACATE IS 426.

a good class of low temperature oils derived from petroleum. Most stable life oxidation studies previously made on this type of mineral oil have been carried out in the temperature range of 200° to 300°F. Under these conditions, using a low molecular weight (gas oil fraction) naphthenic oil, good oxidation stability has been noted. At temperatures above 300°F. the hindered phenol type inhibitors give less protection in a naphthenic light oil fraction than can be obtained readily from a phenothiazine-inhibited ester. The solubility of phenothiazine in mineral oil limits its use here.

The data on Table 52 show the results of a Spec. MIL-L-7808 oxidation and corrosion test with Voltesso 36 containing various oxidation inhibitors. The approximate stable life, or induction period, is shown on Table 52 for comparison. Reference data for a typical blend of a commercial grade di-2-ethylhexyl sebacate inhibited with 0.5 weight per cent phenothiazine are also shown as a basis of comparison. Voltesso 36 is a highly refined naphthenic white oil of about 10 centistokes viscosity at 100°F. Two batches of Voltesso 36 (PRL 3456 and PRL 3134) are used interchangeably in this study.

The data on Table 52 indicate that all of the inhibitors evaluated show some improvement in the 72 hour test over the Voltesso 36 without an inhibitor. The inhibitor types represented by the trade names are: Paranox 441, a hindered phenol; Antioxidant 2246, a hindered phenol; Paranox 1, an alkyl phenol sulfide; and Lubrizol 328, a metallic salt of an organic dithiophosphate. The only inhibitors showing a stable life in excess of the 72 hour test time are phenyl alpha naphthylamine and the dibutyl acid phosphite-hindered phenol mixed inhibitor. None of these three blends meet entirely the Spec. MIL-L-7808 oxidation and corrosion requirements. All three fluids would probably be considered operational after this 72 hour test.

The data on Table 52 illustrate the advantages of the hindered phenol-alkyl acid phosphite mixture as an oxidation inhibitor for mineral oils. The studies of the synergistic effect of the alkyl acid phosphites on Paranox 441 and on Antioxidant 2246 are shown on Tables 53 and 54, respectively. These data emphasize the effect of varying the size of the alkyl group in the alkyl acid phosphite. These tests are standard Spec. MIL-L-7808 oxidation and corrosion tests of 72 hours' duration. Again the approximate stable life or induction period of the finished composition is shown on Tables 53 and 54 as a basis of comparison. The stable life curves in which neutralization number is plotted as a function of time are shown on Figures 28 and 29.

Interpretation of the data on Table 53 is somewhat involved by the fact that the tests shown, with the exception of the two containing dimethyl acid phosphite and dibutyl acid phosphite, indicate by the final neutralization number that the point of incipient oxidation has been reached. The effect of alkyl group size on the dialkyl phosphite appears to be much less pronounced in the mineral oil than in the di-2-ethylhexyl sebacate as reported in PRL 5.8-Sep53. There is, however, a trend to indicate that a decrease in alkyl group size improves both

oxidation stability and corrosion properties toward metals. The same size alkyl group in a dialkyl acid phosphite has correspondingly less coating or more corrosion tendency in the Voltesso 36 than in the di-2-ethylhexyl sebacate.

The reduction of sludge formation in the Paranox 441-alkyl acid phosphite blends is appreciable. It has been noted previously that one of the principle functions of the acid phosphite synergist in an ester fluid is that of a metal coating agent or deactivator in the ester. For this reason, a blend of 1.0 weight per cent Paranox 441 in Voltesso 36 has been tested without metal catalysts. This test shows signs of incipient oxidation. These tests indicate that, while metal deactivation may be a function of the alkyl acid phosphites, this is not the sole mechanism of the synergistic effect of the Paranox 441-dialkyl acid phosphite inhibitor. The very low values of sludge, or dirtiness, in the Paranox 441-dialkyl acid phosphite additives are noteworthy. The data on Figure 28 also emphasize the reduced effect of alkyl group size in the dialkyl acid phosphites in the mineral oil as compared to the ester. In a di-2-ethylhexyl sebacate blend containing 1.0 weight per cent Paranox 441 and 0.5 weight per cent dialkyl acid phosphite, a stable life at 347°F. of 65 hours is noted for di-2-ethylhexyl acid phosphite compared with a stable life in excess of 290 hours for dimethyl acid phosphite.

The data presented on Table 54 are for the mineral oil-alkyl acid phosphite blends to which Antioxidant 2246 instead of Paranox 441 has been added in 1.0 weight per cent concentration. The results with Antioxidant 2246 are similar to those obtained with the same base materials containing Paranox 441 with two notable exceptions. There is an increase in the stable life of the fluids containing Antioxidant 2246 over those containing Paranox 441 as shown in Figure 29. There is also an increase in the dirtiness tendencies of the blends containing the Antioxidant 2246. These data indicate that sludge formation during the stable life, or induction period, is encountered.

Data are presented on Table 55 to illustrate the changes in fluid properties encountered in Voltesso 36 blends which are subjected to oxidation and corrosion tests in excess of the stable life. These blends contain Paranox 441-alkyl acid phosphite inhibitors. In general, these data as compared with the data on Table 53, indicate that all of the fluid properties as well as the metal coating or corroding trends are increasing more rapidly in the period following the stable life. The stable life interval is determined by a plot of neutralization number versus time. The point at which the neutralization number shows a sharp increase in rate of change with time is considered the end of the stable life or induction period. In general, more evidence of oxidative deterioration and metal corrosion are noted within the stable life, or induction period, with Voltesso 36 and mineral oils of this type than with dibasic acid esters as discussed in previous reports.

The tests discussed on Tables 52 through 55 have been conducted with a low viscosity naphthenic mineral oil (Voltesso 36). Additional oxidation and corrosion data, using the same inhibitor combinations and

test conditions, have been determined for two more viscous naphthenic mineral oils. These naphthenic oils are Esstic 45 and Necton 55. All of these naphthenic mineral oils have been obtained as commercial products of the Standard Oil Company of New Jersey. Esstic 45 has a 100°F. viscosity of 44.6 centistokes compared with a value of 98.0 centistokes for Necton 55. These fluids have been evaluated in the 72 hour, 347°F., oxidation and corrosion test of Spec. MIL-L-7808.

The data for Esstic 45 blends are shown on Table 56. Similar data for Necton 55 are shown on Table 57. Samples of Esstic 45 and Necton 55 without an anti-oxidant have been run as a basis of comparison. The property changes of the non-additive Esstic 45 compare favorably with those of Voltesso 36 (Table 52) and Necton 55 (Table 57) under the same conditions. There are, however, substantial differences to the response of these three naphthenic oils to oxidation inhibitors. The Esstic 45 and Necton 55 show much less beneficial effect from the addition of oxidation inhibitors than does Voltesso 36. Some of the same inhibitor trends noted with Voltesso 36 are still evident with the heavier naphthenic oils.

The problems of copper corrosion and sludge formation are the property changes most difficult to control in the Esstic 45 and Necton 55 oils. In Esstic 45 and Necton 55, only the alkyl acid phosphite-Paranox 441 combinations show a trend toward reduction in the formation of sludge. The remaining inhibitors, and combinations of inhibitors, tested show as much or more sludge than the uninhibited mineral oils. The phenyl alpha naphthylamine shows good corrosion control in the Esstic 45 and Necton 55 oils. The alkyl-acid phosphite-hindered phenol combinations all show copper corrosion in Necton 55 and Esstic 45 while some of the alkyl acid phosphites with small alkyl groups (methyl and butyl) show a tendency to coat rather than corrode copper in combination with a hindered phenol in Voltesso 36.

In view of the difference in behavior noted for the same additives in naphthenic mineral oils of different molecular weight ranges, several stable life tests were attempted in one of the more viscous mineral oils (Esstic 45). The data for neutralization number increase versus time for these tests are shown in Figure 30. These curves do not show a characteristic break in the rate of change of neutralization number normally considered indicative of an induction period or stable life. The curve for the Antioxidant 2246-dimethyl acid phosphite combination indicates a reduced rate of neutralization number increase, but again there is no break in the curve indicative of induction period.

The Paranox 441-dialkyl acid phosphite inhibitor combination has been evaluated in a finished Spec. MIL-O-5606 fluid in accordance with the Spec. MIL-L-7808 oxidation and corrosion test. These data are shown on Table 58. They show that the blend of 1.0 weight per cent Paranox 441 and 0.5 weight per cent dimethyl acid phosphite in a Spec. MIL-O-5606 formulation shows adequate stability in this severe oxidation and corrosion test. The blend containing Paranox 441 and dibutyl acid phosphite shows indications of incipient oxidation.

Table 52

OXIDATION AND CORROSION PROPERTIES OF A NAPHTHENIC TYPE MINERAL OIL 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 ~ 10 ± 1 LITERS PER HOUR; FLUID CHARGE = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM AND MAGNESIUM.
TEST FLUID: PRL 3134 AND PRL 3456 = A HIGHLY REFINED NAPHTHENIC GAS OIL FRACTION (VOLTESOL 36).
PRL 3371 = DI-2-ETHYLHEXYL SEBACATE.

| TEST FLUID | PRL 3456 | PRL 3134 | | | | | | | PRL 3371 |
|---|---|---|---|---|---|---|---|---|---|
| OXIDATION INHIBITOR, WT.% | — | 1.0 PARANOX 441 | 1.0 PARANOX 441 + 0.5 DIBUTYL ACID PHOSPHITE | 1.0 ANTI-OXIDANT 2246 | 1.0 ANTI-OXIDANT 2246 + 0.5 DIBUTYL ACID PHOSPHITE | 1.0 PHENYL-α-NAPHTHYLAMINE | 1.0 PARANOX I | 1.0 LUBRIZOL 328 | 0.5 PHENO-THIAZINE |
| APPROX. STABLE LIFE, HRS.(1) | <5 | 56 | 90 | 30 | 150 | 110 | <72 | <72 | 150 |
| LIQUID LOSS, WT.% | 3 | 10 | 4 | - | 2 | - | - | - | 2 |
| % CHANGE IN VISCOSITY | | | | | | | | | |
| AT 130°F. | +50 | +45 | +7 | +29 | +2 | +12 | +5 | +23 | +2 |
| AT 0°F. | +150 | +202 | +19 | +110 | +4 | +39 | +19 | +88 | +5 |
| A.S.T.M. COLOR | | | | | | | | | |
| ORIGINAL | 1 | 1 | 2 | 1 | 1 | 7 | 1-1/2 | 1 | 1 |
| FINAL | >8 | >8 | 7 | >8 | >8 | 8 | >8 | >8 | >8 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | | | | | | |
| ORIGINAL | 0.0 | 0.0 | 0.1 | 0.1 | 0.1 | 0.1 | 1.2 | 0.9 | 0.1 |
| FINAL | 12.7 | 4.6 | 0.6 | 7.7 | 0.6 | 0.2 | 2.1 | 7.1 | 1.2 |
| WT.% OIL INSOLUBLE MATERIAL | 5.8 | 1.1 | 0.2 | 4.7 | 0.8 | 0.5 | 3.6 | 4.2 | 0.5 |
| FINAL CATALYST CONDITION | | | | | | | | | |
| APPEARANCE | | | | | | | | | |
| COPPER | CORRODED | CORRODED | CORRODED | DULL | COATED | DULL | CORRODED | CORRODED | DULL |
| STEEL | DULL | DULL | CORRODED | DULL | COATED | DULL | DULL | COATED | DULL |
| ALUMINUM | DULL | BRIGHT | DULL | DULL | DULL | DULL | COATED | COATED | DULL |
| MAGNESIUM | DULL | BRIGHT | COATED | DULL | COATED | DULL | COATED | COATED | BRIGHT |
| WT. LOSS (MG./SQ. CM.) | | | | | | | | | |
| COPPER | 0.46 | 0.24 | 0.20 | 0.09 | +0.29 | 0.00 | 0.28 | 1.76 | 0.00 |
| STEEL | +0.01 | 0.00 | 0.65 | 0.00 | +0.16 | 0.00 | +0.06 | +0.15 | 0.00 |
| ALUMINUM | +0.06 | 0.00 | +0.11 | +0.01 | +0.02 | 0.01 | +0.15 | +0.11 | +0.02 |
| MAGNESIUM | +0.09 | +0.02 | +0.53 | +0.06 | +0.64 | 0.01 | +0.30 | +0.13 | 0.00 |

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

Table 53

OXIDATION AND CORROSION CHARACTERISTICS OF A NAPHTHENIC TYPE MINERAL OIL AT 347°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDICTIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F.; TEST TIME = 72 HOURS; AIR RATE [illegible] ± [illegible] LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF [illegible]R, STEEL, ALUMINUM AND MAGNESIUM EXCEPT IN TEST NOTED.
TEST FLUID VOLTESSO 36 = A HIGHLY REFINED NAPHTHENIC GAS OIL FRACTION (PRL 3134 OR PRL 3456).

| TEST FLUID | VOLTESSO 36 + 1.0 WT.% PARANOX 441 | | | | | |
|---|---|---|---|---|---|---|
| ALKYL ACID PHOSPHITE, WT.% | NONE | NONE | 0.5 DIMETHYL ACID PHOSPHITE | 0.5 DIETHYL ACID PHOSPHITE | 0.5 DIBUTYL ACID PHOSPHITE | 0.5 PHOSPHOROUS ACID |
| APPROX. STABLE LIFE, HOURS(1) | 50 | 45 | 75 | 75 | 80 | - |
| OVERALL LIQUID LOSS, WT.% | 10 | - | - | - | - | - |
| % CHANGE IN VISCOSITY | | | | | | |
| AT 130°F. | +45 | +32 | +5 | +27 | +7 | +16 |
| AT 0°F. | +202 | +175 | +17 | +86 | +19 | +54 |
| NEUT. NO. (MG. KOH/GM. OIL): | | | | | | |
| ORIGINAL | 0.0 | 0.0 | 0.3 | 0.2 | 0.1 | 0.1 |
| FINAL | 4.6 | 7.2 | 1.0 | 3.1 | 0.6 | 2.9 |
| A.S.T.M. UNION COLOR: | | | | | | |
| ORIGINAL | 1 | 1 | 2 | 2 | 2 | 2 |
| FINAL | >8 | >8 | 7 | 8 | 7 | 8 |
| WT.% OIL INSOLUBLE MATERIAL | 1.1 | 1.2 | 0.1 | 0.2 | 0.2 | 0.2 |
| FINAL CATALYST CONDITION | | | | | | |
| APPEARANCE | | | | | | |
| COPPER | CORRODED | - | DULL | DULL | CORRODED | DULL |
| STEEL | DULL | - | DULL | DULL | CORRODED | DULL |
| ALUMINUM | BRIGHT | - | DULL | DULL | DULL | BRIGHT |
| MAGNESIUM | BRIGHT | - | COATED | COATED | COATED | COATED |
| WT. LOSS (MG./SQ. CM.) | | | | | | |
| COPPER | 0.24 | - | +0.08 | +0.09 | 0.20 | 0.10 |
| STEEL | 0.00 | - | +0.02 | +0.02 | 0.65 | 0.05 |
| ALUMINUM | 0.00 | - | 0.04 | 0.02 | +0.11 | 0.01 |
| MAGNESIUM | +0.02 | - | +0.36 | +0.70 | +0.53 | +0.13 |

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

Table 54

OXIDATION AND CORROSION CHARACTERISTICS OF A NAPHTHENIC MINERAL OIL FRACTION AT 347°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-6387.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F.; TEST TIME = 72 HOURS; AIR RATE = 10 ± 1 LITERS PER HOUR; TEST FLUID = 100 ML.; CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.
TEST FLUID VOLTESSO 36 = A HIGHLY REFINED NAPHTHENIC GAS OIL FRACTION (PRL 3134 OR PRL 3456).

| TEST FLUID | <---------- VOLTESSO 36 + 1.0 WT.% ANTIOXIDANT 2246 ------ | | | |
|---|---|---|---|---|
| ALKYL ACID PHOSPHITE, WT.% | NONE | 0.5 DIMETHYL ACID PHOSPHITE | 0.5 DIBUTYL ACID PHOSPHITE | 0.5 BIS (2-ETHYL HEXYL) ACID PHOSPHITE |
| APPROX. STABLE LIFE, HOURS(1) | 30 | 150 | 140 | 80 |
| LIQUID LOSS, WT.% | - | 1 | 1 | 1 |
| % CHANGE IN CENTISTOKE VISCOSITY | | | | |
| AT 130°F. | +29 | +2 | +3 | +2 |
| AT [illegible]°F. | +110 | +4 | +4 | +3 |
| A.S.T.M. UNION COLOR | | | | |
| ORIGINAL | 1 | 1 | 1 | 1 |
| FINAL | 7 | >8 | >8 | >8 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | |
| ORIGINAL | 0.1 | 0.3 | 0.5 | 0.5 |
| FINAL | 7.7 | 0.9 | 0.7 | 0.3 |
| WT.% OIL INSOLUBLE MATERIAL | 4.7 | 1.6 | 1.4 | 1.4 |
| FINAL CATALYST CONDITION | | | | |
| APPEARANCE | | | | |
| COPPER | DULL | COATED | COATED | CORRODED |
| STEEL | DULL | DULL | DULL | DULL |
| ALUMINUM | DULL | BRIGHT | DULL | BRIGHT |
| MAGNESIUM | DULL | COATED | COATED | DULL |
| WT. LOSS (MG./SQ. CM.) | | | | |
| COPPER | 0.09 | +0.18 | +0.61 | 0.20 |
| STEEL | 0.00 | 0.06 | 0.00 | 0.03 |
| ALUMINUM | +0.01 | 0.02 | 0.04 | 0.02 |
| MAGNESIUM | +0.05 | +0.43 | +0.70 | +0.02 |

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

Figure 28

OXIDATION STABILITY OF A NAPHTHENIC MINERAL OIL FRACTION AT 347°F.

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

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F.; TEST TIME AS INDICATED; AIR RATE = 10 ± 1 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; AND CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

| SYMBOL | ALKYL ACID PHOSPHITE | TEST FLUID |
|---|---|---|
| ▽ | NONE | 1.0 WT.% PARANOX 441 IN VOLTESSO 36 (A HIGHLY REFINED NAPHTHENIC GAS OIL; 9 CS. AT 100°F.) |
| ○ | 0.5 DIMETHYL ACID PHOSPHITE | |
| △ | 0.5 DIETHYL ACID PHOSPHITE | |
| ▲ | 0.5 DIISOPROPYL ACID PHOSPHITE | |
| □ | 0.5 DIBUTYL ACID PHOSPHITE | |
| ■ | 0.5 DI-2-ETHYLHEXYL ACID PHOSPHITE | |

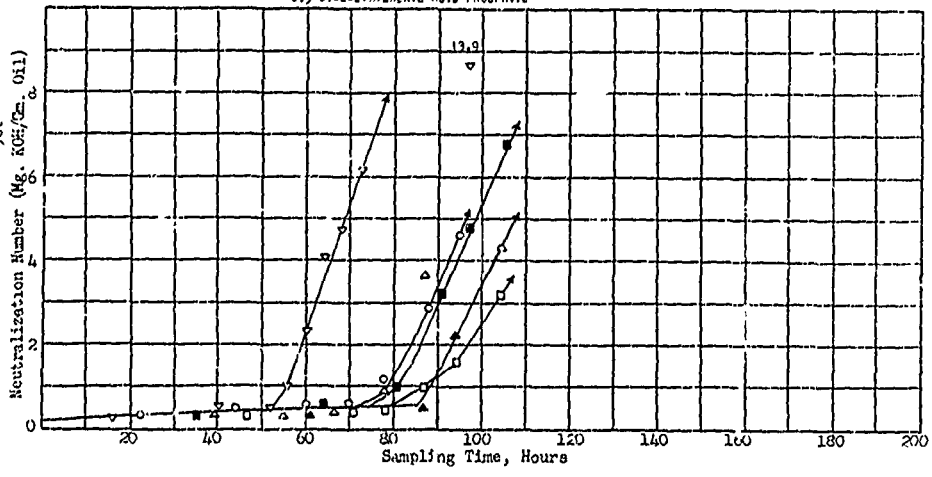


Figure 29

OXIDATION STABILITY OF A NAPHTHENIC TYPE MINERAL OIL FRACTION 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 = 10 ± 1 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; AND CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

| SYMBOL | ALKYL ACID PHOSPHITE, WT.% | TEST FLUID |
|---|---|---|
| ○ | NONE | VOLTESSO 36 |
| △ | NONE | VOLTESSO 36 (1.0 WT.% ANTIOXIDANT 2246 IN VOLTESSO 36 (A HIGHLY REFINED NAPHTHENIC GAS OIL; 9 CS. AT 100°F.) |
| ● | 0.5 DIMETHYL ACID PHOSPHITE | |
| ▲ | 0.5 DIBUTYL ACID PHOSPHITE | |
| ▽ | 0.5 BIS(2-OCTYL) ACID PHOSPHITE | |

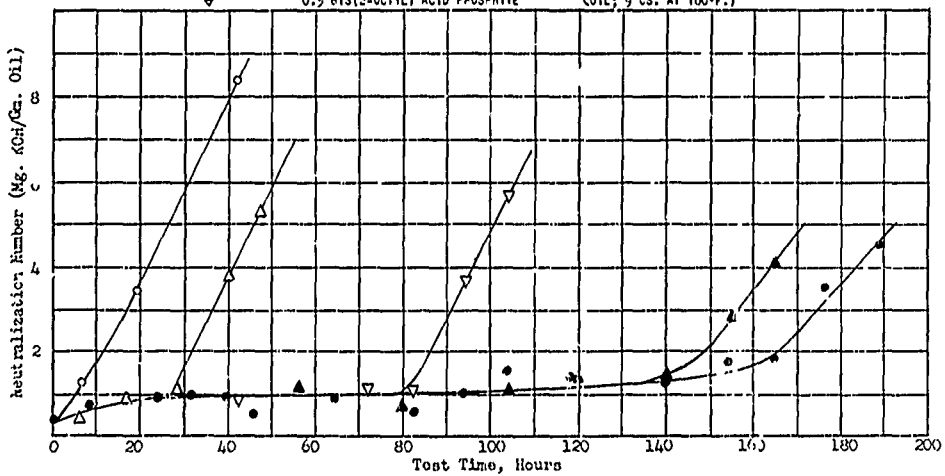


Table 55

OXIDATION AND CORROSION CHARACTERISTICS OF A NAPHTHENIC MINERAL OIL FRACTION AT 347°F.

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F.; TEST TIME AS INDICATED; AIR RATE = 10 ± 1 LITERS PER HOUR;
TEST FLUID CHARGE = 100 ML.; AND CATALYST = A 1 INCH SQUARE EACH OF METALS INDICATED.
TEST FLUID VOLTESSO 36 = A HIGHLY REFINED NAPHTHENIC GAS OIL FRACTION (PRL 3134 OR PRL 3456).

| TEST FLUID | VOLTESSO 36 | <- - - - - - - - - - - - 1.0 WEIGHT PER CENT PARANOX 441 IN VOLTESSO 36 - - - - - - - - - - - - -> | | | | | |
|---|---|---|---|---|---|---|---|
| ALKYL ACID PHOSPHITE, WT.% | NONE | NONE | 0.5 DIMETHYL ACID PHOSPHITE | 0.5 DIETHYL ACID PHOSPHITE | 0.5 DIISOPROPYL ACID PHOSPHITE | 0.5 DIBUTYL ACID PHOSPHITE | 0.5 DI-2-ETHYLHEXYL ACID PHOSPHITE |
| TEST TIME, HOURS | 96 | 97 | 98 | 94 | 113 | 113 | 113 |
| APPROX. STABLE LIFE, HOURS(1) | <5 | 50 | 75 | 75 | 90 | 85 | 75 |
| % CHANGE IN VISCOSITY | | | | | | | |
| AT 130°F | +75 | +40 | +18 | +19 | +20 | +16 | +32 |
| AT 0°F. | +253 | +205 | +68 | +95 | +132 | +111 | +119 |
| NEUT. NO. (MG. KOH/GM. OIL): | | | | | | | |
| ORIGINAL | 0.0 | 0.1 | 0.2 | 0.2 | 0.1 | 0.2 | 0.1 |
| FINAL | 17.4 | 13.9 | 4.3 | 4.6 | 4.6 | 3.3 | 7.1 |
| A.S.T.M. UNION COLOR: | | | | | | | |
| ORIGINAL | 1 | 1-1/2 | 2 | 2 | 2 | 2 | 2 |
| FINAL | >8 | >8 | >8 | >8 | 8 | 8 | >8 |
| WT.% INSOLUBLE MATERIAL | 15.1 | 5.1 | 1.6 | 0.8 | 0.8 | 0.5 | 3.4 |
| FINAL CATALYST CONDITION | | | | | | | |
| APPEARANCE | | | | | | | |
| COPPER | CORRODED | DULL | COATED | CORRODED | COATED | COATED | CORRODED |
| STEEL | COATED | DULL | DULL | COATED | COATED | COATED | COATED |
| ALUMINUM | DULL | DULL | DULL | COATED | DULL | COATED | COATED |
| MAGNESIUM | DULL | DULL | COATED | COATED | COATED | COATED | COATED |
| WT. LOSS (MG./SQ. CM.) | | | | | | | |
| COPPER | 0.37 | 0.34 | +0.12 | 1.09 | +1.19 | +3.30 | 1.60 |
| STEEL | +0.15 | +0.03 | +0.08 | +0.22 | +0.44 | +0.29 | +0.11 |
| ALUMINUM | +0.06 | +0.01 | +0.08 | +0.16 | +0.02 | +0.10 | +0.10 |
| MAGNESIUM | 0.00 | +0.04 | +0.62 | +0.98 | +0.53 | +1.15 | +0.12 |

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

Table 56

OXIDATION AND CORROSION PROPERTIES OF A NAPHTHENIC TYPE MINERAL OIL A 3457.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F.; TEST TIME = 72 HOURS; AIR RATE = 10 ± 1 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.
TEST FLUID: PRL 3457 = FOSTIC 45, A NAPHTHENIC MINERAL OIL OF 45 CENTISTOKES VISCOSITY AT 100°F. OBTAINED FROM THE STANDARD OIL COMPANY OF NEW JERSEY.

| TEST FLUID | PRL 3457 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| OXIDATION INHIBITOR, WT.% | - | 1.0 PARANOX 441 | 1.0 PHENYL-α-NAPHTHYL-AMINE | 1.0 ANTIOXIDANT 2246 | 1.0 ANTIOXIDANT 2246 | | | 1.0 PARANOX 441 | | |
| ACID PHOSPHITE, WT.% | - | - | - | - | 0.5 DIMETHYL ACID PHOSPHITE | 0.5 DIETHYL ACID PHOSPHITE | 0.5 DI-2-ETHYLHEXYL ACID PHOSPHITE | 0.5 DIMETHYL ACID PHOSPHITE | 0.5 DIBUTYL ACID PHOSPHITE | 0.5 PHOSPHOROUS ACID |
| OVERALL LIQUID LOSS, WT.% | - | 2 | 2 | 2 | 1 | 2 | 1 | 1 | 1 | 2 |
| % CHANGE IN VISCOSITY AT 130°F. | +35 | +40 | +37 | +29 | +12 | +11 | +11 | +17 | +21 | +26 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | | | | | | | |
| ORIGINAL | 0.3 | 0.2 | 0.2 | 0.1 | 0.5 | 0.9 | 0.4 | 0.1 | 0.7 | 0.6 |
| FINAL | 5.5 | 5.5 | 6.8 | 7.2 | 2.3 | 2.1 | 2.2 | 2.2 | 3.2 | 4.3 |
| A.S.T.M UNION COLOR: | | | | | | | | | | |
| ORIGINAL | 2 | 2 | 3 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| FINAL | >8 | >8 | >8 | >8 | >8 | >8 | >8 | >8 | >8 | >8 |
| WT.% OIL INSOLUBLE MATERIAL | 4.4 | 5.1 | 5.9 | 5.8 | 5.9 | 5.3 | 6.1 | 1.6 | 3.6 | 6.7 |
| FINAL CATALYST CONDITION | | | | | | | | | | |
| APPEARANCE | | | | | | | | | | |
| COPPER | CORRODED | CORRODED | DULL | DULL | CORRODED | CORRODED | CORRODED | CORRODED | CORRODED | CORRODED |
| STEEL | DULL | DULL | DULL | DULL | COATED | DULL | DULL | COATED | COATED | COATED |
| ALUMINUM | BRIGHT | BRIGHT | DULL | DULL | COATED | COATED | DULL | COATED | COATED | COATED |
| MAGNESIUM | - | BRIGHT | DULL | BRIGHT | COATED | COATED | DULL | COATED | COATED | COATED |
| WT LOSS (MG./SQ. CM.) | | | | | | | | | | |
| COPPER | 0.34 | 0.29 | 0.06 | 0.11 | 1.11 | 0.25 | 0.53 | 1.35 | 2.01 | 1.13 |
| STEEL | +0.01 | +0.06 | +0.09 | +0.02 | +0.14 | +0.09 | +0.01 | +0.11 | +0.43 | +0.77 |
| ALUMINUM | 0.00 | +0.02 | 0.00 | +0.02 | +0.13 | +0.10 | +0.04 | +0.19 | +0.15 | +0.17 |
| MAGNESIUM | - | +0.06 | +0.07 | 0.00 | +0.56 | +0.91 | +0.02 | +0.74 | +0.94 | +1.14 |

Table 57

OXIDATION AND CORROSION PROPERTIES OF A NAPHTHENIC TYPE MINERAL OIL AT 347°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F.; TEST TIME = 72 HOURS, AIR RATE = 10 [illegible] LITERS PER HOUR; TEST FLUID CHANGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.
TEST FLUID: PRL 2054 = NICTON 55, A NAPHTHENIC MINERAL OIL OF 98 CENTISTOKES VISCOSITY AT 100°F. OBTAINED FROM THE STANDARD OIL COMPANY OF NEW JERSEY.

| TEST FLUID | PRL 2054 | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| OXIDATION INHIBITOR, WT.% | NONE | 1.0 PARANOX 441 | 1.0 PHENYL-α-NAPHTHYLAMINE | 1.0 ANTI-OXIDANT 2246 | 1.0 ANTIOXIDANT 2246 | | 1.0 PARANOX 441 | |
| ACID PHOSPHITE, WT.% | NONE | NONE | NONE | NONE | 0.5 DIMETHYL ACID PHOSPHITE | 0.5 DIBUTYL ACID PHOSPHITE | 0.5 DIMETHYL ACID PHOSPHITE | 0.5 DIBUTYL ACID PHOSPHITE |
| OVERALL LIQUID LOSS, WT.% | 0 | 7 | 2 | 5 | 0 | 5 | 0 | 0 |
| % CHANGE IN VISCOSITY AT 130°F. | +111 | +129 | +43 | +74 | +5 | +26 | +63 | +20 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | | | | | |
| ORIGINAL | 0.1 | 0.1 | 0.1 | 0.1 | 0.7 | 0.0 | 0.2 | 0.2 |
| FINAL | 6.2 | 6.2 | 2.5 | 4.9 | 1.9 | 2.1 | 5.2 | 1.6 |
| A.S.T.M. UNION COLOR: | | | | | | | | |
| ORIGINAL | 3 | 3 | 4 | 3 | 3 | 3 | 2 | 2 |
| FINAL | >8 | >8 | >8 | >8 | >8 | >8 | >8 | >8 |
| WT % OIL INSOLUBLE MATERIAL | 4.4 | 5.8 | 3.6 | 4.2 | 2.7 | 2.9 | 2.1 | 0.3 |
| FINAL CATALYST CONDITION | | | | | | | | |
| APPEARANCE | | | | | | | | |
| COPPER | DULL | CORRODED | DULL | DULL | CORRODED | CORRODED | CORRODED | CORRODED |
| STEEL | DULL | DULL | DULL | DULL | DULL | COATED | DULL | DULL |
| ALUMINUM | DULL | DULL | DULL | BRIGHT | DULL | COATED | DULL | DULL |
| MAGNESIUM | DULL | DULL | DULL | BRIGHT | COATED | COATED | COATED | COATED |
| WT. LOSS (MG./SQ. CM.) | | | | | | | | |
| COPPER | 0.19 | 0.29 | 0.05 | 0.06 | 0.64 | 0.61 | 1.40 | 1.20 |
| STEEL | 0.02 | 0.02 | +0.01 | +0.02 | +0.04 | +0.35 | +0.08 | +0.02 |
| ALUMINUM | +0.01 | 0.02 | 0.02 | 0.00 | +0.07 | +0.50 | +0.08 | +0.01 |
| MAGNESIUM | 0.03 | +0.02 | 0.00 | 0.00 | +0.48 | +0.73 | +0.42 | +0.04 |

Figure 30

OXIDATION STABILITY OF A NAPHTHENIC TYPE MINERAL OIL FRACTION 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 = 10 ± 1 LITERS PER HOUR, TEST FLUID CHARGED = 100 ML.; AND CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, ALUMINUM, AND MAGNESIUM.

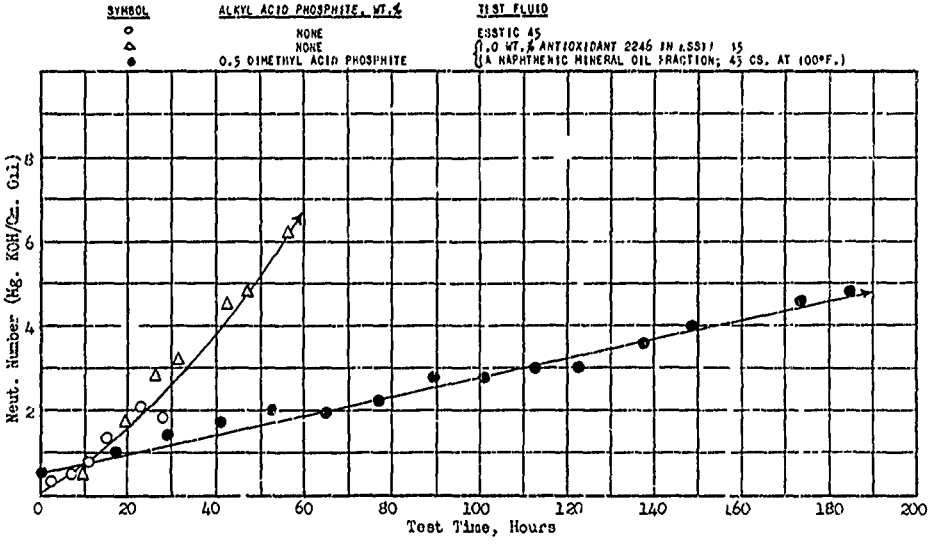


Table 58

OXIDATION AND CORROSION CHARACTERISTICS OF A SPEC. MIL-O-5606 TYPE HYDRAULIC FLUID AT 347°F.

PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347 ± 3°F.; TEST TIME = 72 HOURS; AIR RATE = 10 ± 1 LITERS PER HOUR; TEST FLUID = 100 ML.; AND CATALYST = A 1 INCH SQUARE EACH OF THE INDICATED METALS.
TEST FLUID: PRL 3453 = A SPEC. MIL-O-5606 TYPE HYDRAULIC FLUID WITHOUT AN ANTI-OXIDANT.

| TEST FLUID | <- - - - - - - - - - - - PRL 3453 - - - - - - - - - - - -> | | |
|---|---|---|---|
| ANTI-OXIDANT, WT.% | <- - - - - - - - - - - 1.0 PARANOX 441 - - - - - - - - - - -> | | |
| ALKYL ACID PHOSPHITE, WT.% | NONE | 0.5 DIMETHYL ACID PHOSPHITE | 0.5 DIBUTYL ACID PHOSPHITE |
| OVERALL LIQUID LOSS, WT.% | 0 | 0 | 2 |
| % CHANGE IN VISCOSITY | | | |
| AT 130°F. | -25 | +3 | -4 |
| AT 0°F. | +40 | +10 | +15 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | |
| ORIGINAL | 0.0 | 0.3 | 0.2 |
| FINAL | 6.0 | 0.4 | 2.2 |
| WT.% INSOLUBLE MATERIAL | 0.1 | 0.1 | 1.7 |
| FINAL CATALYST CONDITION | | | |
| APPEARANCE | | | |
| COPPER | DULL | COATED | COATED |
| STEEL | DULL | DULL | COATED |
| ALUMINUM | BRIGHT | DULL | COATED |
| MAGNESIUM | BRIGHT | COATED | DULL |
| WT. LOSS (MG./SQ. CM.) | | | |
| COPPER | 0.12 | +0.20 | +0.29 |
| STEEL | +0.04 | +0.03 | +0.20 |
| ALUMINUM | +0.05 | +0.02 | +0.20 |
| MAGNESIUM | 0.02 | +0.33 | +0.03 |

Alkyl acid phosphite-hindered phenol inhibitor combinations offer enhanced oxidation and corrosion stability at high temperatures in mineral oils as well as in diester compositions. Phenyl alpha naphthylamine is also a good high temperature oxidation inhibitor for mineral oils. There are, in general, more indications of oxidative deterioration and corrosion in the 347°F. oxidation and corrosion tests for the mineral oils during the so-called induction period, or stable life, than is the case in the diester fluids evaluated previously by this laboratory. The effect of a given inhibitor to control property changes and corrosion of metals during the induction period of a 347°F. oxidation and corrosion test decreases as the molecular weight, or viscosity grade, of the same type of mineral oil increases.

4. Oxidation Stability After Storage. It has been noted that synthetic fluids containing acid phosphate or acid phosphite lubrication additives show an increase in neutralization number on storage. This neutralization number increase on storage has been investigated for acid phosphates and acid phosphites prepared from primary alcohols and for acid phosphites prepared from secondary alcohols. A more complete discussion of neutralization number increase and change in lubricity on storage has been given previously in this report.

A summary of the observed neutralization number increases is shown in Table 59. These samples have been stored in stoppered glass bottles at room temperature (70° to 80°F.) and opened only for sampling. PRL 3379 is an Acryloid-ester blend containing phenothiazine as an antioxidant.

Table 59

NEUTRALIZATION NUMBER CHANGE AFTER STORAGE

| Base Fluid | Phosphorus Cmpd., Wt.% | | Orig. Neut. No. | Storage Time, Mos. | Neut. No. After Storage |
|---|---|---|---|---|---|
| PRL 3379 | 0.5 | Dilauryl Acid Orthophosphate | 2.0 | 15 | 12.0 |
| PRL 3379 | 0.5 | Dimethyl Acid Phosphite | 0.6 | 13 | 19.1 |
| PRL 3379 | 0.5 | Diisopropyl Acid Phosphite | 0.2 | 13 | 2.5 |
| PRL 3379 | 0.5 | Dibutyl Acid Phosphite | 0.1 | 13 | 12.9 |
| PRL 3379 | 0.5 | Di-2-Ethylhexyl Acid Phosphite | 0.1 | 13 | 6.7 |
| PRL 3379 | 0.5 | Bis (2-Octyl) Acid Phosphite | 0.5 | 13 | 2.0 |

It can be noted from Table 59 that the two acid phosphites prepared from secondary alcohols (diisopropyl and bis (2-octyl) acid phosphites) are much more stable to neutralization number change with storage than the other materials shown. This may be due to the fact that the esters prepared from secondary alcohols would be expected to be more stable to hydrolysis. Previous data have shown that this phenomenon of neutralization number increase on storage may be related to hydrolysis stability.

Some Spec. MIL-L-7808 type oxidation tests conducted with storage samples of fluids containing acid phosphate and acid phosphite lubricity

additives are discussed in report PRL 5.8-Sep53. In general, fluids containing acid phosphates, which have been stored at room temperature for approximately one year, exhibit increased metal corrosion and sludge formation in the Spec. MIL-L-7808 oxidation test at 347°F. Blends containing acid phosphites also show a trend toward metal corrosion after storage. However, the resulting metal corrosion is not as severe as that encountered with the acid phosphate-containing blends.

The blends containing the two secondary acid phosphites, which have been stored at room temperature for approximately 13 months, have now been evaluated for oxidative behavior in the Spec. MIL-L-7808 oxidation and corrosion test (72 hours at 347°F.). The properties of the fluids following these tests along with the properties obtained with the same blend when it was freshly prepared, are shown on Table 60.

Both of these blends show good oxidation stability following the 13 months storage period. There appears to be no trend toward increased sludging. In the fluid containing the diisopropyl acid phosphite, the catalyst coating tendency is still present following storage. In the case of the fluid containing the bis (2-octyl) acid phosphite, the coating tendency is no longer present. However, there is no appreciable tendency to corrode any of the test metals under the oxidation conditions.

Wear tests carried out in the Shell four-ball E.P. lubricant test with the stored blend indicate that there is little change in the activity of the acid phosphite as an anti-wear additive following the Spec. MIL-L-7808 oxidation and corrosion test over that of the freshly prepared blend.

5. Interrelation of Copper-Beryllium Alloy and Oxidation and Corrosion Deterioration. It has been requested that this Laboratory investigate the effect of copper-beryllium alloy on the oxidation stability of hydraulic fluids and lubricants. This request has been made primarily with respect to hydraulic fluid evaluations. The detailed discussion of these studies is given in the section of this report dealing with hydraulic fluids. The results of these studies are here summarized briefly. Mineral oil- and ester-base fluid and lubricant compositions have been included in this study. Some of the ester-base compositions include gear lube formations containing alkyl acid phosphate and phosphite type additives. Oxidation tests were conducted at 347°F. and 500°F.

The data indicate that copper-beryllium alloy does have some effect on the oxidation stability of hydraulic fluids and lubricants of the types evaluated. This effect appears to be intermediate between that exerted by metals such as copper and bronze and that shown by metals such as steel and aluminum. The copper-beryllium alloy does not appear to be affected adversely by the types of hydraulic fluids used in this study under the test conditions outlined. That is, in terms of corrosion by the fluids, copper-beryllium appears to be somewhat better than pure copper.

6. Oxidation and Corrosion Evaluation at 500°F. The studies of oxidation at 500°F. as a function of oxygen assimilated and oxidation

Table 60

OXIDATION AND CORROSION PROPERTIES OF SOME SYNTHETIC GEAR LUBRICANTS AFTER STORAGE AT ROOM TEMPERATURE

TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 347°F.; TEST TIME = 72 HOURS; AIR RATE = 10 ± 1 LITERS PER HOUR; FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF THE METALS INDICATED.
TEST FLUID PRL 3379 - 9.0 WT.% ACRYLOID PF-25 + 0.5 WT.% PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE.

| TEST FLUID | 0.5 WT.% DIISOPROPYL ACID PHOSPHITE IN PRL 3379 | | 0.5 WT.% BIS(2-OCTYL) ACID PHOSPHITE IN PRL 3379 | |
|---|---|---|---|---|
| STORAGE TIME, MOS. | 0 | 13 | 0 | 13 |
| LIQUID LOSS, WT.% | 2 | 3 | 1 | 3 |
| % CHANGE IN VISCOSITY | | | | |
| AT 130°F. | +5 | +9 | +7 | +8 |
| AT 0°F. | +7 | +11 | +11 | +11 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | |
| ORIGINAL | 0.2 | 2.5 | 0.7 | 2.0 |
| FINAL | 3.7 | 5.4 | 2.9 | 5.3 |
| A.S.T.M. UNION COLOR: | | | | |
| ORIGINAL | 1-1/2 | 3 | 1-1/2 | 3 |
| FINAL | >8 | >8 | >8 | >8 |
| WT.% OIL INSOLUBLE MATERIAL | 0.9 | 0.4 | TRACE | 0.1 |
| FINAL CATALYST CONDITION | | | | |
| APPEARANCE | | | | |
| COPPER | COATED | COATED | COATED | DULL |
| STEEL | COATED | COATED | COATED | DULL |
| ALUMINUM | COATED | COATED | COATED | DULL |
| MAGNESIUM | COATED | COATED | COATED | DULL |
| WT. LOSS (MG./SQ. CM.) | | | | |
| COPPER | +0.33 | +0.47 | +0.65 | 0.09 |
| STEEL | +0.93 | +0.15 | +0.27 | 0.01 |
| ALUMINUM | +0.14 | +0.11 | +0.29 | +0.03 |
| MAGNESIUM | +0.02 | +0.99 | +1.05 | 0.02 |

rate have been continued along the same lines discussed in report PRL 5.8-Sep53. The same group of chemical classes studied as high temperature hydraulic fluids and discussed in the previous section of this report are also included in this preliminary evaluation of 500°F. oxidation and corrosion properties. The following classes of compounds are included in this study.

1. Silicones
2. Silicate esters
3. Dibasic acid esters
4. Mineral oils
5. Pentaerythritol esters
6. Synthetic hydrocarbons
7. Polyglycol ether (Ucon)
8. Chlorinated biphenyl (Aroclors)

This series of semi-quantitative tests have been conducted with each test fluid under the same test conditions for different time intervals. During the test, the oxygen assimilated by the test fluid is determined by periodic analysis of the exhaust gas composition. The common test conditions include a test temperature of 500°F.; an air rate of 5 liters per hour at standard conditions; a 100 ml. sample of test fluid; and the presence of a one inch square each of copper, steel, and aluminum sheet. The procedures and techniques used, with the exception of time and temperature, are essentially those of Spec. MIL-L-7808. The results of these tests can be compared either on the basis of the same times (oxidation rate) or the same degree of oxygen assimilated. Previous data obtained with these techniques are summarized in Table 61. In all cases, an attempt has been made to show the test for the longest estimated useful life and an additional test representing extensive fluid deterioration. Additional oxidation and corrosion data of this type are presented in Tables 62 through 76. These oxidation data continue to indicate that, with very few exceptions, extensive oxidation occurs at 500°F. The materials evaluated exhibit no appreciable stable life or induction period at 500°F.

Aroclor 1248 shows the best oxidation stability of the materials evaluated thus far at 500°F. Data for this fluid are shown on Table 62. Moderate copper corrosion is the only substantial evidence of oxidation or corrosion even after 120 hours at 500°F. The copper corrosion occurs even under short time tests and does not increase in rate of corrosion in the 120 hour test as compared with the 12 hour test. A very small but measurable amount of oxygen is absorbed at a steady rate throughout the oxidation. This same material shows excellent thermal stability to temperatures of 750°F. in the absence of air (under a nitrogen blanket). Aroclor 1248 has several properties which are limitations under current specification jet engine oil properties. Aroclor 1248 attacks current low temperature rubbers causing excessive swelling and softening. This material also has a relatively limited liquid range, exhibiting a pour point of 20°F. and a boiling point of about 700°F. It should be noted, however, that Aroclor 1248 shows excellent non-inflammability properties. In addition, this material shows little or no volatile product formation on thermal stability. Hence, it is believed that the excellent non-inflammability

properties of the Aroclor 1248 would be maintained with use at high temperature.

Silicone fluids have been evaluated at 500°F. as shown on Tables 61, 63, 64 and 65. A 510 type silicone obtained from the Dow Corning Corporation shows very good oxidation and corrosion stability at 500°F. This material is believed to be a methylphenyl silicone. This material shows good oxidation and corrosion stability for 124 hours in the 500°F. test (Table 63). The rate of oxygen assimilated and the resultant rate of property changes appear to be about constant over the entire test period. There is no indication of dirtiness or sludging tendencies with the 510 type silicone even under the most severe 500°F. tests. Methylphenyl silicones of this general character can be prepared to have a wide liquid range, excellent viscosity-temperature characteristics, and good thermal stability. It is generally conceded, however, that the major weak spot in the methylphenyl silicone properties is the limited lubricity properties particularly for steel-on-steel. The other silicone compositions are designed specifically to gain improved lubricity.

Oxidation and corrosion data for General Electric Silicones No. 81406 and No. 81451 are shown on Tables 61 and 64. These silicones have been modified chemically to obtain greatly improved steel-on-steel lubricity in laboratory lubricity testers such as the Shell four-ball wear and E.P. lubricant testers. These two improved lubricity silicones exhibit oxidation properties intermediate between the methylphenyl silicones and the Spec. MIL-L-7808 type ester base stocks. In general, the rate of oxygen assimilation is about the same for the methylphenyl silicones and the two improved lubricity silicones. However, the resultant property changes, primarily viscosity increase, are much more severe for the improved lubricity silicones. Moderate copper corrosion has been noted in all 500°F. evaluations with the two silicones with improved lubricity. It would appear that the modification of the silicone to improve lubricity results in a reduction in oxidation and corrosion stability. In terms of tests of equal time, these improved lubricity silicones still show an improved oxidation stability at 500°F. by a factor of 2 to 3 over a typical Spec. MIL-L-7808 ester base stock. However, on the basis of property changes for a given amount of oxygen assimilated, these silicones appear to be among the poorest lubricants evaluated in the 500°F. test. Gellation occurs with relatively small quantities of oxygen assimilated for these improved lubricity silicones.

Lubricant SD-17 is a silicone 510-di-2-ethylhexyl sebacate blend developed by the NACA to overcome the lubricity deficiencies of the silicones by the addition of a solvent. The composition of SD-17 comprises a 2:1 (by volume) mixture of Dow Corning 510 silicone of 100 centistokes viscosity grade and di-2-ethylhexyl sebacate. This mixture is inhibited against oxidation with 0.5 weight per cent phenothiazine. Oxidation and corrosion tests with SD-17 composition are shown on Table 65. These data indicate severe oxidative deterioration for SD-17 under relatively short 500°F. tests This composition exhibits excessive sludge or dirtiness under the mildest test conditions. The oxidized fluid also appears to separate upon standing to form two liquid phases. It is interesting to note by comparing the data on Tables 61, 63 and 65 that the

oxidative deterioration of SD-17 composition is far more severe for a given time or a given amount of oxygen assimilated than for either of its two components. On the basis of lubricity tests in the four-ball testers and a high temperature Vickers vane pump, the lubricity of SD-17 appears to be much poorer than that of di-2-ethylhexyl sebacate itself.

Oxidation and corrosion tests at 500°F. have been conducted with several silicate ester-base formulations. Fluids O.S. 45 and MLO 8200 are commercial silicate ester-base formulations. MLO 5277 is also a complete fluid formulation while tetra-2-ethylhexyl silicate (PRL 3455, is an uninhibited silicate ester. These oxidation data are shown on Tables 61, 66 and 67. The silicates, in general, tend to form excessive amounts of volatile oxidation products.

Isopentane is a conventional sludge precipitant for mineral oils. It is also a satisfactory precipitant for esters and polyglycol ethers but is not a satisfactory sludge precipitant for silicates and silicones. That is, the oxidized silicates and silicones show the conventional high viscosity increase on oxidation but essentially no isopentane insolubles. This does not necessarily mean that the oxidized fluids do not contain small quantities of relatively highly oxidized materials. The neutralization numbers after oxidation are low with silicates and silicones indicating a lack of non-volatile acidic oxidation products. The acidity of the volatile fragments of oxidation are not measured in this test procedure.

The tetra-2-ethylhexyl silicate, O.S. 45, and MLO 5277 show an oxidation stability of the same order of magnitude as that of the typical dibasic acid ester base stocks used in Spec. MIL-L-7808 fluids. MLO 8200 silicate fluid shows a substantial improvement in oxidation stability over the other silicate fluids evaluated. It is believed that this improvement is achieved primarily by the use of additives to reduce the oxidation rate rather than the use of a more inherently stable silicate ester base stock. The loss in viscosity with mild oxidation noted for MLO 5277 and MLO 8200 as compared to the substantial viscosity increase noted with the other two silicates evaluated under the same test conditions is probably due to the additive used to improve the viscosity-temperature properties employed in the former fluids. Some of the silicate ester fluids studied show moderate steel corrosion and slight copper corrosion under severe 500°F. oxidation tests. These same trends are evident with dibasic acid esters of the Spec. MIL-L-7808 type.

Tridecyl pelargonate, which is a monobasic acid, has been evaluated in the 500°F. oxidation and corrosion test and compared with a typical dibasic acid ester of the Spec. MIL-L-7808 type. These comparative data are shown on Tables 61 and 68. The behavior of tridecyl pelargonate and di-2-ethylhexyl sebacate are quite similar under the same 500°F. oxidation and corrosion test conditions. It is interesting to note that both esters show the same trend toward slight copper corrosion and moderate steel corrosion with increasing test severity. The relationship between viscosity increase and sludge formation for the tridecyl pelargonate resembles that of the dibasic acid esters. That is, these esters show a relatively low rate of sludge formation accompanied by a buildup of larger

oxidized molecules which are isopentane insoluble and appear to cause the large viscosity increase in the oxidized fluid.

Results of 500°F. oxidation tests with a Ucon (LB-135) polyglycol-ether type lubricant are summarized on Table 61. These data indicate that the Ucon, like the silicates, tends to form excessive amounts of volatile oxidation products. The rate of oxidation and the oxygen tolerance for this Ucon lubricant appears to be about the same order of magnitude as di-2-ethylhexyl sebacate. It is also interesting to note that the Ucon lubricant, like the dibasic acid ester, shows some steel corrosion with severe oxidation. Recent 500°F. tests with a Ucon LB-170X show the same trends as the Ucon LB-135.

Several synthetic hydrocarbons prepared by polymerizing olefins have been included in this study. These materials are polybutenes received from the Standard Oil Company of Indiana. Hydrocarbons as a class are of interest in this high temperature lubricant study because of the promising results obtained in high temperature oxidation tests with a well refined mineral oil fraction (Necton 45) as shown on Table 61. These mineral oil data indicate that as the temperature of the test increases the margin of difference between the mineral oils and synthetics diminishes. The olefin polymers have been chosen to represent essentially an isoparaffinic structure. Two viscosity levels (110 and 15 centistokes at 100°F.) are represented by the three polybutenes. PRL 3440 and PRL 3473 are polybutenes containing some unsaturation, presumably one olefinic linkage per molecule. PRL 3474 has been saturated to the isoparaffin by hydrogenation.

The 500°F. oxidation and corrosion data for these three polybutenes are shown on Tables 69, 70 and 71. The rate of oxygen assimilation for these materials is about the same as that of the esters and mineral oil fraction (Necton 45). No corrosion is noted even under severe oxidation for these materials. The amount of oxygen assimilated, and the time of ultimate failure of the three polybutenes are the same for the saturated and unsaturated samples. However, there appears to be a significant difference in the behavior of the unsaturated and saturated samples in terms of the related phenomena of sludge formation and viscosity increase. The unsaturated samples show a very low rate of sludge formation and isopentane insoluble formation. The viscosity increase noted is moderately high and is not reduced by the removal of the isopentane insolubles. The saturated polybutene (PRL 3474) shows a low value for viscosity increase but a relatively high rate of sludge and isopentane insoluble product formation. These data indicate that the oxidative attack on the unsaturated molecules is more general (widely distributed) than in the case of the saturated polybutene. That is a high viscosity increase accompanied by little or no sludge or isopentane insoluble material indicates that essentially all of the molecules show some attack by oxygen. In the case of the saturated polybutene, it would appear that a molecule once attacked by oxygen is more susceptible to further attacks than the starting material, resulting in a small amount of sludge compared to the general viscosity increase. At the high temperatures of this oxidation test, the unsaturated polybutenes would appear to be more desirable than the saturated polybutene. It is believed that viscosity increase of the fluid is more desirable with oxidation than is sludge formation.

Several specific hydrocarbon types have been evaluated at 500°F. in the oxidation test. These data are presented on Tables 72, 73, 74, 75 and 76. These data may be compared with the data for Necton 45 (a well-refined naphthenic mineral oil) shown on Table 61. Paraffin, naphthene, and aromatic hydrocarbons are represented in this study. These data confirm the fact that hydrocarbons exhibit good corrosion characteristics at 500°F. even under severe oxidation. In general, the cetane and triamylcyclohexane show a higher rate of oxygen absorbed than the aromatic materials evaluated. Sovaloid is a commercial aromatic mineral oil concentrate obtained from the Socony-Vacuum Oil Company. The material was described by Socony-Vacuum as follows:

> A synthetic product made by a chemical rearrangement of petroleum hydrocarbons. It is composed entirely of polycyclic aromatic hydrocarbons, in which three- and four-ring compounds predominate.

It is interesting to note that, of the three aromatic compounds evaluated, the Sovaloid shows a substantially higher rate of isopentane insolubles and sludge formation than the other two. These data indicate that dirtiness or sludge formation is characteristic of the more complicated polynuclear aromatics.

The compounds chosen to evaluate hydrocarbon types are in most cases not applicable directly to jet engine oil use. They have been evaluated to establish trends in oxidation for comparison with typical low pour point naphthenic mineral oils (e.g. Necton 45) and low pour point synthetic hydrocarbons (polybutene). No substantial improvement in high temperature oxidation stability would be expected from the further refining of Necton 45 on the basis of the study on pure hydrocarbons. The polybutene products may represent an improvement in dirtiness characteristics over Necton 45 in the 500°F. oxidation and corrosion tests. The polybutene fractions are not as thermally stable as the Necton 45 or naphthenic mineral oils in general.

These high temperature oxidation data indicate that essentially all of the fluids evaluated undergo extensive oxidation at 500°F. The fluids (Aroclor 1248 and a methylphenyl silicone) showing the best high temperature oxidation properties exhibit the most serious deviations from the other desired properties of a jet engine oil. Thus, it would appear that the use of either of these lubricants with good oxidation stability would require substantial mechanical changes or lubricant system component changes.

A comparison of the oxidation stability of the remaining fluids with the thermal stability data shown on Tables 4 and 5 of this report as well as data presented in previous reports shows clearly the large advantages to be gained in fluid stability and useful life by the elimination or severe limitation of oxygen in the fluid system. Thus, it appears that any mechanical steps that can be taken to seal completely or at least seal partially the lubricant system from the surrounding atmosphere will result in improved lubricant behavior or permit an increased maximum operating temperature.

Oxidation at 500°F. for the lubricants evaluated appears to be a strong function of the amount of oxygen in contact and the degree of contact between the oxygen and fluid. Foaming or spraying the fluid into an oxygen containing atmosphere increases air-oil contact and oxidation rate. Thus, in mechanical systems that are not completely sealed, reductions in oxidative deterioration would be expected from any improvements in foaming and/or elimination of spray type lubrication.

If oxygen, and hence the rate of oxidation, in the lubricant system can not be adequately controlled, advantage might be taken of the fact that most of the lubricants tested can assimilate a reasonable amount of oxygen before becoming excessively dirty. This suggests a limited pass lubricant system where the quantity of lubricant being circulated is not returned to the main oil tank and can be discarded after a reasonable number of passes through the bearing and replaced with unused lubricant. In other words, the oil in the main oil storage tank does not circulate. Oil systems of this type are conventionally used on aircraft piston engines. Piston engines, in general, differ from jet engines on the basis of oil consumption. The high oil consumption of the piston engine automatically takes care of discarding the used oil. It may be desirable to build in high oil consumption in a jet engine. The high oil consumption or discarded lubricant, at least in the case of mineral oils, esters, and polyethers could be fed back into the fuel stream and burned. The additional lubricant required in such a system would not represent a severe weight penalty.

A panel coking apparatus has been ordered in accordance with the suggestion of the Materials Laboratory of the Wright Air Development Center. This apparatus will be used to supplement the oxidation and thermal stability tests described in this report. This apparatus has now been received and is being set up for operation.

D. THERMAL STABILITY. Preliminary thermal stability data for the various chemical classes considered for hydraulic fluids and jet lubricants are summarized in the preceding section on hydraulic fluids. These data indicate clearly the advantages of purely thermal stability as compared to oxidation stability.

Jet engine lubricants are formulated to give a higher degree of lubricity than hydraulic fluids. Phosphorus-containing anti-wear and E.P. additives have been extensively investigated as lubricity additives in jet engine lubricants. It has been noted that fluids containing tricresyl phosphate, or acid phosphites, as anti-wear additives tend to be less stable thermally than the base fluid to which these materials have been added. Studies are being conducted to determine the extent to which the presence of these phosphorus-containing additives affect the thermal stability of finished fluids and lubricants. Exploratory tests have been conducted with blends of tricresyl phosphate or dibutyl acid phosphite in di-2-ethylhexyl sebacate. These tests are conducted in a glass thermal stability apparatus at 500°F. for a period of 20 hours. A diagram of the apparatus is shown in report PRL 5.8-Sep53. The test is carried out under a nitrogen atmosphere. The tube is sealed with a U-tube containing approximately three milliliters of the test fluid.

Table 61

OXIDATION AND CORROSION PROPERTIES OF SEVERAL FLUIDS AT 500°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.

| TEST FLUID (COMPOSITIONS IN WT.%) | PRL 3207 DI-2-ETHYLHEXYL SEBACATE + 0.5 PHENOTHIAZINE | | PRL 3057 HERCOFLEX 600 + 0.5 PHENOTHIAZINE | | PRL 2782 NECTON 45 (MINERAL OIL) | | PRL 3416 SILICATE BASE HYDRAULIC FLUID (MIL 5277) | |
|---|---|---|---|---|---|---|---|---|
| TEST TIME, HOURS | 20 | 60 | 20 | 40 | 20 | 40 | 40 | 60 |
| LIQUID LOSS, WT.% | 9 | 0 | 9 | 15 | 2 | 0 | 12 | 36 |
| APPROX. AMOUNT $O_2$ CHARGED, GMS.(1) | 39.3 | 78.6 | 26.2 | 52.4 | 26.2 | 52.4 | 52.4 | 78.6 |
| APPROX. AMOUNT $O_2$ USED, GMS.(1) | 8.7 | 17.4 | 6.0 | 13.7 | 5.2 | 10.5 | 4.1 | 7.7 |
| MOLS $O_2$ USED/426 GMS. FLUID(4) | 1.30 | 2.60 | 0.05 | 1.05 | 0.77 | 1.57 | 0.62 | 1.06 |
| % CHANGE IN VISCOSITY | | | | | | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | | | | | | | |
| AT 130°F. | +116 | SOLID(5) | +66 | +45.0 | +86 | SOLID(5) | -24 | +587 |
| AT 0°F. | +240 | SOLID(5) | 180 | SOLID | - | - | -7 | +1670 |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) | | | | | | | | |
| AT 130°F. | +51 | +50 | +59 | - | +5 | - | - | +858 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | | | | | |
| ORIGINAL | 0.1 | 0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.0 | 0.0 |
| FINAL | 16.8 | 36.2 | 3.7 | 17.7 | 2.8 | 2.7 | 1.2 | 2.2 |
| WT.% OIL INSOLUBLE MATERIAL(2) | 0.8 | -(5) | TRACE | 1.7 | 0.3 | -(5) | 1.7 | 0.7 |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 6.9 | 25 | 1.2 | 23.5 | 4.6 | 49 | 4.8 | 1.9 |
| FINAL CATALYST CONDITION | | | | | | | | |
| APPEARANCE | | | | | | | | |
| COPPER | DULL | CORRODED | DULL | DULL | DULL | COATED | DULL | DULL |
| STEEL | COATED | CORRODED | DULL | CORRODED | DULL | DULL | COATED | DULL |
| ALUMINUM | BRIGHT | BRIGHT | DULL | DULL | BRIGHT | DULL | BRIGHT | DULL |
| WT. LOSS (MG./SQ. CM.) | | | | | | | | |
| COPPER | 0.07 | 0.52 | 0.06 | 0.13 | 0.13 | +0.12 | 0.07 | +0.03 |
| STEEL | +0.23 | 3.26 | 0.02 | 12.05 | +0.02 | 0.00 | +0.14 | +0.06 |
| ALUMINUM | 0.00 | 0.03 | +0.01 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 |

(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) 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.
(3) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.
(4) THE MOLS OF $O_2$ FOR 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE $O_2$ ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYLHEXYL SEBACATE IS 426.
(5) OXIDIZED FLUID WAS AN INTIMATE MIXTURE OF INSOLUBLE MATERIAL AND OXIDIZED LIQUID. OIL INSOLUBLES COULD NOT BE DETERMINED WITHOUT DILUTION.

(TABLE CONCLUDED ON NEXT PAGE)

Table 61 (Concluded)

OXIDATION AND CORROSION PROPERTIES OF SEVERAL FLUIDS AT 500°F.

| TEST FLUID (COMPOSITIONS IN WT.%) | PF 3455 TETRA (2-ETHYLHEXYL) SILICATE | | PRL 2801 UCON LUBRICANT LB-135 + 1.0 PHENYL-α-NAPHTHYLAMINE | | PRL 3475 SILICONE NO. 81406 (G.E.) | |
|---|---|---|---|---|---|---|
| TEST TIME, HOURS | 20 | 40 | 20 | 60 | 40 | 75 |
| LIQUID LOSS, WT.% | 25 | 38 | 15 | 44 | 2 | 3 |
| APPROX. AMOUNT $O_2$ CHARGED, GMS.(1) | 26.2 | 52.4 | 26.2 | 78.6 | 52.4 | 98.3 |
| APPROX. AMOUNT $O_2$ USED, GMS.(1) | 8.2 | 13.8 | 10.2 | 26.0 | 2.4 | 4.4 |
| MOLS $O_2$ USED/426 GMS. FLUID(4) | 1.22 | 2.05 | 1.44 | 3.70 | 0.21 | 0.58 |
| % CHANGE IN VISCOSITY | | | | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | | | | | |
| AT 130°F. | +199 | SOLID(5) | | SOLID(5) | +82 | +15,400 |
| AT 0°F. | +444 | SOLID(5) | | SOLID(5) | +125 | - |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) AT 130°F. | +234 | - | -14 | -10 | - | - |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | | | |
| ORIGINAL | 0.1 | 0.1 | 0.3 | 0.3 | 0.1 | 0.1 |
| FINAL | 1.2 | 1.2 | 7.4 | 9.1 | 0.9 | 1.0 |
| WT.% OIL INSOLUBLE MATERIAL(2) | 0.[illegible] | -(5) | 0.1 | -(5) | TRACE | - |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 1.1 | 8.3 | 3.8 | 30.6 | TRACE | 0.1 |
| FINAL CATALYST CONDITION | | | | | | |
| APPEARANCE | | | | | | |
| COPPER | BRIGHT | BRIGHT | DULL | BRIGHT | CORRODED | CORRODED |
| STEEL | CORRODED | CORRODED | DULL | CORRODED | DULL | DULL |
| ALUMINUM | BRIGHT | BRIGHT | DULL | BRIGHT | BRIGHT | BRIGHT |
| WT. LOSS (MG./SQ. CM.) | | | | | | |
| COPPER | 0.02 | 0.00 | 0.00 | 0.00 | 0.49 | 1.35 |
| STEEL | 0.26 | 0.55 | 0.05 | 0.74 | 0.05 | +0.06 |
| ALUMINUM | 0.01 | +0.02 | 0.00 | 0.00 | 0.00 | +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) 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.

(3) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.

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

(5) OXIDIZED FLUID WAS AN INTIMATE MIXTURE OF INSOLUBLE MATERIAL AND OXIDIZED LIQUID. OIL INSOLUBLES COULD NOT BE DETERMINED WITHOUT DILUTION.

Table 62

OXIDATION AND CORROSION PROPERTIES OF AROCLOR 1248 AT 500°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.
TEST FLUID PRL 3508 = AROCLOR 1248 OBTAINED FROM THE MONSANTO CHEMICAL COMPANY.

| TEST FLUID | AROCLOR 1248 (PRL 3508) | | | | |
|---|---|---|---|---|---|
| TEST TIME, HOURS | 12 | 20 | 40 | 60 | 120 |
| LIQUID CHARGED, GRAMS | 137 | 134 | 137 | 138 | 140 |
| LIQUID LOSS, WT.% | 0 | +1 | 0 | 0 | 4 |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 15.7 | 26.2 | 52.4 | 78.6 | 157.2 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | 0.5 | 1.0 | 1.5 | 2.4 | 3.1 |
| MOLS $O_2$ USED/426 GMS. OF FLUID(4) | 0.05 | 0.08 | 0.15 | 0.22 | 0.30 |
| % CHANGE IN VISCOSITY | | | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) AT 130°F. | +2 | +2 | +2 | +2 | +12 |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) AT 130°F. | +7 | +1 | +1 | +2 | +12 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | | |
| ORIGINAL | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| FINAL | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| WT.% OIL INSOLUBLE MATERIAL(2) | NONE | TRACE | TRACE | TRACE | TRACE |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | TRACE | TRACE | TRACE | TRACE | TRACE |
| FINAL CATALYST CONDITION | | | | | |
| APPEARANCE | | | | | |
| COPPER | CORRODED | CORRODED | CORRODED | CORRODED | CORRODED |
| STEEL | DULL | DULL | DULL | DULL | DULL |
| ALUMINUM | BRIGHT | DULL | DULL | DULL | DULL |
| WT. LOSS (MG./SQ. CM.) | | | | | |
| COPPER | 0.60 | 0.33 | 2.09 | 2.86 | 6.37 |
| STEEL | +0.08 | 0.00 | 0.02 | 0.02 | 0.09 |
| ALUMINUM | +0.05 | 0.00 | 0.00 | 0.03 | 0.03 |

(1) AMOUNT OXYGEN SUPPLIED CALCULATED AS FOLLOW: AIR RATE (L./HR. AT 0, 1 ATM.) 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) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING THE OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.
(3) THE ISOPENTANE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF THE OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.
(4) 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.

Table 63

## OXIDATION AND CORROSION CHARACTERISTICS OF A SILICONE AT 500°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST TIME AS INDICATED; FLUID CHARGED = 100 ML.;
CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.
TEST FLUID PRL 5-97 = SILICONE FLUID 510 OBTAINED FROM THE DOW-CORNING CORPORATION

| TEST FLUID | PRL 3497 | | | |
|---|---|---|---|---|
| TEST TIME, HOURS | 20 | 40 | 60 | 124 |
| LIQUID CHARGED, GRAMS | 98 | 97 | 98 | 97 |
| LIQUID LOSS, WT.% | 0 | 0 | 0 | 6 |
| APPROX. AMOUNT $O_2$ SUPPLIED, GMS.(1) | 26.2 | 52.4 | 78.6 | 163.1 |
| APPROX. AMOUNT $O_2$ USED, GMS.(1) | 1.2 | 2.1 | 3.9 | 10.2 |
| MOLS $O_2$ USED/426 GMS. FLUID(4) | 0.1[illegible] | 0.29 | 0.45 | 1.40 |
| % CHANGE IN VISCOSITY | | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | | | |
| AT 130°F. | +[illegible] | +24 | +30 | +112 |
| AT 0°F. | +12 | +28 | +36 | +126 |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) | | | | |
| AT 130°F. | +4 | +8 | +29 | +104 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | |
| ORIGINAL | 0.[illegible] | 0.0 | 0.0 | 0.0 |
| FINAL | 0.0 | 0.0 | 0.0 | 0.2 |
| WT.% OIL INSOLUBLE MATERIAL(2) | NONE | NONE | NONE | NONE |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 0.4 | 0.2 | 0.2 | NONE |
| FINAL CATALYST CONDITION | | | | |
| APPEARANCE | | | | |
| COPPER | DULL | DULL | DULL | COATED |
| STEEL | DULL | DULL | DULL | DULL |
| ALUMINUM | DULL | BRIGHT | BRIGHT | BRIGHT |
| WT. LOSS (MG./SQ. CM.) | | | | |
| COPPER | +0.04 | +0.03 | +0.06 | +0.18 |
| STEEL | +0.02 | +0.02 | +0.05 | +0.02 |
| ALUMINUM | 0.02 | 0.02 | 0.02 | 0.01 |

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 OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR $O_2$.
(2) 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.
(3) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. THE ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.
(4) THE MOLS OF $O_2$ FOR 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE $O_2$ ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYLHEXYL SEBACATE IS 426.

Table 64

OXIDATION AND CORROSION PROPERTIES OF A SILICONE AT 500°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.
TEST FLUID PRL 3491 = AN EXPERIMENTAL SILICONE FLUID WITH IMPROVED LUBRICITY (NO. 81451) OBTAINED FROM THE GENERAL ELECTRIC COMPANY.

| TEST FLUID | PRL 3491 | |
|---|---|---|
| TEST TIME, HOURS | 20 | 40 |
| LIQUID CHARGED, GRAMS(1) | 102 | 104 |
| LIQUID LOSS, WT % | 2 | 7 |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 26.2 | 52.4 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | 0.9 | 1.7 |
| MOLES $O_2$ USED/426 GMS. OF FLUID(4) | 0.12 | 0.21 |
| % CHANGE IN VISCOSITY | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | |
| AT 130°F | +67 | +510 |
| AT 0°F. | +84 | +736 |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) | | |
| AT 130°F. | 54 | +480 |
| NEUT. NO. (MG. KOH/GM. OIL) | | |
| ORIGINAL | 0.1 | 0.1 |
| FINAL | 0.7 | 0.7 |
| WT.% OIL INSOLUBLE MATERIAL(2) | NONE | NONE |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 0.1 | 0.1 |
| FINAL CATALYST CONDITION | | |
| APPEARANCE | | |
| COPPER | CORRODED | CORRODED |
| STEEL | DULL | DULL |
| ALUMINUM | DULL | DULL |
| WT LOSS (MG./SQ. CM.) | | |
| COPPER | 1.42 | .24 |
| STEEL | 0.02 | 0.07 |
| ALUMINUM | 0.00 | 0.02 |

(1) AMOUNT 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 OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR $O_2$.
(2) 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.
(3) THE ISOPENTANE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. THE ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.
(4) THE MOLS OF $O_2$ FOR 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE $O_2$ ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYLHEXYL SEBACATE IS 426.

Table 65

OXIDATION AND CORROSION CHARACTERISTICS OF AN SD-17 FLUID AT 500°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST TIME AS INDICATED, FLUID CHARGE = 100 ML.
CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.
TEST FLUID: PRL 3529 = 2:1 (BY VOL.) SILICONE TYPE 510 (PRL 3497):DI-2-ETHYLHEXYL SEBACATE + 0.5 WT. % PHENOTHIAZINE (NACA DESIG. = SD-17).

| TEST FLUID | <- - - -

Table 66

OXIDATION AND CORROSION CHARACTERISTICS OF O.S. 45 SILICATE FLUID AT 500°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST TIME AS INDICATED. LIQUID CHARGED = 100 ML.; CATALYST = A 1-INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.
TEST FLUID PRL 3505 = O.S. 45 SILICATE FLUID OBTAINED FROM THE MONSANTO CHEMICAL COMPANY.

| TEST FLUID | PRL 3505 | |
|---|---|---|
| TEST TIME, HRS. | 20 | 40 |
| LIQUID CHARGED, GMS. | 87 | 88 |
| LIQUID LOSS, WT % | 21 | 45 |
| APPROX. AMOUNT $O_2$ SUPPLIED, GMS.(1) | 26.2 | 52.4 |
| APPROX. AMOUNT $O_2$ USED, GMS.(1) | 5.0 | 11.1 |
| MOLS $O_2$ USED/426 GMS. FLUID(4) | 0.76 | 1.62 |
| % CHANGE IN VISCOSITY | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | |
| AT 130°F. | +50 | +1500 |
| AT 0°F. | +224 | +11,700 |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) | | |
| AT 130°F. | +103 | - |
| NEUT. NO. (MG. KOH/GM. OIL) | | |
| ORIGINAL | 0.0 | 0.0 |
| FINAL | 0.5 | 0.6 |
| WT. % OIL INSOLUBLE MATERIAL(2) | TRACE | 0.2 |
| WT. % ISOPENTANE INSOLUBLE MATERIAL(3) | 0.1 | 0.2 |
| FINAL CATALYST CONDITION | | |
| APPEARANCE | | |
| COPPER | BRIGHT | BRIGHT |
| STEEL | CORRODED | CORRODED |
| ALUMINUM | BRIGHT | BRIGHT |
| WT. LOSS (MG./SQ. CM.) | | |
| COPPER | 0.00 | 0.05 |
| STEEL | 0.43 | 0.59 |
| ALUMINUM | 0.00 | 0.00 |

(1) AMOUNT OF OXYGEN SUPPLIED CALCULATED AS FOLLOWS: AIR RATE (L./MIN. 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 ANALYSED FOR $O_2$.
(2) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE O. INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.
(3) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF THE OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.
(4) THE MOLS OF $O_2$ FOR 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE $O_2$ ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYLHEXYL SEBACATE IS 426.

Table 67

OXIDATION AND CORROSION OF MLO 8200 SILICATE FLUID AT 500°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST TIME AS INDICATED; FLUID CHARGED = 100 ML.,
CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL AND ALUMINUM.
TEST FLUID: PRL 3506 = MLO 8200 SILICATE FLUID OBTAINED FROM THE OFONITE CHEMICAL COMPANY.

| TEST FLUID | PRL 3506 | | | |
|---|---|---|---|---|
| TEST TIME, HRS. | 20 | 40 | 60 | 117 |
| LIQUID CHARGED, GMS. | 89 | 89 | 92 | 89 |
| LIQUID LOSS, WT.% | 7 | 10 | 27 | 33 |
| APPROX. AMOUNT $O_2$ SUPPLIED, GMS.(1) | 26.2 | 52.4 | 78.6 | 153.4 |
| APPROX. AMOUNT $O_2$ USED, GMS.(1) | 3.4 | 4.4 | 8.3 | 12.3 |
| MOLS $O_2$ USED/426 GMS. FLUID(4) | 0.51 | 0.65 | 1.20 | 1.83 |
| % CHANGE IN VISCOSITY | | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | | | |
| AT 130°F. | 18 | -32 | +90 | +120 |
| AT 0°F. | -15 | +6 | +315 | +475 |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) | | | | |
| AT 130°F. | -21 | -19 | +99 | +343 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | |
| ORIGINAL | 0.1 | 0.1 | 0.1 | 0.1 |
| FINAL | 0.6 | 0.1 | 0.6 | 2.4 |
| WT.% OIL INSOLUBLE MATERIAL(2) | TRACE | TRACE | 0.8 | 7.9 |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | TRACE | TRACE | 1.1 | 8.0 |
| FINAL CATALYST CONDITION | | | | |
| APPEARANCE | | | | |
| COPPER | CORRODED | CORRODED | CORRODED | CORRODED |
| STEEL | DULL | DULL | DULL | DULL |
| ALUMINUM | DULL | DULL | BRIGHT | BRIGHT |
| WT. LOSS (MG./SQ. CM.) | | | | |
| COPPER | 0.20 | 0.34 | 0.44 | 0.53 |
| STEEL | 0.00 | +0.03 | +0.02 | +0.02 |
| ALUMINUM | 0.00 | +0.02 | +0.01 | 0.00 |

(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) 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.
(3) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. THE ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF THE OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.
(4) THE MOLS OF $O_2$ PER 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE $O_2$ ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYLHEXYL SEBACATE IS 426.

Table 68

## OXIDATION AND CORROSION CHARACTERISTICS OF TRIDECYL PELARGONATE AT 500°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL AND ALUMINUM.

| TEST FLUID | <--------- 0.5 WT.% PHENOTHIAZINE IN TRIDECYL PELARGONATE (PPL 3444) ---------> | | | | |
|---|---|---|---|---|---|
| TEST TIME, HOURS | 12 | 20 | 30 | 40 | 60 |
| LIQUID CHARGED, GRAMS | 86 | 86 | 86 | 86 | 86 |
| LIQUID LOSS, WT.% | 5 | 6 | 12 | 13 | 23 |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 15.7 | 26.2 | 39.3 | 52.4 | 78.6 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | 3.4 | 5.5 | 10.4 | 12.8 | 24.8 |
| MOLES $O_2$ USED/426 GRAMS OF FLUID(4) | 0.52 | 0.84 | 1.61 | 1.98 | 3.84 |
| % CHANGE IN VISCOSITY | | | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | | | | |
| AT 130°F. | +23 | +99 | +258 | +506 | SOLID(5) |
| AT 0°F. | +55 | +188 | +610 | +180 | SOLID(5) |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) | | | | | |
| AT 130°F. | +9 | +11 | +45 | +21 | +30 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | | |
| ORIGINAL | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| FINAL | 6.9 | 9.8 | 11.8 | 15.8 | 12.5 |
| WT.% OIL INSOLUBLE MATERIAL(2) | 0.2 | 0.3 | 0.4 | 1.2 | -(5) |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 2.8 | 3.6 | 10.0 | 10.5 | 19.5 |
| FINAL CATALYST CONDITION | | | | | |
| APPEARANCE | | | | | |
| COPPER | DULL | DULL | DULL | CORRODED | CORRODED |
| STEEL | DULL | DULL | CORRODED | CORRODED | CORRODED |
| ALUMINUM | DULL | DULL | DULL | DULL | DULL |
| WT. LOSS (MG./SQ. CM.) | | | | | |
| COPPER | 0.06 | 0.11 | 0.12 | 0.20 | 0.29 |
| STEEL | 0.00 | 0.00 | 1.32 | 3.20 | 10.53 |
| ALUMINUM | 0.00 | 0.00 | 0.00 | +0.03 | 0.02 |

(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 ANALYSIS OF EXHAUST GASES AND ANALYSIS FOR $O_2$.
(2) 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.
(3) THE ISOPENTANE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. THE ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY WEIGHING A SAMPLE OF THE OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.
(4) THE MOLS OF $O_2$ FOR 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE $O_2$ ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYL-HEXYL SEBACATE IS 426.
(5) OXIDIZED FLUID WAS AN INTIMATE MIXTURE OF INSOLUBLE MATERIAL AND OXIDIZED FLUID. OIL INSOLUBLES COULD NOT BE DETERMINED WITHOUT DILUTION.

Table 69

OXIDATION AND CORROSION PROPERTIES OF A POLYBUTENE TYPE FLUID AT 500°F

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F ; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; FLUID CHARGED = 100 ML.;
CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL, AND ALUMINUM.
TEST FLUID: PRL 3440 = INDOPOL L-50 POLYBUTENE POLYMER OF 110 CENTISTOKES VISCOSITY AT 100°F.

| TEST FLUID | PRL 3440 | | |
|---|---|---|---|
| TEST TIME, HRS. | 20 | 40 | 60 |
| LIQUID CHARGED, GMS. | 81 | 81 | 81 |
| LIQUID LOSS, WT.% | 13 | 20 | 31 |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 26.2 | 52.4 | 78.6 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | 7.2 | 13.0 | 23.4 |
| MOLES $O_2$ USED/426 GMS. OF FLUID(4) | 1.18 | 2.14 | 3.82 |
| % CHANGE IN VISCOSITY | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) AT 130°F. | +63 | +255 | SOLID(5) |
| AT 0°F. | +354 | - | SOLID(5) |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) AT 130°F. | +71 | +255 | - |
| NEUT. NO. (MG. KOH/GM. OIL) | | | |
| ORIGINAL | 0.0 | 0.0 | 0.0 |
| FINAL | 2.2 | 3.8 | 10.6 |
| WT.% OIL INSOLUBLE MATERIAL(2) | TRACE | TRACE | -(5) |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 0.1 | 1.3 | 27.5 |
| FINAL CATALYST CONDITION | | | |
| APPEARANCE | | | |
| COPPER | DULL | DULL | DULL |
| STEEL | DULL | DULL | DULL |
| ALUMINUM | BRIGHT | DULL | DULL |
| WT. LOSS (MG./SQ. CM.) | | | |
| COPPER | 0.01 | 0.02 | 0.12 |
| STEEL | 0.01 | 0.00 | 0.06 |
| ALUMINUM | 0.00 | 0.00 | 0.04 |

(1) AMOUNT 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 OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR $O_2$.
(2) OIL INSOLUBLE MATERIAL IS DETERMINED BY CENTRIFUGING OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.
(3) THE ISOPENTANE INSOLUBLE MATERIAL IS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DILUTING A SAMPLE OF THE OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLE MATERIAL HAS BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.
(4) THE MOLS OF $O_2$ FOR 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE $O_2$ ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYLHEXYL SEBACATE IS 426.
(5) OXIDIZED FLUID WAS AN INTIMATE MIXTURE OF INSOLUBLE MATERIAL AND OXIDIZED FLUID. OIL INSOLUBLES COULD NOT BE DETERMINED WITHOUT DILUTION.

Table 70

OXIDATION AND CORROSION PROPERTIES OF A POLYBUTENE TYPE FLUID AT 500°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL AND ALUMINUM.
TEST FLUID: PRL 3473 = SAMPLE LF-0741 POLYBUTENE POLYMER OF 15 CENTISTOKES VISCOSITY AT 100°F.

| | PRL 3473 | | |
|---|---|---|---|
| TEST FLUID | | | |
| TEST TIME, HRS. | 20 | 40 | 40 |
| LIQUID CHARGED, GMS. | 80 | 81 | 80 |
| LIQUID LOSS, WT.% | 14 | 23 | 28 |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 26.2 | 52.4 | 52.4 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | 9.3 | 11.9 | 17.5 |
| MOLS $O_2$ USED/426 GMS. OF FLUID(4) | 1.55 | 1.98 | 2.92 |
| % CHANGE IN VISCOSITY | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | | |
| AT 130°F. | +129 | +840 | +2900 |
| AT 0°F. | +820 | +19900 | SOLID |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) | | | |
| AT 130°F. | +129 | +670 | +1390 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | |
| ORIGINAL | 0.0 | 0.0 | 0.1 |
| FINAL | 1.9 | 8.9 | 8.5 |
| WT.% OIL INSOLUBLE MATERIAL(2) | TRACE | 0.1 | 0.2 |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 0.1 | 3.6 | 3.9 |
| FINAL CATALYST CONDITION | | | |
| APPEARANCE | | | |
| COPPER | DULL | DULL | DULL |
| STEEL | DULL | DULL | DULL |
| ALUMINUM | BRIGHT | DULL | BRIGHT |
| WT. LOSS (MG./SQ. CM.) | | | |
| COPPER | 0.04 | 0.08 | 0.08 |
| STEEL | 0.11 | 0.02 | 0.00 |
| ALUMINUM | 0.00 | 0.00 | 0.02 |

(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 CONSUME DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR $O_2$.

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

(3) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DILUTING A SAMPLE OF THE OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLE MATERIAL HAS BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.

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

## Table 71

### OXIDATION AND CORROSION PROPERTIES OF A POLYBUTENE TYPE FLUID AT 500°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL AND ALUMINUM.
TEST FLUID: PRL 3474 = SAMPLE NO. LF-0742 POLYBUTENE POLYMER (PRODUCT OF HYDROGENATION OF SAMPLE NO. LF-0741, SEE TABLE 70).

| TEST FLUID | PRL 3474 | | | |
|---|---|---|---|---|
| TEST TIME, HOURS | 20 | 40 | 44 | 60 |
| LIQUID CHARGED, GMS. | 79 | 80 | 80 | 80 |
| LIQUID LOSS, WT.% | 20 | 29 | 27 | 30 |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 26.2 | 52.4 | 58.3 | 78.6 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | 8.1 | 13.4 | 14.9 | 22.0 |
| MOLES $O_2$ USED/426 GMS. OF FLUID(4) | 1.37 | 2.23 | 2.46 | 3.64 |
| % CHANGE IN VISCOSITY | | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | | | |
| AT 130°F. | +33 | +47 | +53 | +46 |
| AT 0°F. | +149 | +168 | +230 | +174 |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) | | | | |
| AT 130°F. | +35 | +37 | +43 | +40 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | |
| ORIGINAL | 0.0 | 0.0 | 0.0 | 0.0 |
| FINAL | 3.2 | 4.3 | 3.1 | 3.2 |
| WT.% OIL INSOLUBLE MATERIAL(2) | 0.1 | 4.9 | 5.2 | 3.4 |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 0.7 | 6.8 | 6.8 | 4.9 |
| FINAL CATALYST CONDITION | | | | |
| APPEARANCE | | | | |
| COPPER | BRIGHT | DULL | BRIGHT | DULL |
| STEEL | DULL | DULL | DULL | DULL |
| ALUMINUM | BRIGHT | COATED | DULL | DULL |
| WT. LOSS (MG./SQ. CM.) | | | | |
| COPPER | 0.02 | 0.01 | 0.00 | 0.05 |
| STEEL | 0.02 | +0.03 | +0.06 | +0.03 |
| ALUMINUM | 0.00 | +0.12 | +0.02 | 0.02 |

(1) 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 OF OXYGEN CONSUMED DETERMINED BY FREQUENT SAMPLING OF EXHAUST GASES AND ANALYSIS FOR $O_2$.
(2) 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.
(3) THE ISOPENTANE INSOLUBLE MATERIAL IS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.
(4) THE MOLS OF $O_2$ FOR 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR THE $O_2$ ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYLHEXYL SEBACATE IS 426.

Table 72

OXIDATION AND CORROSION CHARACTERISTICS OF CETANE AT 500°F.

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL AND ALUMINUM.

| TEST FLUID | CETANE | | | |
|---|---|---|---|---|
| TEST TIME, HOURS | 6 | 20 | 32 | 40 |
| LIQUID CHARGED, GMS. | 76 | 76 | 77 | 77 |
| LIQUID LOSS, WT.% | 7 | 18 | 35 | 35 |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 7.9 | 26.2 | 39.3 | 52.4 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | 6.3 | 17.2 | 22.5 | 28.2 |
| MOLS $O_2$ USED/426 GMS. FLUID(4) | 1.11 | 3.02 | 3.95 | 4.95 |
| % CHANGE IN VISCOSITY | | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) AT 130°F. | +24 | +128 | +732 | +1950 |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) AT 130°F. | +32 | +133 | +360 | +170 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | |
| ORIGINAL | 0.0 | 0.0 | 0.0 | 0.0 |
| FINAL | 4 | 8.8 | 12.8 | 12.2 |
| WT.% OIL INSOLUBLE MATERIAL(2) | TRACE | TRACE | 0.2 | 0.2 |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 0.1 | 0.1 | 9.6 | 12.6 |
| FINAL CATALYST CONDITION | | | | |
| APPEARANCE | | | | |
| COPPER | DULL | DULL | BRIGHT | DULL |
| STEEL | DULL | DULL | DULL | DULL |
| ALUMINUM | DULL | DULL | BRIGHT | DULL |
| WT. LOSS (MG./SQ. CM.) | | | | |
| COPPER | 0.12 | 0.03 | 0.02 | 0.07 |
| STEEL | 0.02 | 0.05 | 0.07 | 0.04 |
| ALUMINUM | 0.03 | 0.02 | 0.00 | +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) OIL INSOLUBLE MATERIAL IS REMOVED BY CENTRIFUGING THE OXIDIZED FLUID IMMEDIATELY AFTER COMPLETION OF TEST. THE OIL INSOLUBLES ARE WASHED WITH A LOW BOILING PETROLEUM NAPHTHA AND DRIED BEFORE WEIGHING.

(3) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF THE OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.

(4) THE MOLS OF $O_2$ FOR 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE $O_2$ ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYL-HEXYL SEBACATE IS 426.

Table 73

OXIDATION AND CORROSION CHARACTERISTICS OF TRIAMYL CYCLOHEXANE AT 500°F.

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL AND ALUMINUM.

| | TRIAMYL CYCLOHEXANE | | | | |
|---|---|---|---|---|---|
| TEST FLUID | 12 | 20 | 30 | 40 | 58 |
| TEST TIME, HOURS | 82 | 82 | 83 | 82 | 82 |
| LIQUID CHARGED, GRAMS | 6 | 13 | 13 | 16 | 20 |
| LIQUID LOSS, WT.% | | | | | |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 15.7 | 26.2 | 39.3 | 52.4 | 75.9 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | 7.4 | 13.9 | 15.8 | 20.5 | 26.3 |
| MOLS $O_2$ USED/426 GMS. OF FLUID(4) | 1.19 | 2.26 | 2.54 | 3.31 | 4.27 |
| % CHANGE IN VISCOSITY | | | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) | | | | | |
| AT 130°F. | +66 | +172 | +393 | +544 | +805 |
| AT 0°F. | +321 | +132 | +5,000 | +12,500 | +17400 |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) | | | | | |
| AT 130°F. | +61 | +128 | +173 | +179 | +194 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | | |
| ORIGINAL | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| FINAL | 2.8 | 4.8 | 5.7 | 6.3 | 6.2 |
| WT.% OIL INSOLUBLE MATERIAL(2) | TRACE | 0.1 | 0.5 | 0.9 | 3.4 |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 0.3 | 2.6 | 6.4 | 10.5 | 15.6 |
| FINAL CATALYST CONDITION | | | | | |
| APPEARANCE | | | | | |
| COPPER | BRIGHT | BRIGHT | BRIGHT | BRIGHT | DULL |
| STEEL | DULL | DULL | DULL | DULL | DULL |
| ALUMINUM | BRIGHT | BRIGHT | BRIGHT | BRIGHT | DULL |
| WT. LOSS (MG./SQ. CM.) | | | | | |
| COPPER | 0.00 | 0.00 | 0.00 | 0.00 | 0.16 |
| STEEL | 0.00 | 0.02 | 0.01 | 0.01 | 0.00 |
| ALUMINUM | 0.00 | +0.02 | 0.00 | 0.00 | 0.00 |

(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) 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.

(3) THE ISOPENTANE INSOLUBLE MATERIAL IS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF THE OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.

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

Table 74

OXIDATION AND CORROSION CHARACTERISTICS OF POLYAMYL NAPHTHALENE AT 500°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL AND ALUMINUM.

| | POLYAMYL NAPHTHALENE | | | |
|---|---|---|---|---|
| TEST FLUID | 12 | 20 | 4 | 60 |
| TEST TIME, HOURS | 87 | 87 | 87 | 87 |
| LIQUID CHARGED, GRAMS | 1 | 0 | 0 | 0 |
| LIQUID LOSS, WT.% | 15.7 | 26.2 | 52.4 | 78.6 |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 3.3 | 5.2 | 9.3 | 14.5 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | 0.56 | 0.86 | 1.40 | 2.22 |
| MOLS $O_2$ USED/426 GMS. OF FLUID(4) | | | | |
| % CHANGE IN VISCOSITY | | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) AT 130°F. | +69 | +134 | +895 | SOLID(5) |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) AT 130°F. | +55 | +104 | +333 | - |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | |
| ORIGINAL | 0.0 | 0.0 | 0.0 | 0.0 |
| FINAL | 1.3 | 2.0 | 5.6 | 13.4 |
| WT.% OIL INSOLUBLE MATERIAL(2) | 0 | 0.2 | 0.8 | 6.7 |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 0 | 1.4 | 5.2 | 25.6 |
| FINAL CATALYST CONDITION | | | | |
| APPEARANCE | | | | |
| COPPER | DULL | DULL | DULL | DULL |
| STEEL | DULL | DULL | DULL | DULL |
| ALUMINUM | BRIGHT | BRIGHT | BRIGHT | BRIGHT |
| WT. LOSS (MG./SQ. CM.) | | | | |
| COPPER | 0.00 | 0.04 | 0.06 | 0.03 |
| STEEL | 0.00 | 0.02 | 0.00 | 0.00 |
| ALUMINUM | 0.03 | +0.02 | 0.00 | 0.00 |

(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) 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.

(3) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.

(4) THE MOLS OF $O_2$ FOR 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE $O_2$ ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYL-HEXYL SEBACATE IS 426.

(5) OXIDIZED FLUID WAS AN INTIMATE MIXTURE OF INSOLUBLE MATERIAL AND OXIDIZED LIQUID. OIL INSOLUBLES COULD NOT BE DETERMINED WITHOUT DILUTION.

Table 75

OXIDATION AND CORROSION CHARACTERISTICS OF m-TERPHENYL AT 500°F.

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; AIR RATE = 5 ± 0.5 LITERS/HR.; TEST TIME AS INDICATED; TEST FLUID CHARGED = 100 GRAMS; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL AND ALUMINUM.

| TEST FLUID | <- - - - - - - - m-TERPHENYL - - - - - - -

Table 76

OXIDATION AND CORROSION CHARACTERISTICS OF SOVALOID AT 500°F

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS INCLUDE: TEST TEMPERATURE = 500 ± 5°F.; TEST TIME AS INDICATED; AIR RATE = 5 ± 0.5 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; CATALYST = A 1 INCH SQUARE EACH OF COPPER, STEEL AND ALUMINUM.

| TEST FLUID | SOVALOID | | |
|---|---|---|---|
| TEST TIME, HOURS | 20 | 40 | 50 |
| LIQUID CHARGED, GMS. | 103 | 102 | 103 |
| LIQUID LOSS, WT.% | 0 | 0 | 0 |
| APPROX. AMOUNT OF $O_2$ SUPPLIED, GMS.(1) | 26.2 | 52.4 | 65.4 |
| APPROX. AMOUNT OF $O_2$ USED, GMS.(1) | 4.5 | 3.0 | 11.1 |
| MOLS $O_2$ USED/426 GMS. OF FLUID(4) | 0.53 | 1.03 | 1.44 |
| % CHANGE IN VISCOSITY | | | |
| AFTER REMOVAL OF OIL INSOLUBLE MATERIAL(2) AT 130°F. | +199 | +3770 | SOLID(5) |
| AFTER REMOVAL OF ISOPENTANE INSOLUBLE MATERIAL(3) AT 130°F. | +28 | +12 | - |
| NEUT. NO. (MG. KOH/GM. OIL) | | | |
| ORIGINAL | 0.0 | 0.0 | 0.0 |
| FINAL | 2.2 | 4.2 | 2.8 |
| WT.% OIL INSOLUBLE MATERIAL(2) | 0.4 | 5.7 | -(5) |
| WT.% ISOPENTANE INSOLUBLE MATERIAL(3) | 20.8 | 57.9 | 90.1 |
| FINAL CATALYST CONDITION | | | |
| APPEARANCE | | | |
| COPPER | DULL | COATED | DULL |
| STEEL | DULL | DULL | DULL |
| ALUMINUM | DULL | DULL | DULL |
| WT. LOSS (MG./SQ. CM.) | | | |
| COPPER | +0.02 | +0.14 | 0.02 |
| STEEL | 0.00 | +0.03 | +0.03 |
| ALUMINUM | 0.09 | +0.03 | 0.04 |

(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) 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.

(3) THE ISOPENTANE INSOLUBLE MATERIAL IS REPORTED AS THE SUM OF THE OIL INSOLUBLE MATERIAL PLUS THE ISOPENTANE INSOLUBLE MATERIAL. ISOPENTANE INSOLUBLE MATERIAL IS DETERMINED BY DISSOLVING A SAMPLE OF THE OXIDIZED FLUID (FROM WHICH THE OIL INSOLUBLES HAVE BEEN REMOVED) IN ISOPENTANE AND WEIGHING THE INSOLUBLE MATERIAL WHICH SETTLES OUT.

(4) THE MOLS OF $O_2$ FOR 426 GRAMS OF OIL HAS BEEN TABULATED AS A COMMON BASIS FOR COMPARING THE $O_2$ ABSORBED. THE MOLECULAR WEIGHT OF DI-2-ETHYL-HEXYL SEBACATE IS 426.

(5) OXIDIZED FLUID WAS AN INTIMATE MIXTURE OF INSOLUBLE MATERIAL AND OXIDIZED LIQUID. OIL INSOLUBLES COULD NOT BE DETERMINED WITHOUT DILUTION.

The test results obtained with these fluids are shown in Table 77. Test fluid PRL 3103 is di-2-ethylhexyl sebacate and PRL 3207 is a blend of 0.5 weight per cent phenothiazine in di-2-ethylhexyl sebacate.

Table 77

THERMAL STABILITY TESTS AT 500°F.

TESTS CONDUCTED FOR 20 HOURS IN GLASS EQUIPMENT UNDER A NITROGEN ATMOSPHERE

| TEST FLUID | PHOSPHORUS CONT'G. ADDITIVE, WT.% | % CHANGE IN VISC. AT 100°F. | NEUT. NO. INCREASE | CATALYST WT. LOSS, MG./SQ. CM. CU | STEEL | AL | MG | AG |
|---|---|---|---|---|---|---|---|---|
| PRL 3103 | NONE | -3 | 2.7 | 0.01 | 0.49 | 0.00 | 0.80 | 0.02 |
| | NONE | -0 | 2.7 | - | - | - | - | - |
| PRL 3207 | 1.0 TRICRESYL PHOSPHATE | 0 | 3.2 | - | - | - | - | - |
| | 5.0 TRICRESYL PHOSPHATE | 0 | 3.2 | - | - | - | - | - |
| PRL 3207 | 0.1 DIBUTYL ACID PHOSPHITE | 0 | 4.9 | - | - | - | - | - |
| | 0.5 DIBUTYL ACID PHOSPHITE | -2 | 8.6 | - | - | - | - | - |
| | 1.0 DIBUTYL ACID PHOSPHITE | -21 | 43.9 | - | - | - | - | - |
| | 1.0 DIBUTYL ACID PHOSPHITE | +4 | 33.1 | +0.07 | +1.85 | -0.40 | - | - |

The presence of 1.0 or 5.0 weight per cent tricresyl phosphate does not appear to affect the thermal stability of di-2-ethylhexyl sebacate under these test conditions, namely 500°F. for 20 hours.

Increasing the concentration of dibutyl acid phosphite from 0.1 to 1.0 weight per cent decreases the thermal stability of the resulting fluid. It has been determined that the dibutyl acid phosphite itself is not stable at 500°F. However, in the case of the blend containing 1.0 weight per cent dibutyl acid phosphite, the maximum neutralization number which can be attributed to the decomposition of the phosphite to phosphorous acid would be about 8.8 milligrams potassium hydroxide per gram of fluid. These data indicate that the presence of the acid phosphite affects the thermal stability of the base stock adversely.

The effect of tricresyl phosphate on the thermal stability of a Spec. MIL-L-7808 type fluid (PRL 3161) has been investigated at 600°F. in the stainless steel pressure cylinder. The apparatus in which these tests are conducted is described in report PRL 5.8-Sep53. The test fluids used are (1) PRL 3161, Commercial Batch 5380 (contains 5.0 weight per cent tricresyl phosphate) and (2) PRL 3076, a PRL 3161 type fluid prepared from stocks at this Laboratory and containing no tricresyl phosphate. These tests are conducted at 600°F. for six hours or until the system pressure approaches 250 p.s.i., whichever is sooner. That is, the test is terminated when the pressure approaches 250 p.s.i. for safety reasons. A summary of the results obtained for these two fluids is shown in Table 78.

Table 78

THERMAL STABILITY TESTS AT 600°F.

Tests conducted at 600°F. in the stainless steel pressure cylinder

| Test Fluid | Test Time, Hrs. | Neut. No. Increase | Max. System Pressure, p.s.i. | Residual Press., at Room Temp., p.s.i. |
|---|---|---|---|---|
| PRL 3076 | 6 | 46 | 110 | 6 |
| PRL 3161 | 3.25 | 147 | 238 | - |
| | 2.75 | 109 | 215 | 10 |

The test with PRL 3076 was conducted for the conventional six hour period with a maximum pressure of 110 p.s.i. The tests with PRL 3161 approached 250 p.s.i. after approximately 3 hours test time. The neutralization number increase is considerably greater for PRL 3161 after three hours than that shown by PRL 3076 after six hours.

These data indicate that, at 600°F., the presence of 5.0 weight per cent tricresyl phosphate has an adverse effect on the thermal stability of this synthetic gear lubricant.

E. ESTERS EVALUATED AS BASE STOCKS FOR FLUIDS AND LUBRICANTS. A group of four pelargonate esters along with one azelate ester have been obtained from Emery Industries, Inc. These pelargonate esters are the first commercial monobasic esters in the desired viscosity range to be evaluated in this manner. The behavior of these esters relative to their oxidation stability and wear characteristics is discussed in report PRL 5.8-Sep53. In general, the dibasic acid ester (di-tridecyl azelate) behaves in a manner similar to the other good quality dibasic acid esters studied by this Laboratory. The four monobasic acid esters (2-ethylhexyl pelargonate, isooctyl pelargonate, tridecyl pelargonate, and iso-decyl pelargonate), however, show reduced stability toward oxidation and are not as susceptible to tricresyl phosphate as an anti-wear additive as are the dibasic acid esters evaluated previously.

These esters have been further evaluated in terms of their viscosity properties, viscosity-temperature behavior, and their blending efficiency with Acryloid HF-25 polymer. The di-tridecyl azelate has a viscosity of 37.4 centistokes at 100°F. This material has a molecular weight of 552 compared with a value of 426 for di-2-ethylhexyl sebacate. The tridecyl azelate might, therefore, be considered for use as a base stock or base stock component where low volatility is desirable in synthetic lubricants.

Each of the pelargonate esters has been blended with Acryloid HF-25 to obtain approximately the same final viscosities. The viscosity properties and the viscosity-temperature characteristics have been determined for each of the blends. Blending curves have then been constructed

showing the 100°F. viscosity level as a function of the viscosity-temperature characteristics for the different Acryloid concentrations. A plot of this data is shown on Figure 31.

A summary of the properties of the various pelargonate esters and an Acryloid blend of each ester is shown in Table 79. Two dibasic acid esters in the same viscosity range are included for comparison.

Table 79

PROPERTIES OF SEVERAL ESTERS AND ESTER BLENDS

Ester Properties

| PRL NO. | ESTER | CENTISTOKE VISCOSITY AT 100°F. | A.S.T.M. SLOPE (210° TO 100°F.) | FLASH POINT, °F. |
|---|---|---|---|---|
| PRL 3442 | 2-ETHYLHEXYL PELARGONATE | 3.47 | 0.829 | 295 |
| PRL 3443 | ISOOCTYL PELARGONATE | 3.78 | 0.787 | 310 |
| PRL 2996 | DI-3-METHYLBUTYL ADIPATE | 4.87 | 0.736 | 345 |
| PRL 3445 | ISODECYL PELARGONATE | 4.95 | 0.779 | 345 |
| PRL 2438 | DI-SEC-AMYL SEBACATE | 7.58 | 0.752 | 410 |
| PRL 3444 | TRIDECYL PELARGONATE | 7.77 | 0.760 | 370 |

Blend Properties

| ESTER | PRL 3442 | PRL 3443 | PRL 2996 | PRL 3445 | PRL 2438 | PRL 3444 |
|---|---|---|---|---|---|---|
| ACRYLOID CONC., WT.% | 12 | 11 | 10 | 9.0 | 5.3 | 7.0 |
| DI-2-ETHYLHEXYL SEBACATE, WT.%(1) | 12 | 11 | 10 | 9.0 | 5.3 | 7.0 |
| CENTISTOKE VISCOSITY AT | | | | | | |
| 210°F. | 6.01 | 5.74 | 6.90 | 5.32 | 4.51 | 5.45 |
| 100°F. | 18.0 | 16.9 | 22.4 | 16.7 | 15.4 | 19.4 |
| A.S.T.M. SLOPE (210° TO 100°F.) | 0.483 | 0.484 | 0.488 | 0.523 | 0.586 | 0.563 |

(1) ACRYLOID SOLVENT.

In general, the blending efficiency of the pelargonates appears to be similar to that shown by the dibasic acid esters in the same viscosity range. That is, in base stocks of the same viscosity level, approximately the same amount of polymer is needed to give final blend viscosities of the same magnitude. The volatility properties of the base stocks, as indicated by flash point, have about the same values for the pelargonates as those of the dibasic acid esters of similar molecular weight.

More complete properties of the esters obtained from Emery Industries, Inc. are shown on Table 80. Good low temperature properties are shown by the various esters as evidenced by cloud and pour point determinations as well as by their storage stability for 168 hours (one week) at -65°F. Included on Table 80 are wear values determined for these esters on the Shell four-ball wear tester both alone and with 1.0 weight per cent tricresyl phosphate as an anti-wear additive. This concentration of tricresyl phosphate gives maximum wear improvement with the dibasic acid ester (PRL 3441). However, this concentration of the

Figure 31

BLENDING CHARACTERISTICS OF ACRYLOID HF-25 IN SEVERAL PELARGONATE ESTERS

PELARGONATE ESTERS RECEIVED FROM EMERY INDUSTRIES, INC.

NUMBERS ADJACENT TO SYMBOLS INDICATE THE WEIGHT PER CENT ACRYLOID REQUIRED TO GIVE THE INDICATED 100°F. CENTISTOKE VISCOSITY.

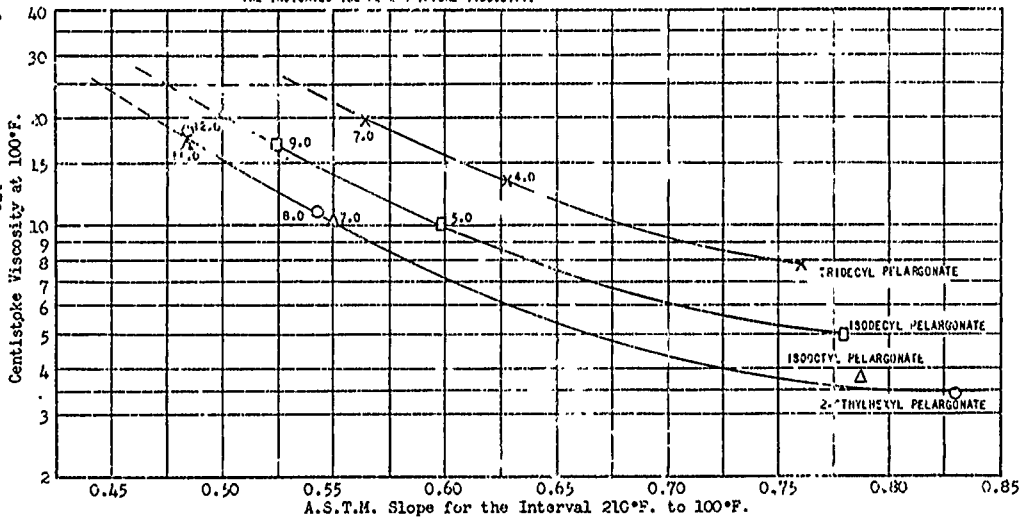


Table 80

PROPERTIES OF SEVERAL ESTERS

ESTERS RECEIVED FROM EMERY INDUSTRIES, INC.

| TEST FLUID<br>PRL DESIGNATION<br>ESTER | PRL 3441<br>DI-TRIDECYL<br>AZELATE | PRL 3442<br>2-ETHYLHEXYL PELARGONATE | | | PRL 3443<br>ISOOCTYL PELARGONATE | | | PRL 3445<br>ISODECYL PELARGONATE | | | PRL 3444<br>TRIDECYL PELARGONAT | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ACRYLOID HF-25 CONCENTRATION, WT.%(1) | NONE | NONE | 8 | 12 | NONE | 7 | 11 | NONE | 5 | 9 | NONE | 4 | 7 |
| DI-2-ETHYLHEXYL SEBACATE, WT.%(1) | NONE | NONE | 8 | 12 | NONE | 7 | 11 | NONE | 5 | 9 | NONE | 4 | 7 |
| CENTISTOKE VISCOSITY | | | | | | | | | | | | | |
| AT 210°F. | 6.62 | 1.33 | 3.85 | 5.01 | 1.46 | 3.64 | 5.74 | 1.73 | 3.35 | 5.32 | 2.31 | 3.85 | 1.45 |
| AT 130°F. | 20.4 | 2.54 | - | - | 2.76 | - | - | 3.49 | - | - | 5.15 | - | - |
| AT 100°F. | 37.4 | 3.47 | 10.9 | 18.0 | 3.78 | 10.2 | 16.9 | 4.95 | 10.0 | 16.7 | 7.77 | 13.3 | 19.4 |
| AT 0°F. | 1430 | 22.3 | - | - | 23.5 | - | - | 39.3 | - | - | 92.5 | - | |
| A.S.T.M. SLOPE (210° TO 100°F.) | 0.672 | 0.829 | 0.542 | 0.483 | 0.787 | 0.549 | [illegible]84 | 0.779 | 0.597 | 0.523 | 0.760 | 0.627 | 0.563 |
| NEUT. NO. (MG. KOH/GM. FLUID) | 0.2 | 0.2 | - | - | 0.1 | - | - | 0.1 | - | - | 0.1 | - | - |
| CLOUD POINT, °F.(2) | NONE | <-100 | - | - | -85 | - | - | -90 | - | - | <-100 | - | - |
| POUR POINT, °F.(2) | -70 | <-100 | - | - | -90 | - | - | -100 | - | - | <-100 | - | - |
| FLASH POINT, °F.(2) | 455 | 295 | - | - | 310 | - | - | 345 | - | - | 370 | - | - |
| FIRE POINT, °F.(2) | 535 | 325 | - | - | 335 | - | - | 380 | - | - | 405 | - | - |
| APPEARANCE AFTER STORAGE AT -65°F. | | | | | | | | | | | | | |
| 24 HOURS | TURBID | SL. TURBID | - | - | CLEAR | - | - | CLEAR | - | - | CLEAR | - | - |
| 72 HOURS | TURBID | SL. TURBID | - | - | CLEAR | - | - | CLEAR | - | - | SL. TURBID | - | - |
| 168 HOURS | TURBID | SL. TURBID | - | - | CLEAR | - | - | CLEAR | - | - | SL. TURBID | - | - |
| AVERAGE WEAR SCAR DIAMETER FOR STEEL-ON-STEEL BEARING SURFACES, MM. | | | | | | | | | | | | | |
| 1 KILOGRAM LOAD | 0.23 | 0.26 | - | - | 0.27 | - | - | 0.25 | - | - | 0.25 | - | - |
| 10 KILOGRAM LOAD | 0.61 | 0.44 | - | - | 0.44 | - | - | 0.44 | - | - | 0.46 | - | - |
| 40 KILOGRAM LOAD | 0.71 | 0.47 | - | - | 0.49 | - | - | 0.50 | - | - | 0.54 | - | - |
| TEST FLUID + 1.0 WT.% TRICRESYL PHOSPHATE | | | | | | | | | | | | | |
| 1 KILOGRAM LOAD | 0.19 | 0.30 | - | - | 0.28 | - | - | 0.26 | - | - | 0.30 | - | - |
| 10 KILOGRAM LOAD | 0.33 | 0.42 | - | - | 0.39 | - | - | 0.42 | - | - | 0.40 | - | - |
| 40 KILOGRAM LOAD | 0.42 | 0.64 | - | - | 0.60 | - | - | 0.54 | - | - | 0.59 | - | - |

anti-wear additive has essentially no effect on the pelargonate esters. Increased concentrations of tricresyl phosphate, on the order of 5.0 weight per cent, will produce maximum wear improvement with the pelargonate esters.

F. PREPARATION OF JET ENGINE OIL COMPOSITIONS FOR INTER-LABORATORY TESTS. The overall data on synthetic gear lubricants of the Spec. MIL-L-7808 type formulated by this Laboratory to contain alkyl acid phosphite lubricity additives are being reviewed. These data have been presented in previous reports covering about a two year period. Several of the more promising compositions have been formulated and sent to Southwest Research Institute and the Wright Air Development Center for further testing. The additional testing of these samples will include the Ryder gear tester and the panel coking test. These tests are not currently available at this Laboratory. The panel coking apparatus is currently being installed and will be ready for use at this Laboratory in the near future.

Four samples of synthetic lubricants have been sent to Southwest Research Institute and one to the Wright Air Development Center. The samples supplied to Southwest Research Institute have been sent in cooperation with the Materials Laboratory and the Power Plant Laboratory of the Wright Air Development Center. The compositions of these 5 fluids are shown on Table 81. PRL 3161 and PRL 3313 have been sent as reference fluids for these proposed tests. Both of these fluid compositions have received widespread testing in both laboratory testers and actual aircraft engines. The remaining three fluids GTO 16, GTO 17 and MLO 7010 are fluids formulated on the basis of studies with alkyl acid phosphite lubricity additives. All three of these fluids have been formulated to meet the property requirements of Spec. MIL-L-7808. Particular emphasis has been placed on the conformance of the -65°F. viscosity value of these fluids to Spec. MIL-L-7808.

Wear characteristics of these fluids are shown on Table 82. These data are for the Shell four-ball wear and E.P. lubricant testers. These test fluids include as a lubricity additive a good primary alkyl acid phosphite (GTO 16), a good primary alkyl acid phosphite plus tricresyl phosphite (GTO 17), and a good secondary alkyl acid phosphite (MLO 7010). This latter composition exhibits the best storage stability of the Spec. MIL-L-7808 type fluids containing an acid phosphate or acid phosphite lubricity additive. The wear characteristics given on Table 82 are actual data determined on these specific blends in July 1954. These were freshly prepared blends in all cases. The alkyl acid phosphate (Ortholeum 162) and alkyl acid phosphites used in these blends have been stored neat by this Laboratory for a period of one to three years. As indicated in a previous section of this report, this storage of the additive results in an increase in lubricity for the blends containing the additive without an apparent increase in neutralization number (see Table 32). The important point is that changes in effectiveness as a lubricity additive with storage time appear to occur whether or not the alkyl acid phosphite is stored by itself or blended as a lubricity additive in the finished formulation. It should be noted that the blend of PRL 3161 was prepared by this Laboratory from materials

which show excellent storage stability and no differences in lubricity after several years storage. Commercial fluids of this Spec. MIL-L-7808 type do not necessarily show this good storage stability. Storage stability of Spec. MIL-L-7808 type fluids has been discussed previously in this report.

Oxidation and corrosion characteristics of fluids of these types have been adequately discussed in reports PRL 5.4-Sep52 and PRL 5.8-Sep53. Oxidation and corrosion characteristics of MLO 7010 and a new and stored sample of ester gear lubricant containing 0.5 weight per cent diisopropyl phosphite are essentially the same, as indicated in Table 83. The diisopropyl acid phosphite tends to coat, rather than corrode, the metal catalysts. It can be noted that in one case silver is corroded somewhat and in a second case it is coated by MLO 7010. In the case where silver was corroded, the specimen was touching all five of the other metals present. In the case where silver was coated, silver and lead were the only specimens present. Lead is corroded in this test, but it should be noted that the lead corrosion is less under the same conditions with MLO 7010 than with PRL 3161. PRL 3161 shows a quate lead corrosion resistance to meet Spec. MIL-L-7808. Under sim ar test conditions, compositions similar to GTO 16 and GTO 17 show less corrosion and somewhat more coating tendencies than MLO 7010.

The sludge or dirtiness in this oxidation test is lower for MLO 7010 than for PRL 3161 or the other blends on Table 83 containing diisopropyl acid phosphite. It should be emphasized that MLO 7010 contains 1.0 weight per cent Paranox 441 while the other compositions contained 0.5 weight per cent phenothiazine. Blends equivalent to GTO 16 and GTO 17 show a very low dirtiness level similar to MLO 7010.

These data indicate in laboratory tests that GTO 16, GTO 17, and MLO 7010 are superior to PRL 3161 and PRL 3313 in lubricity, trace dirtiness characteristics, and active metal corrosion.

G. CONCLUSIONS. It appears that high temperature stability and lubricity are the most important properties in an improved jet engine oil. In conjunction with these required high temperature properties, current low temperature standards should be maintained or improved if possible.

The acid hydrogen in the alkyl acid phosphites appears to be responsible to a large extent for the excellent lubricity properties imparted by small concentrations of these additives. The affinity of the acid hydrogen for metal surfaces appears to be responsible for the preferential presence of the additive in the wearing area. Several organic acids containing either chlorine or sulfur show some anti-wear and anti-seize properties. These materials are not as effective as the alkyl acid phosphites.

Essentially all of the ester and mineral oil blends containing alkyl acid phosphates and phosphites show an increase in neutralization number on storage in stoppered glass bottles at room temperature

Table 81

COMPOSITIONS AND PROPERTIES OF SEVERAL GEAR LUBRICANTS

| FLUID DESIGNATION | PRL 3161 BATCH NO. 2 | PRL 3313 BATCH NO. 2 | GTO 16 | GTO [illegible] | MLO 7010 |
|---|---|---|---|---|---|
| COMPOSITION, WT.% | | | | | |
| ACRYLOID RF-25 | 3.9 | 3.0 | 7.5 | 1.5 | 3.5 |
| DI-2-ETHYLHEXYL SEBACATE | 90.6 | 85.0 | 95.0 | 92.0 | 95.0 |
| OXIDATION INHIBITOR | 0.5 PHENOTHIAZINE | 0.5 PHENOTHIAZINE | 1.0 PARANOX 441 | 1.0 PARANOX 441 | 1.0 PARANOX 441 |
| LUBRICITY ADDITIVE | 5.0 TRICRESYL PHOSPHATE | 0.5 DATHCLEUM 162 + 5.0 TRICRESYL PHOSPHATE | 0.5 DIETHYL ACID PHOSPHITE | 0.5 DIETHYL ACID PHOSPHITE + 5.0 TRI-CRESYL PHOSPHATE | 0.5 DIISOPROPYL ACID PHOSPHITE |
| PROPERTIES | | | | | |
| CENTISTOKE VISCOSITY | | | | | |
| AT 130°F. | 13.7 | [illegible] | [illegible] | 15.7 | 12.7 |
| AT 100°F. | 20.8 | 42.2 | [illegible] | [illegible] | 20.4 |
| AT [illegible]°F. | 374 | 792 | 12,000 | 11,800 | 316 |
| AT -65°F. | 16,000 | 44,000 | | | 13,000 |
| NEUT. NO. (MG. KOH/GM. OIL) | 0.1 | 1.6 | 0.3 | 0.3 | 0.2 |

Table 82

WEAR CHARACTERISTICS OF SOME EXPERIMENTAL GEAR LUBRICANTS

TEST CONDITIONS INCLUDE: FOUR-BALL WEAR TESTER: TEST TIME = 1 HOUR; TEST TEMPERATURE = 75°C.; AND TEST SPEED = 1350 R.P.M.
EXTREME-PRESSURE LUBRICANT TESTER: TEST TIME = 1 MINUTE; TEST TEMPERATURE = ROOM TEMPERATURE (70°-80°F.); TEST SPEED = 1750 R.P.M.

STEEL BALLS = SKF INDUSTRIES GRADE #1 (0.5 INCH DIAMETER) STEEL BALLBEARINGS, PRL BATCH #12.
TEST FLUID COMPOSITIONS: SEE TABLE 81.

| FLUID DESIG. | WEAR TESTER: AVE. WEAR SCAR DIAM., MM., STEEL-ON-STEEL BEARING SURFACES | | | EXTREME PRESSURE LUBRICANT TESTER: APPROX. LOAD FOR | | EXTREME PRESSURE LUBRICANT TESTER: AVERAGE WEAR SCAR DIAMETER, MM. STEEL ON STEEL BEARING SURFACES | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 KG. | 10 KG. | 40 KG. | INCIPIENT SEIZURE KG. | PERMANENT WELDING, KG. | 80 KG. | 100 KG. | 120 KG. | 140 KG. | 160 KG. | 180 KG. | 200 KG. |
| PRL 3161 BATCH NO. 2 | 0.16 | 0.22 | 0.37 | 80 | 120 | 0.38 | 2.88 | WELDED | | | | |
| PRL 3313 BATCH NO. 2 | 0.18 | 0.26 | 0.39 | 130 | 160 | - | 0.45 | 0.47 | 2.75 | WELDED | | |
| GTO 16 | 0.18 | 0.28 | 0.40 | 170 | 180 | - | - | - | 0.49 | 0.54 | WELDED | |
| GTO 17 | 0.16 | 0.25 | 0.39 | 170 | 180 | - | 0.44 | - | 0.45 | 0.52 | WELDED | |
| MLO 7010 | 0.15 | 0.24 | 0.40 | 190 | 200 | - | - | - | - | 0.52 | 0.55 | WELDED |

Table 83

OXIDATION AND CORROSION CHARACTERISTICS OF SEVERAL GEAR LUBRICANTS

TEST PROCEDURES AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-L-7808.
TEST CONDITIONS AND SPEC: TEST TEMPERATURE = 347 ± 3°F.; TEST TIME = 72 HOURS; AIR RATE = 10 ± 1 LITERS PER HOUR; TEST FLUID = 100 ML., AND CATALYST = 4 : INCH SQUARE EACH : METALS INDICATED.
TEST FLUID COMPOSITIONS: SEE TABLE 81.

| FLUID DESIGNATION | <- - - PRL 3161 - - - > | | | <- - - MIL 7010 - > | | PRL 3515 | PRL 3515(1) |
|---|---|---|---|---|---|---|---|
| OVERALL LIQUID LOSS, WT.% | 2 | 3 | 4 | 2 | 3 | 2 | 3 |
| % CHANGE IN VISCOSITY | | | | | | | |
| AT 130°F. | +5 | +3 | +6 | +5 | +5 | +5 | +9 |
| AT 0°F. | +7 | +6 | +8 | +7 | +7 | +7 | +11 |
| NEUT. NO. (MG. KOH/GM. OIL) | | | | | | | |
| ORIGINAL | 0.2 | 0.1 | 0.2 | 0.2 | 0.2 | 0.2 | 2.5(1) |
| FINAL | 2.2 | 1.5 | 1.2 | 3.0 | 3.3 | 3.7 | 5.4 |
| A.S.T.M. UNION COLOR: | | | | | | | |
| ORIGINAL | 2 | 2 | 2 | 1 | 1 | 1-1/2 | 3 |
| FINAL | >8 | >3 | >8 | >8 | >8 | >8 | >8 |
| WT.% INSOLUBLE MATERIAL | 0.2 | 0.3 | 0.4 | 0.1 | 0.1 | 0.9 | 0.4 |
| FINAL CATALYST CONDITION | | | | | | | |
| APPEARANCE | | | | | | | |
| COPPER | DULL | DULL | CORRODED | COATED | - | COATED | COATED |
| STEEL | DULL | DULL | DULL | COATED | - | COATED | COATED |
| ALUMINUM | DULL | DULL | DULL | COATED | - | COATED | COATED |
| MAGNESIUM | DULL | DULL | DULL | COATED | - | COATED | COATED |
| AG-PLTD. STEEL | - | DULL | - | CORRODED | COATED | - | - |
| LEAD | - | - | CORRODED | CORRODED | CORRODED | - | - |
| WT. LOSS (MG./SQ. CM.) | | | | | | | |
| COPPER | +0.05 | +0.02 | 0.27 | +1.29 | - | +0.33 | +0.47 |
| STEEL | +0.05 | +0.03 | +0.02 | +0.76 | - | +0.53 | +0.15 |
| ALUMINUM | 0.02 | +0.02 | 0.00 | +0.11 | - | +0.14 | +0.11 |
| MAGNESIUM | +0.05 | +0.01 | 0.01 | +0.19 | - | +0.02 | +0.29 |
| AG-PLTD. STEEL | - | 0.02 | - | 0.76 | +0.14 | - | - |
| LEAD | - | - | 10.22 | 3.87 | 6.25 | - | - |

(1) TEST FLUID FOR THIS TEST WAS STORED AT ROOM TEMPERATURE FOR 13 MONTHS IN A STOPPERED GLASS BOTTLE.

(70° to 80°F.). This phenomenon appears to be related to the hydrolysis stability of the additives. Some commercial Spec. MIL-L-7808 type fluids containing tricresyl phosphate show a neutralization number increase on storage. All of the fluids containing alkyl acid phosphites and the commercial Spec. MIL-L-7808 fluids showing a neutralization number increase on storage show improved lubricity after storage. Several alkyl acid phosphite additives stored neat appear to give improved lubricity properties when blended in ester-base fluids. These fresh blends show improved lubricity but not an increased neutralization number. The changes in the alkyl acid phosphite which cause increased lubricity with storage appear to be changes in the additive as opposed to changes in a completed blend induced by the additive.

Preliminary studies indicate that M-10 tool steel and heat stabilized 52-100 steel ball bearings can successfully be used as specimens for the Shell four-ball wear tester. The effect of fluids containing tricresyl phosphate is the same for 52-100 E.P. type and 52-100 heat stabilized steel ball bearings. The effect of tricresyl phosphate lubricity additive on M-10 steel ball bearings is the same at low loads but more effective at high loadings than with the 52-100 E.P. type steel ball bearings.

Suitable specimens for the Shell four-ball wear tester have been prepared from titanium and titanium alloys. No effective lubricants have been found for titanium-on-titanium bearing systems. Conventional E.P. lubricity additives generally improve steel-on-titanium lubrication. The mechanism of improved steel-on-titanium lubrication appears to include a chemical erosion action on the steel member which keeps to a minimum titanium pickup by the steel. Steel-on-titanium alloy systems appear to be somewhat harder to lubricate than steel-on-pure titanium systems.

The overall effect of increasing the phenothiazine concentration to at least 2.0 weight per cent is to improve the stable life or induction period. At temperatures of 500°F., where the induction period or stable life is too short to measure as a significant number, increased phenothiazine concentration is effective in reducing the rate of oxidation. The effect of the phenothiazine shows good persistence for periods of 30 to 60 hours at 500°F. All accelerated oxidation and corrosion conditions give indication of "trace dirtiness" within the stable life of the fluid. There are indications that this "trace dirtiness" increases with increasing phenothiazine.

In all cases evaluated in the region of incipient oxidation, uninhibited di-2-ethylhexyl sebacate appears to be cleaner on oxidation than a phenothiazine-inhibited di-2-ethylhexyl sebacate. Analysis of the oxidation products indicates that the presence of phenothiazine concentrates the effects of incipient oxidation on a relatively few fluid molecules causing sludge, while in the uninhibited ester, the same amount of oxygen is spread out over a much larger portion of the molecules resulting in some viscosity increase but less sludge. These data would indicate, in general, that it is desirable to obtain as much inherent stability as possible by ester and bulk fluid refining so that

the concentration of phenothiazine may be held to a minimum.

All of the phosphorus-containing ester fluids evaluated at 500°F. in an accelerated oxidation test show increased sludging tendencies. The use of Paranox 441 instead of phenothiazine does not alter substantially these sludge forming tendencies. There is no appreciable difference in sludge forming tendencies between compositions of the PRL 3161 type prepared to the same lubricity level in the one case with 5.0 weight per cent tricresyl phosphate and in the second case with 0.1 weight per cent of an alkyl acid phosphite.

Alkyl acid phosphite-hindered phenol inhibitor combinations offer enhanced oxidation and corrosion stability at high temperatures in mineral oils as well as in diester compositions. Phenyl alpha naphthylamine is also a good high temperature oxidation inhibitor for mineral oils. There are, in general, more indications of oxidative deterioration and corrosion in the 347°F. oxidation and corrosion tests for the mineral oils during the so-called induction period, or stable life, than is the case in the diester fluids evaluated previously by this Laboratory. The effect of a given inhibitor to control property changes and corrosion of metals during the induction period of a 347°F. oxidation and corrosion test decreases as the molecular weight, or viscosity grade, of the same type of mineral oil increases.

The problem of developing a satisfactory jet engine oil for operation in the temperature range of 500° to 600°F. (bulk oil temperature) requires the same basic property evaluations as the development of a high temperature hydraulic fluid. More emphasis will be placed on low temperature, oxidation, and corrosion properties for the jet engine oil development.

Preliminary oxidation and corrosion data indicate that an extended useful life at 500°F. will be extremely difficult to provide in the presence of large amounts of air or oxygen. Some of the compositions showing maximum oxidation and corrosion stability have not as yet been shown to possess adequate lubricity (silicones) or rubber seal compatibility (Aroclor). Silicates, esters, polyglycol ethers, synthetic hydrocarbons, and mineral oil fractions fall in the same general area of oxidation and corrosion stability at 500°F.

Increased jet lubricant life at high temperatures may best be achieved by a combination of fluid improvements coupled with mechanical changes to emphasize the strong properties of the improved fluids.

Fluids of adequate thermal stability for jet engine oils at 500° to 600°F. bulk oil temperatures have been shown in the hydraulic fluid section of this report. The use of alkyl acid phosphites and to a lesser extent tricresyl phosphate tends to increase the rate of thermal degradation of dibasic acid esters at 500°F. and above. The alkyl acid phosphites and tricresyl phosphate are added to the lubricant to improve the lubricity level.

A series of monobasic acid esters (pelargonic acid esters) have been evaluated as base stock materials for jet engine oils. In general,

these monobasic acid esters compare favorably in properties with conventional dibasic acid esters as base stocks for jet engine oil formulations. The pelargonate esters show poor tricresyl phosphate susceptibility, similar to diesters prepared from glycols and monobasic acids.

Several jet engine oils with improved lubricity have been formulated for further testing in high temperature stability and lubricity by the Wright Air Development Center and the Southwest Research Institute. These fluids contain alkyl acid phosphite additives and are based on the basic research on compositions of this type covering the past three years.

H. FUTURE WORK. Work on the development of a thermally stable polymeric additive for improving the viscosity-temperature characteristics of fluids and lubricants will be applied to jet engine oils as well as hydraulic fluids. The maximum temperatures estimated for engine oils of 600°F. is lower than the 700°F. maximum estimated for hydraulic fluids.

Major emphasis in future work will be concentrated on oxidation and corrosion at high temperatures. A program will be undertaken to study the effect of increased oxygen availability and increased intimacy of air-oil mixing on the rate of oxidation. All general trends established, thus far, indicate that increased intimacy of air-oil mixing and increased air circulation rate increase oxidation severity at 500°F. An attempt will be made to extend these studies into the regions which might be encountered in open and partially sealed lubricant systems.

It has been clearly shown that the quality margins between fluids decrease rapidly with increasing temperature at 500°F. and above. Many fluids do appear to have substantial oxygen tolerance at these elevated temperatures. Further studies will be directed to a study of various sequences of oxidation tests to determine how best to take advantage of the oxygen tolerance of various fluids. These data would be useful to guide engine designers in lubricating higher temperature engines in case mechanical changes are required in the lubricant system.

A panel coking apparatus is being installed. This unit will be used to measure high temperature stability under varying conditions.

High temperature hydraulic pump tests will be continued. Jet engine oils will be included in this test program along with hydraulic fluid compositions. The main points of emphasis will be lubricity at high temperatures and minimum pumpable viscosities in the jet engine oil studies. Lubricity studies are currently limited for the most part to low bulk oil temperatures.

Further work on the jet engine oils with alkyl acid phosphite lubricity additives will be dependent to a large extent upon the outcome of current evaluations being conducted by the Wright Air Development Center and the Southwest Research Institute.

## III. JET FUEL DIRTINESS

A. GENERAL. It has been indicated that the Air Force is encountering some difficulty with jet fuel dirtiness in current operations. These problems are noted primarily as deposits in portions of the fuel system in which the fuel is heated usually on its way to the burner. This includes the portion of the system between the fuel-oil heat exchanger and the fuel nozzle. In these cases, the fuel is heated in the presence of dissolved air in an environment including metal surfaces. This high temperature dirtiness of jet fuels is not adequately predicted or defined by conventional low temperature storage stability evaluations and ASTM gum tests. There is, however, some indication that these overall dirtiness trends of jet fuel are increased with storage time.

The Materials Laboratory, WCRTRI, of the Wright Air Development Center requested that this Laboratory make a study of the high temperature deposit forming tendencies of jet fuels. It was indicated that this study should include various classes of hydrocarbons which are not now being used in the preparation of JP-4 fuel. In general, the JP-4 fuel, as it is supplied currently, is believed to be a straight run product. That is, no cracked components are present. This is the first fuel study undertaken by this Laboratory under the current Air Force Contract AF33(038)18193. This Laboratory has maintained a project concerned with the composition and physical separation of fuels in the gasoline and jet fuel range for the past 20 years.

The dirtiness or deposit problem has been considered in these initial studies on the basis of existent and potential gum. Gum is the term conventionally applied to the formation of essentially non-volatile and/or insoluble products in fuels. These materials are products of oxidation and/or condensation of the fuel noted under storage and accelerated oxidation conditions. The term gum as used in this discussion is, therefore, more inclusive than sludge or insolubles normally used to characterize oxidative deterioration of hydraulic fluids and lubricants. Existent gum comprises non-volatile and insoluble material that is present in the fuel at the time of evaluation. Potential gum refers to the relative ease and quantity of non-volatile and insoluble products formed upon storage or upon subjection of the fuel to thermal and oxidative treatment.

The control of existent gum is a problem of removal of the gum from the fuel by physical processes, or of the dispersion or suspension of the gum in the fuel to prevent undesirable deposits at critical surfaces such as heat exchangers, filters, and nozzles. In the long range program, the problem of potential gum is probably the more important of the two. Control of potential gum is probably a more complex problem than removal of existent gum. Potential gum control can be attacked by the use of oxidation inhibitors, and by a basic study into the type of compounds required to produce gum on oxidation.

The study of chemical species and their relation to gum formation has been approached from two general directions. First, a JP-4

standard (dirty) referee fuel has been subjected to various physical separation processes to determine the effect of these separations on potential gum formation. These physical separation processes include distillation, silica gel adsorption, and liquid extraction with a liquid ammonia-amine solvent. The second approach is to study pure hydrocarbons and possible types of mineral oil impurities, both alone and in synthetic fuel blends, to determine the potential gum formation. This latter approach is made practical by the large inventory of pure hydrocarbon types accumulated over the years by this Laboratory in conjunction with research in the physical separations processes.

The JP-4 referee fuel was obtained from the Baltimore Refinery of the Esso Standard Oil Company. Approximately 200 gallons of this JP-4 referee fuel were purchased for use in this study. It is believed that this JP-4 referee fuel is designed to exhibit maximum dirtiness allowed under the JP-4 specification.

B. LIQUID EXTRACTION UNIT USED IN THE SEPARATION OF JP-4 REFEREE FUEL. This unit consists of a 20 stage extractor with auxiliary equipment for solvent and product recovery. It is designed primarily for continuous operation, but it has been used satisfactorily for batch operation. In the present study, continuous operation was used.

The extractor has 20 individual stages stacked on top of one another. Efficiency tests indicate these stages approach theoretical stages, i.e., equilibrium between the two phases is reached on each stage and separation of the phases is complete. The extractor is constructed so that the location of the feed point can be changed to give various combinations of enriching (above the feed) and stripping (below the feed) stages. The extractor is equipped with sampling lines for both phases on each stage. Each stage has a water injection point to decrease the hydrocarbon solubility in the extractor since water acts as an anti-solvent.

The predominant constituent of the solvent is ammonia. Monomethylamine is added to ammonia to increase the solubility of the hydrocarbons in the solvent. The light phase, or solvent plus hydrocarbon, leaves the top of the extractor to be separated in the recovery system. The heavy phase, or hydrocarbon saturated with solvent, is pumped from the bottom of the extractor to the recovery system. The solvent from these two streams are combined to be used over again in the extractor.

The hydrocarbon from the light or solvent phase is split into two streams: (1) extract product, and (2) reflux to be returned to the extractor. The hydrocarbon from the heavy phase is the raffinate product. The extract product is combined with the raffinate product to be used over again as hydrocarbon feed. In this way extensive separational studies can be made on an original charge of 25 to 30 gallons of hydrocarbon feed.

1. Operating Conditions. Six separate extractions were made on the "topped" JP-4 fuel. Of these, five extractions (runs 231, 232, 233, 234 and 235) were of an exploratory nature and three of the main

extraction variables were studied. The operating conditions for these extractions are shown on Table 84. These variables are product proportionment or extract yield, solvent-to-oil ratio, and stage distribution. Approximately one to two liters of extract product along with the corresponding amount of raffinate were collected in these runs for analysis and for a study of their properties.

Runs 236 and 237 were production extractions in which large amounts (approx. 15 gals. of extract) of end products were produced. The raffinate product of run 236 was used as feed for run 237. In this way, the more easily extracted compounds were removed by the first extraction (run 236), and in the subsequent extraction (run 237), compounds more difficult to extract were removed. The average operating condition for runs 236 and 237 are given in Table 84.

The solvent used contained 9 to 25 weight per cent monomethyamine in ammonia. Water injection was used in run 232 to reduce the hydrocarbon solubility above the feed stage. The water was necessary for this run since a small proportion of the feed (8.5 vol. %) was taken as extract product and the operating conditions were such that this product was pure aromatics. In such an extraction, the solubility of the more soluble compounds increases rapidly as they concentrate toward the top of the extractor, thus requiring an antisolvent to maintain two liquid phases.

In these six extractions, the solvent-to-oil (feed) weight ratio was varied from 1:1 to 3:1. The temperature range in the extractor during operation was 61° to 102°F. Actually the temperature gradient between the feed stage and the top stage of the extractor ranged from about 25° to 34°F. This helped to maintain the hydrocarbon solubility in the solvent within the limits of 10 to 30 weight per cent.

Four different stage distributions were used in an effort to determine the effect of enriching and stripping stages on the separation. The most effective stage distribution will vary with operational conditions. Therefore, when other conditions are altered it is often necessary to relocate the feed point, or change the stage distribution, to use effectively all the stages.

The effects of these principal variables will be discussed later together with graphs showing the results.

C. EXTRACTION OF JP-4 FUEL. The main purpose or objective of this work was to determine whether the "dirty" portion of the fuel, as well as the potential "dirty" compounds, could be removed from the fuel by liquid ammonia extraction using an extractor with 20 stages. Another objective of the work was to prepare a sufficient quantity of the extraction products so that practical "mock-up" tests could be made in addition to the laboratory gum and oxidation evaluations. The effectiveness of the separation of the type hydrocarbons for this rather wide boiling range fuel evolved as probably the most fruitful result of the study.

The referee fuel was purchased from the Esso Standard Oil Company. The exact origin of the fuel is not known but, from the analyses made, it appears to be made up partially of a cracked stock. This is indicated mainly by the presence of olefinic hydrocarbons to the extent of eight volume per cent.

A number of separation steps were used in the preparation of the samples for "mock-up" tests. These steps are shown schematically in the flow sheet of Figure 32 and are discussed below.

1. Fractionation and Analysis of Fuel. As the sample was received at this laboratory, the ASTM boiling range was 122° to 518°F. Actually, the atmospheric pressure boiling range is wider than this because, by fractionation, it is about 80° to 520°F. The fractionation data for the fuel are given in Table 85 along with some physical properties on the fractions. From these data, and from silica gel adsorption data that are not included, the following analysis has been arrived at for the fuel.

| Hydrocarbon | Vol. % |
|---|---|
| Olefins | 8 |
| Mononuclear aromatics | 26 |
| Polynuclear aromatics | 2 |
| Saturates | 64 |
| Total | 100 |

A further analysis of the aromatic portion is as follows:

| Aromatic Group | Vol.% of Fuel |
|---|---|
| Toluene | 1 |
| C-8 | 2 |
| C-9 | 6 |
| C-10 | 7 |
| C-11, C-12 and higher mononuclear | 10 |
| C-10, C-11 and C-12 | 2 |
| Total | 28 |

The polynuclear aromatics referred to above consist mainly of the homologs of naphthalene.

It is realized that in making the aromatic analysis by absorption in sulfuric acid, some error may be introduced, due to the presence of olefins. However, since the olefin content is rather low, this error is probably not appreciable. Furthermore, the total aromatic content by the acid absorption of the fractions and by the silica gel adsorption of the overall fuel agree quite well.

2. Topping of Fuel for Liquid Extraction. As mentioned previously, the boiling range of the fuel as received included hydrocarbons boiling as low as about 80°F. Ammonia forms azeotropic mixtures with

some hydrocarbons boiling below about 200°F. In the solvent recovery system of the extraction unit, the solvent is separated from the hydrocarbon and purified for reuse by distillation. Therefore, any hydrocarbons that are present in the extraction products that form azeotropes with ammonia will contaminate the solvent that is returned to the extractor. This means that an impure solvent would be used which might be objectionable in making a very sharp separation. Hydrocarbons boiling above about 200°F. do not form azeotropes with ammonia.

For these reasons the material boiling below about 200°F. was removed from the fuel by fractional distillation to prepare the feed for the liquid extraction study. This was done only because it was more convenient to operate the extraction unit with this lower boiling material removed. It is believed that this lower boiling material would have little or no affect on the dirtiness of the fuel.

Four barrels (180 gallons) of this fuel were "topped" to remove the material boiling below about 200°F. This was done in this Laboratory's 75-plate column which is equipped with a still having a capacity of 45 gallons. This distillation is shown as step A in the flow sheet of Figure 32. In Table 86, the data are given for one of the distillations which is typical of the other three that were also made. The "topped" fuel, or the feed for the liquid extractions, represents 85 volume per cent of the original JP-4 fuel. This material is shown as product 3 in Figure 32. In other words, 15 volume per cent of the JP-4 fuel was discarded (product 2 in Figure 32). The estimated composition of the material below about 200°F. is 15 volume per cent olefins with the balance being naphthenes and paraffins. Essentially no benzene appears to be present.

3. Liquid Extraction of "Topped" Fuel (200°-520°F.). A total of six extractions was made on the "topped" jet fuel. In this series of runs, some of the principal operating variables were studied, namely, solvent-to-oil ratio, stage distribution, and product yield. The detailed operating conditions for these runs has been given previously on Table 84. The analyses of the products from these six runs (Nos. 231 to 236), as well as a summarization of the operating conditions, are given in Table 87.

One method that was used for evaluating some aspects of the "dirtiness" of this JP-4 fuel is existent gum number (ASTM Method D381-52T). This property for the extraction products is also included in Table 87. It will be noted that the gum content of both the extraction products from the individual runs is higher than the original JP-4 referee fuel and this gum content is not greatly altered by changes in the extraction conditions. On the other hand, the hydrocarbon type analyses for the extraction products are quite different with changing extraction conditions. For example, in run 232 (8.5 vol. % of feed to extract) the aromatic content of the extract is 100 per cent, while in run 235 (31 vol.% of feed to extract) it is about 74 volume per cent. These two runs represent the extreme differences in the analyses for this series of runs. The analyses of the products from the other runs are within these two extremes.

In Figure 33, the aromatic content of the extract and the per cent of the feed aromatics in the extract are plotted against the extract yield (% of feed to extract) for the two different solvent-to-oil ratios used. These curves show clearly the effect of the two variables, solvent-to-oil ratio and extract yield, on the aromatic:non-aromatic separation. The other principal variable studied, stage distribution, does not appear to affect greatly the nature of the end products.

As mentioned previously, the first six runs (231 to 236) were made on the "topped" fuel. The first five of these runs were experimental with rather small end product samples being removed. In run 236 (step B in Figure 32), about 100 gallons were processed through the extractor, resulting in about 15 gallons of extract product (product No. 4 in Figure 32) and 85 gallons of raffinate product (product No. 5 in Figure 32). This run was made principally to produce an extract that represented the most soluble compounds present in the feed, so that the dirtiness characteristics of this portion could be determined. If the polarity of the compounds has anything to do with deposit formation and dirtiness, then the "dirty" qualities of this sample should be magnified over that of the original JP-4 fuel.

This extract represents 15 volume per cent of the topped fuel, consists of 96 volume per cent aromatics, and contains about 45 per cent of the aromatics present in the topped fuel. As noted in Table 87, it also contains about 50 per cent of the feed polynuclear aromatics.

The raffinate from run 236 was then used as the feed for liquid extraction run 237 so that a second extract product could be produced. This step is shown in Figure 32 as step C. In this run (237), the extract product (product 6 in Figure 32) represents 18 volume per cent of the feed or 15 volume per cent of the topped JP-4 fuel. The aromatic content of this extract is 69 volume per cent as compared to 96 per cent for the first extract. Also, the nature and relative proportions of the aromatics in these two extracts are probably quite different. The aromatic content of the raffinate from run 237 (product 7 in Figure 32) has been reduced to 9 volume per cent, as compared to 21 per cent for run 236 raffinate, and 33 per cent for the feed. The olefin content is about the same in all three cases, so as the aromatic content is decreased, the saturated (paraffins and naphthenes) hydrocarbon content is correspondingly increased.

From these two extractions the following four products were made:

1. Extract from run 236. Represents the first 15 volume % of the topped JP-4 fuel removed by extraction.

2. Extract from run 237. Represents the second 15 volume % (15 to 30%) of the topped JP-4 fuel removed by extraction.

3. Raffinate from run 236. Represents 85 volume % of the topped JP-4 fuel. The other 15% of the feed is aromatics removed by extraction.

4. Raffinate from run 237. Represents 70 volume % of the topped JP-4 fuel. The other 30% of the feed was removed as extracts and consisted of about 80 per cent aromatics.

The hydrocarbon type analyses listed in Table 87 were made chiefly from the refractive index and bromine number measurements of fractions from the fractional distillation and fractional silica gel adsorption of the products.

The data for all the individual silica gel adsorptions and fractional distillations are not included here, but plots are given for both adsorption and distillations that illustrate these two methods of analysis. Figure 34 is a plot of the analyses for the fractional silica gel adsorption of the feed, the extract product, and the raffinate product from a typical extraction run (235) on this topped fuel. This plot shows clearly that the hydrocarbon type separations by this method are quite sharp. This analytical method has proved to be very useful in making these and similar analyses, especially when olefins are present.

In Figure 35, the boiling point data are plotted for the raffinate and extract products from a typical extraction (232). These data illustrate that there is a substantial difference in the boiling points of the two extraction products. This difference decreases somewhat as the extract yield is increased, or as more of the aromatic hydrocarbons are removed into the extract product.

The flow sheet for the separation of JP-4 referee fuel indicates that the raffinate and extract products have been subjected to further distillation. This additional distillation step is necessary to reduce the existent gum value of the products from the extractor which are, in all cases, in excess of the specification limit for JP-4 fuel. The increase in gum number in the extraction process is discussed in more detail in the section on existent gum. To prevent, or limit as much as possible, the formation of additional gum on standing following the extraction and distillation steps, 20 parts per million of U.O.P. Inhibitor No. 5 has been added to the products of extraction and distillation.

Oxidation tests discussed in subsequent paragraphs indicate that any inhibitor originally present in the JP-4 fuel is effectively removed in the liquid ammonia-amine extraction procedure. Therefore, products taken from the extractor must be reinhibited. It has been experimentally shown that U.O.P. Inhibitor No. 5 does not appear as gum in the air jet gum test. Similarly, distillation of extraction products containing U.O.P. Inhibitor No. 5 indicates that this material is volatile. As a safety feature, however, it is planned to add an additional 20 parts per million of U.O.P. Inhibitor No. 5 to the extractor products that are subjected to subsequent distillation.

The composition of the extractor fractions, according to hydrocarbon type, show good separation or concentration of the aromatics and sulfur in the extract fractions, and saturates (naphthenes and paraffins) in the raffinate fractions. A measure of existent gum

indicates, however, that the values for all extractor products are higher than for the topped JP-4 referee fuel used as the starting material. This trend was found to be characteristic of a basic wash of JP-4 referee fuel. Potential gum studies after oxidation, however, indicate that some differences between the raffinate and the extract have been effected by extraction. It is further indicated by preliminary tests, that a simple distillation of the extraction products to produce fractions varying according to increasing molecular size causes still further separation in potential gum values. It has been found that a simple distillation also essentially eliminates existent gum values.

As a result of these studies, which are described in a subsequent section of this report, large scale vacuum distillations have been conducted on the extract and raffinate portions of extractor runs 236 and 237 (runs B and C on Figure 32). These distillations are designed primarily to reduce existent gum values formed or at least increased by contact with the basic ammonia-amine solvent in the extractor. In all cases, the distillations were carried to about 95 volume per cent distilled. Approximately 10 gallons of distilled products have been prepared for each of the four materials discussed, i.e., the extract and the raffinate fractions from runs 236 and 237.

In addition to these four major products, three fractions of run 237 raffinate have been prepared according to boiling range. Three batch distillations were conducted and the same fractions from the various distillations blended. Fraction 1 of the raffinate from run 237 includes the boiling range from 230° to 350°F. (34 vol. %); Fraction 2 from 350° to 450°F. (47 vol. %); and Fraction 3 from 450° to 550°F. (14 vol. %). The remaining 5 vol. % was divided among the loss, holdup, and the residue.

The relationship of these various products from the simple distillation are shown on Figure 32. All of these distilled products have been inhibited with 20 p.p.m. of U.O.P. Inhibitor No. 5 and stored in 15 gallon steel drums under a nitrogen atmosphere. These fractions are the result of efficient separation techniques. The various fractions do, therefore, offer an opportunity to determine how wide or how specific the dirtiness trends are in this JP-4 referee fuel.

The fractions indicated on Figure 32 are being studied in the second phase of the jet fuel test program. That is, these fractions are being evaluated in bench tests to determine their dirtiness characteristics.

D. <u>APPARATUS AND PROCEDURES FOR EXISTENT AND POTENTIAL GUM DETERMINATION</u>. Gum determinations are conducted in accordance with the air jet procedure of ASTM Test Method D381-52T "Test for Existent Gum by Jet Evaporation". A flow diagram of the apparatus used to meet the requirements of the gum determination is shown on Figure 36. This apparatus has been made by modifying the constant temperature bath used in an earlier study relating to slide valve sticking by hydraulic fluids. The construction details of the bath, along with a wiring diagram, have been shown as Figures 7 and 8 of report PRL 5.8-Sep53. These drawings are, therefore, not repeated here. The temperature of

Table 84

OPERATING CONDITIONS FOR THE LIQUID EXTRACTION OF "TOPPED" ESSO JP-4 REFEREE FUEL IN THE 20-STAGE EXTRACTOR USING LIQUID AMMONIA SOLVENTS

(THE "TOPPED" FUEL INCLUDES THE MATERIAL BOILING ABOVE 100°C. (212°F.) AND REPRESENTS 85 VOL.% OF THE JP-4 REFEREE FUEL)

MIXER FREQUENCY, CYCLES PER MINUTE = 405 MIXER AMPLITUDE, INCHES = 0.25

| RUN NO. | 231 | 232(6) | 233 | 234 | 235 | 236(7) | 237(8) |
|---|---|---|---|---|---|---|---|
| STAGE DISTRIBUTION, E/F/S(1) | 15/F/4 | 15/F/4 | 12/F/7 | 12/F/7 | 8/F/11 | 15/F/4 | 8/F/11 |
| SOLVENT FEED | | | | | | | |
| RATE, LBS./HR. | 15 | 45 | 45 | 45 | 45 | 45 | 45 |
| COMPOSITION, WT.% | | | | | | | |
| AMMONIA | 91 | 91 | 91 | 85 | 82 | 85 | 75 |
| MONOMETHYLAMINE | 9 | 9 | 9 | 15 | 18 | 15 | 25 |
| SOLVENT-TO-OIL WT. RATIO | 1.0 | 3.0 | 3.0 | 3.0 | 3.0 | 2.9 | 2.9 |
| HYDROCARBON FEED RATE, LBS./HR. | 15 | 15 | 15 | 15 | 15 | 15.6 | 15.6 |
| VOL.% OF FEED AS EXTRACT PRODUCT | 8 | 8.5 | 20 | 19 | 31 | 15 | 18 |
| EXTRACT PHASE LEAVING EXTRACTOR(2) | | | | | | | |
| RATE, LBS./HR. | 19.5 | 57 | 52 | 59 | 57 | 65 | 55 |
| WT.% SOLVENT | 78 | 78 | 86 | 75 | 78 | 68 | 80 |
| WT.% HYDROCARBON | 22 | 22 | 14 | 25 | 22 | 32 | 20 |
| RAFFINATE PRODUCT(3) (SOLVENT-FREE) | | | | | | | |
| RATE, LBS./HR. | 13.7 | 13.6 | 11.7 | 11.8 | 10 | 13.1 | 12.6 |
| HYDROCARBON REFLUX | | | | | | | |
| RATE, LBS./HR. | 2.9 | 11.1 | 4.2 | 11.5 | 7.5 | 18.2 | 8.0 |
| REFLUX RATIO(4) | | | | | | | |
| TOP STAGE | 2.2 | 8.0 | 1.2 | 3.6 | 1.5 | 7.3 | 2.7 |
| FEED STAGE | 0.3 | 3.7 | 0.5 | 0.9 | 0.7 | 2.4 | 1.6 |
| EXTRACTOR TEMP. RANGE, °F. | 72-97 | 61-95 | 63-95 | 68-102 | 68-99 | 61-97 | 70-100 |
| STAGE 16 - SOL., WT.%(5) | 13 | 19 | 10 | 19 | 16 | 34 | 16 |
| TEMP., °F. | 79 | 65 | 70 | 72 | 77 | 64 | 82 |
| STAGE 12 - SOL., WT.%(5) | 14 | 19 | 10 | 16 | 16 | 33 | 15 |
| TEMP., °F. | 90 | 81 | 81 | 84 | 99 | 77 | 100 |
| STAGE 8 - SOL., WT.%(5) | 12 | 22 | 10 | 13 | 13 | 32 | 15 |
| TEMP., °F. | 92 | 92 | 95 | 102 | 92 | 90 | 99 |
| STAGE 5 - SOL., WT.%(5) | 8 | 13 | 9 | 11 | 10 | 14 | 12 |
| TEMP., °F. | 97 | 95 | 93 | 99 | 92 | 97 | 99 |
| STAGE 1 - SOL., WT.%(5) | 4 | 6 | 5 | 5 | 4 | 7 | 6 |
| TEMP., °F. | 94 | 92 | 93 | 99 | 92 | 92 | 99 |

(1) ENRICHING/FEED/STRIPPING STAGES.
(2) THIS IS THE SOLVENT PHASE AS IT LEAVES THE TOP OF THE EXTRACTOR AND ENTERS THE RECOVERY SYSTEM. THE DIFFERENCE BETWEEN THE HYDROCARBON IN THIS PHASE AND THE EXTRACT PRODUCT IS RETURNED TO THE EXTRACTOR AS REFLUX.
(3) THE RAFFINATE PRODUCT IS THE HYDROCARBON OF THE HEAVY PHASE AS IT LEAVES THE EXTRACTOR. THIS PHASE USUALLY CONTAINS ABOUT 5 WT.% SOLVENT. THE BALANCE IS HYDROCARBON.
(4) REFLUX RATIO IS DEFINED AS THE POUNDS OF HYDROCARBON ENTERING A STAGE FROM THE ONE ABOVE DIVIDED BY THE POUNDS OF EXTRACT HYDROCARBON REMOVED AS PRODUCT PER UNIT TIME.
(5) SOLUBILITY IS THE WT.% HYDROCARBON IN THE EXTRACT PHASE.
(6) IN THIS RUN 1.5 LBS./HR. OF WATER WAS INJECTED ON STAGE 6.
(7) THIS WAS A PRODUCTION RUN. THE OPERATING CONDITIONS LISTED ARE AN AVERAGE FOR THE DURATION OF THE RUN.
(8) THIS WAS A PRODUCTION RUN USING THE RAFFINATE FROM RUN 236 AS THE FEED. THE 18 VOL.% OF RUN 236 RAFFINATE REPRESENTS 15 VOL.% OF THE "TOPPED" REFEREE FUEL.

Table 85

RACTIONAL DISTILLATION OF ESSO JP-4 REFEREE FUEL

FRACTIONATION NO. 85 IN 1.87-INCH I.D. STAINLESS STEEL COLUMN NO. 1
(APPROXIMATELY 35 THEORETICAL PLATES)

| VOL.% DISTILLED | REFLUX RATIO |
|---|---|
| 0-14 | 20:1 |
| 14-63 | 10:1 |
| 63-88 | 20:1 |

DECEMBER 14-17, 1953

CHARGE: 53.5 LITERS OF JP-4 REFEREE FUEL OF FORMULA 192 PURCHASED FROM THE ESSO STANDARD OIL COMPANY.

ESTIMATED ANALYSIS

| HYDROCARBON | VOL.% |
|---|---|
| OLEFINS | 8 |
| MONONUCLEAR AROMATICS | 26 |
| POLYNUCLEAR AROMATICS | 2 |
| SATURATES | 64 |
| TOTAL | 100 |

SULFUR CONTENT, WT.% = 0.29

MATERIAL BALANCE

| | VOL. CC. | VOL.% |
|---|---|---|
| CHARGE | 53,500 | 100 |
| NON-CONDENSABLE GAS | 1,340 | 2.5 |
| DISTILLATE | 49,670 | 85.4 |
| HOLDUP | 300 | 0.6 |
| RESIDUE | 6,160 | 11.5 |
| RECOVERY | 53,470 | 100 |

A.S.T.M. DISTILLATION

| VOL.% DIST. | TEMP., °F., CORR. TO 760 MM. HG |
|---|---|
| I.B.P. | 122 |
| 2 | 1[illegible] |
| 5 | 197 |
| 10 | 226 |
| 20 | 256 |
| 30 | 300 |
| 40 | 332 |
| 50 | 344 |
| 60 | 368 |
| 70 | 389 |
| 80 | 415 |
| 90 | 460 |
| 97 | 518 |
| DISTILLATE | 99.0 |
| RESIDUE | 0.6 |
| RECOVERY | 99.6 |

| FRAC. NO. | CC. PER FRAC. | TOTAL CC. DISTILLED | VOL.% OF CHARGE DIST. | REFLUX TEMP. CORRECTED TO 760 MM. HG °C. | °F. | REFRACTIVE INDEX, BEFORE $H_2SO_4$ | AFTER EXTRACTION | *EST. VOL.% AROMATICS |
|---|---|---|---|---|---|---|---|---|
| 1A | 1340 | 1340 | 2.5 | NON-CONDENSABLE GAS | | | | |
| 1 | 480 | 1820 | 3.4 | 32.0 | 90 | 1.3594 | | |
| 2 | 480 | 2300 | 4.3 | 52.5 | 127 | 1.3703 | | |
| 3 | 480 | 2780 | 5.2 | 59.5 | 139 | 1.3745 | | |
| 4 | 480 | 3260 | 6.1 | 65.0 | 149 | 1.3797 | | |
| 5 | 480 | 3740 | 7.0 | 66.0 | 151 | 1.3889 | 1.3876 | 0 |

(CONTINUED ON NEXT PAGE)

Table 85 (Continued)

| FRAC. NO. | CC. PER FRAC. | TOTAL CC. DISTILLED | VOL.% OF CHARGE DIST. | REFLUX TEMP. CORRECTED TO 760 MM. HG °C. | °F. | REFRACTIVE INDEX, BEFORE $H_2SO_4$ | AFTER EXTRACTION | *EST. VOL.% AROMATICS |
|---|---|---|---|---|---|---|---|---|
| 6 | 480 | 4220 | 7.9 | 74.5 | 167 | 1.4030 | | |
| 7 | 480 | 4700 | 8.8 | 82.0 | 180 | 1.4059 | 1.4068 | 0 |
| 8 | 480 | 5180 | 9.7 | 87.5 | 190 | 1.4005 | | |
| 9 | 480 | 5660 | 10.6 | 90.0 | 195 | 1.3990 | 1.3995 | 0 |
| 10 | [illegible] | 6140 | 11.5 | 91.0 | 196 | 1.4001 | | |
| 11 | [illegible] | 6620 | 12.4 | 95.0 | 205 | 1.4033 | | |
| 12 | [illegible] | 7100 | 13.3 | 99.5 | 211 | 1.4109 | 1.4066 | 5 |
| 13 | 480 | 7580 | 14.2 | 102.5 | 217 | 1.4238 | | |
| 14 | 960 | 8540 | 16.0 | 112.0 | 234 | 1.4314 | 1.4117 | 24 |
| 15 | 960 | 9500 | 17.8 | 118.0 | 244 | 1.4184 | | |
| 16 | 960 | 10,460 | 19.5 | 118.0 | 244 | 1.4178 | 1.4115 | 8 |
| 17 | 960 | 11,420 | 21.3 | 121.5 | 251 | 1.4190 | | |
| 18 | 960 | 12,380 | 23.1 | 127.0 | 260 | 1.4255 | 1.4151 | 13 |
| 19 | 960 | 13,340 | 24.9 | 133.0 | 271 | 1.4370 | | |
| 20 | 960 | 14,300 | 26.7 | 134.5 | 275 | 1.4439 | | |
| 21 | 960 | 15,260 | 28.5 | 137.0 | 279 | 1.4458 | 1.4180 | 37 |
| 22 | 960 | 16,220 | 30.3 | [illegible] | 286 | 1.4456 | | |
| 23 | 960 | 17,180 | 32.1 | [illegible] | 293 | 1.4350 | | |
| 24 | 960 | 18,140 | 33.9 | 149.0 | 300 | 1.4348 | 1.4212 | 17 |
| 25 | 960 | 19,100 | 35.7 | 154.0 | 310 | 1.4380 | | |
| 26 | 960 | 20,060 | 37.4 | 160.0 | 321 | 1.4445 | | |
| 27 | 960 | 21,020 | 39.4 | 160.0 | 321 | 1.4490 | 1.4238 | 33 |
| 28 | 960 | 21,980 | 41.0 | [illegible] | 323 | 1.4550 | | |
| 29 | 960 | 22,940 | 42.8 | 163.5 | 327 | 1.4561 | | |
| 30 | 960 | 23,900 | 44.7 | 167.5 | 334 | 1.4572 | 1.4257 | 40 |
| 31 | 960 | 24,860 | 46.5 | 168.5 | 336 | 1.4564 | | |
| 32 | 960 | 25,820 | 48.3 | 173.0 | 344 | 1.4590 | | |
| 33 | 960 | 26,780 | 50.0 | 176.0 | 349 | 1.4539 | 1.4263 | 35 |
| 34 | 960 | 27,740 | [illegible] | [illegible] | 353 | 1.4533 | | |
| 35 | 960 | 28,700 | 53.7 | 181.5 | 358 | 1.4533 | | |
| 36 | 960 | 29,660 | 55.4 | 183.5 | 362 | 1.4557 | 1.4290 | 35 |
| 37 | 960 | 30,620 | 57.3 | 188.0 | 370 | 1.4567 | | |
| 38 | 960 | 31,580 | 59.0 | 187.[illegible] | 369 | 1.4559 | | |
| 39 | 960 | 32,540 | 60.8 | 189.5 | 374 | 1.4576 | 1.4308 | 35 |
| 40 | 960 | 33,500 | 62.6 | 193.0 | 380 | 1.4564 | | |
| 41 | 480 | 33,980 | 63.5 | 193.0 | 380 | 1.4567 | | |
| 42 | 480 | 34,460 | 64.4 | 195.5 | 384 | 1.4578 | 1.4313 | 35 |
| 43 | 480 | 34,940 | 65.3 | 196.5 | 386 | 1.4600 | | |
| 44 | 480 | 35,420 | 66.3 | 199.5 | 390 | 1.4638 | | |
| 45 | 480 | 35,900 | 67.2 | 200.0 | 392 | 1.4680 | 1.4343 | 45 |
| 46 | 480 | 36,380 | 68.0 | 201.5 | 394 | 1.4718 | | |
| 47 | 480 | 36,860 | 69.0 | 203.5 | 399 | 1.4738 | | |
| 48 | 480 | 37,340 | 69.7 | 203.5 | 398 | 1.4749 | 1.4383 | 46 |
| 49 | 480 | 37,820 | 70.5 | 205.5 | 402 | 1.4749 | | |
| 50 | 480 | 38,300 | 71.6 | 205.5 | 402 | 1.4750 | | |
| 51 | 480 | 38,780 | 72.4 | 208.5 | 407 | 1.4763 | 1.4391 | 46 |
| 52 | 480 | 39,260 | 73.4 | 209.0 | 408 | 1.4783 | | |
| 53 | 480 | 39,740 | 74.3 | 211.0 | 412 | 1.4812 | 1.4388 | 50 |
| 54 | 480 | 40,220 | 75.1 | 211.5 | [illegible] | 1.4824 | | |
| 55 | 480 | 40,700 | 76.1 | 213.0 | 416 | 1.4814 | | |
| 56 | 480 | 41,180 | 76.8 | 214.0 | 418 | 1.4769 | 1.4360 | 48 |
| 57 | 480 | 41,660 | 77.8 | 215.5 | 420 | 1.4597 | | |
| 58 | 480 | 42,140 | 78.8 | 218.0 | 424 | 1.4648 | | |
| 59 | 480 | 42,620 | 79.7 | 219.0 | 428 | 1.4590 | 1.4390 | 32 |
| 60 | 480 | 43,100 | 80.6 | 221.0 | 429 | 1.4643 | | |
| 61 | 480 | 43,580 | 81.[illegible] | 224.0 | 435 | 1.4575 | | |
| 62 | 480 | 44,060 | 82.3 | 226.0 | 439 | 1.4592 | 1.4444 | 33 |
| 63 | 480 | 44,540 | 83.3 | 228.5 | 443 | 1.4704 | | |
| 64 | 480 | 45,020 | 84.1 | 229.5 | 445 | 1.4708 | | |
| 65 | 480 | 45,500 | 85.1 | 235.0 | 455 | 1.4717 | 1.4437 | 30 |

(CONCLUDED ON NEXT PAGE)

Table 85 (Concluded)

| FRAC. NO. | CC. PER FRAC. | TOTAL CC. DISTILLED | VOL.% OF CHARGE DIST. | REFLUX TEMP. CORRECTED TO 760 MM. HG °C. | °F. | REFRACTIVE INDEX, BEFORE $H_2SO_4$ | AFTER EXTRACTION | *EST. VOL.% AROMATICS |
|---|---|---|---|---|---|---|---|---|
| 66 | 480 | 45,980 | 85.9 | 236.5 | 458 | 1.4723 | | |
| 67 | 480 | 46,460 | 86.8 | 240.5 | 465 | 1.4723 | | |
| 68 | 480 | 46,940 | 87.7 | 243.0 | 469 | 1.4700 | 1.4458 | 28 |
| 69 | 70 | 47,010 | 87.9 | - | - | 1.4682 | | |
| COLD TRAP | 300 | 47,310 | 88.4 | - | - | - | | |
| RESIDUE | 6,160 | 53,470 | 100 | - | - | 1.4734 | 1.4510 | 31 |

* THE AROMATIC CONTENT WAS CALCULATED FROM THE REFRACTIVE INDEX BEFORE AND AFTER SULFURIC ACID EXTRACTION.

Figure 32

SCHEMATIC FLOW SHEET FOR THE LIQUID EXTRACTION OF JP-4 REFEREE FUEL

All Percentage Values Indicated are on the Basis of the Original JP-4 Fuel

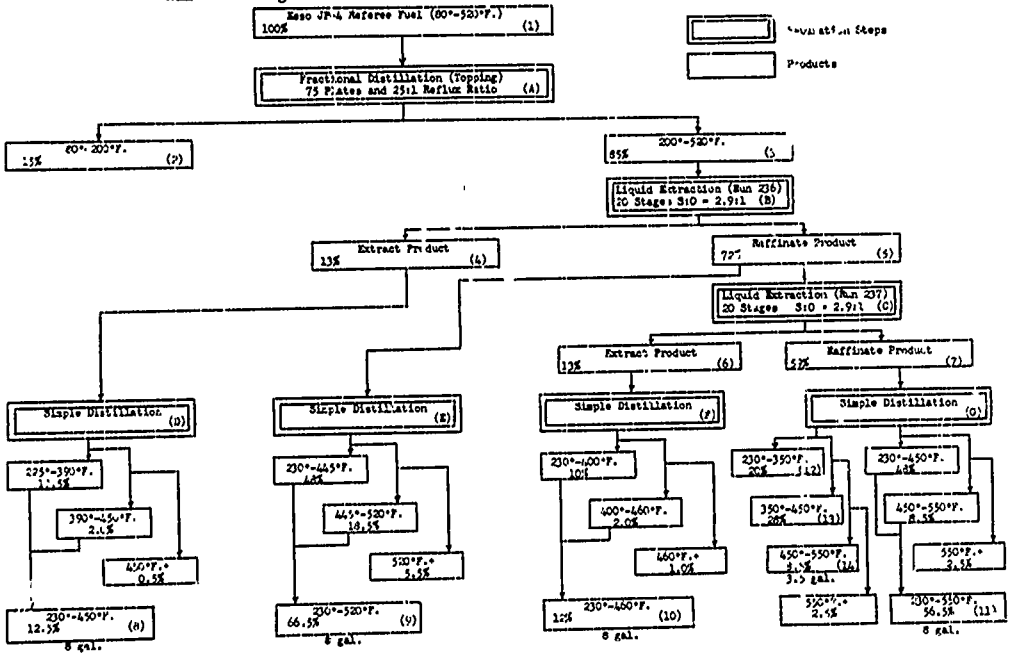


Table 86

FRACTIONAL DISTILLATION OF ESSO JP-4 REFEREE FUEL

ALUMINUM COLUMN
(APPROXIMATELY 75 THEORETICAL PLATES AND 25:1 REFLUX RATIO)

DECEMBER 3-4, 1953

CHARGE: JP-4 REFEREE FUEL OF FORMULA 192 PURCHASED FROM THE ESSO STANDARD OIL COMPANY

VOLUME CHARGED - 170.2 LITERS

PROPERTIES OF CHARGE: REFRACTIVE INDEX AT 20°C., $n_D^{20}$ = 1.4486

A.S.T.M. DISTILLATION

| VOL. % DIST. | TEMP., °F. |
|---|---|
| I.B.P. | 122 |
| 2 | 154 |
| 5 | 197 |
| 10 | 226 |
| 20 | 256 |
| 30 | 300 |
| 40 | 332 |
| 50 | 344 |
| 60 | 358 |
| 70 | 389 |
| 80 | 415 |
| 90 | 450 |
| 97 | 518 |

| | |
|---|---|
| DISTILLATE | 99.0 CC. |
| RESIDUE | 0.5 |
| RECOVERY | 99.6 |

ESTIMATED ANALYSIS

| HYDROCARBON | VOL.% |
|---|---|
| OLEFINS | 8 |
| MONONUCLEAR AROMATICS | 26 |
| POLYNUCLEAR AROMATICS | 2 |
| SATURATES | 64 |
| TOTAL | 100 |

SULFUR CONTENT, WT.% = 0.29

| FRAC. NO. | CC. PER FRAC. | TOTAL CC. DISTILLED | VOL.% OF CHARGE DIST. | 50% COTTRELL B.P. CORRECTED TO 760 MM. HG °C. | °F. | COTTRELL SPREAD I.B.P. 50% PT. °C. | REFRACTIVE INDEX, $n_D^{20}$ |
|---|---|---|---|---|---|---|---|
| 1A | 5110 | 5110 | 3.0 | | | | |
| 1 | 960 | 6070 | 3.6 | 30.75 | 87.4 | 1.00 | 1.3577 |
| 2 | 960 | 7030 | 4.1 | | | | 1.3605 |
| 3 | 960 | 7990 | 4.7 | 36.7 | 98.1 | 0.55 | 1.3670 |
| 4 | 960 | 8950 | 5.3 | | | | 1.3750 |
| 5 | 960 | 9910 | 5.8 | 58.05 | 136.5 | 0.50 | 1.3750 |
| 6 | 960 | 10,870 | 6.4 | | | | 1.3763 |
| 7 | 960 | 11,830 | 6.9 | 64.25 | 147.7 | 1.45 | 1.3800 |
| 8 | 960 | 12,790 | 7.5 | | | | 1.3857 |
| 9 | 960 | 13,750 | 8.1 | 68.90 | 156.0 | 1.15 | 1.3950 |
| 10 | 960 | 14,710 | 8.6 | | | | 1.4068 |
| 11 | 960 | 15,670 | 9.2 | 76.85 | 170.3 | 1.65 | 1.4125 |
| 12 | 960 | 16,630 | 9.8 | | | | 1.4059 |
| 13 | 960 | 17,590 | 10.3 | 87.9 | 190.2 | 1.50 | 1.4000 |
| 14 | 960 | 18,550 | 10.9 | | | | 1.3979 |
| 15 | 960 | 19,510 | 11.4 | 90.95 | 195.7 | 0.70 | 1.3982 |
| 16 | 960 | 20,470 | 12.0 | | | | 1.3990 |
| 17 | 960 | 21,430 | 12.6 | 94.2 | 201.6 | 1.00 | 1.3995 |
| 18 | 960 | 22,390 | 13.1 | | | | 1.4010 |
| 19 | 960 | 23,350 | 13.7 | 98.05 | 208.5 | 0.70 | 1.4040 |
| 20 | 960 | 24,310 | 14.3 | | | | 1.4110 |
| 21 | 960 | 25,270 | 14.8 | 100.9 | 213.6 | 0.45 | 1.4168 |
| 22 | 960 | 26,230 | 15.4 | | | | 1.4279 |
| 23 | 960 | 27,190 | 15.9 | 104.6 | 220.3 | 0.55 | 1.4343 |
| 24 | 960 | 28,150 | 16.5 | | | | 1.4406 |
| 25 | 960 | 29,110 | 17.1 | 108.05 | 227.3 | 0.55 | 1.4457 |
| 26 | 960 | 30,070 | 17.7 | | | | 1.4356 |
| 27 | 960 | 31,030 | 18.2 | 113.65 | 236.5 | 0.75 | 1.4172 |
| 28 | 960 | 31,990 | 18.8 | | | | 1.4092 |
| 29 | 960 | 32,950 | 19.3 | 117.95 | 244.3 | 0.40 | 1.4082 |
| 30 | 950 | 33,910 | 19.9 | | | | 1.4110 |

(CONCLUDED ON NEXT PAGE)

Table 86 (Concluded)

| FRAC. NO. | CC. PER FRAC. | TOTAL CC. DISTILLED | VOL.% OF CHARGE DIST. | 50% COTTRELL B.P. CORRECTED TO 760 MM. HG °C | °F. | COTTRELL SPREAD I.B.P. 50% PT. °C. | REFRACTIVE INDEX, $N_D^{20}$ |
|---|---|---|---|---|---|---|---|
| 31 | 950 | 34,870 | 20.5 | 119.5 | 247.1 | 0.25 | 1.4138 |
| 32 | 950 | 35,820 | 21.0 | | | | 1.4163 |
| 33 | 950 | 36,770 | 21.6 | 121.55 | 250.8 | 0.35 | 1.4174 |
| 34 | 950 | 37,750 | 22.2 | | | | 1.4168 |
| [illegible] | 950 | 38,710 | 22.7 | 124.05 | 255.3 | 0.30 | 1.4158 |
| 36 | 950 | [illegible] | [illegible] | | | | 1.4167 |
| 37 | [illegible] | 40,[illegible] | 23.9 | 127.05 | 260.7 | 0.35 | 1.4214 |
| HOLDUP | 1000 | 42,630 | 25.0 | - | - | - | - |
| RESIDUE | 127,500 | 170,130 | 100 | | | | |

Table 87

SUMMARIZATION OF DATA FOR THE LIQUID EXTRACTION OF "TOPPED" ESSO JP-4 REFEREE FUEL

BOILING RANGE OF FEED: 200°-520°F.

SOLVENT COMPOSITION
WT.% $NH_3$ = 82-91
WT.% AMINE = 9-18

| RUN NO. | JP-4 "TOPPED" REFEREE FUEL | 231 | 232 | 233 | 234 | 235 | 236 | 237(1) |
|---|---|---|---|---|---|---|---|---|
| SOLVENT-TO-OIL WT. RATIO | | 1:1 | 3:1 | 3:1 | 3:1 | 3:1 | 2.9:1 | 2.9:1 |
| STAGE DISTRIBUTION, E/F/S | | 15/F/4 | 15/F/4 | 12/F/7 | 12/F/7 | [illegible] | 15/F/4 | 8/F/1 |
| EXTRACTION TEMPERATURE RANGE, °F. | | 72-97 | 61-95 | 63-95 | 69-102 | 68-93 | 61-97 | 70-100 |
| SOLUBILITY RANGE, WT.% HYDC. IN EXTRACT PHASE | | 4-13 | 6-22 | 5-10 | 5-19 | 4-16 | 7-34 | 6-16 |
| EXTRACT PRODUCT | | | | | | | | |
| VOL.% OF FEED | | 8 | 8.5 | 20 | 19 | 31 | 15 | 18 |
| REFRACTIVE INDEX, $N_D^{20}$ | | 1.4990 | 1.5149 | 1.4971 | 1.5020 | 1.4890 | 1.5110 | 1.4841 |
| ANALYSIS, VOL.% | | | | | | | | |
| MONONUCLEAR AROMATICS | | 74 | 89 | 80 | 81 | 68 | 86 | 62 |
| POLYNUCLEAR AROMATICS* | | 9 | 11 | 8 | 7 | 6 | 10 | 7 |
| OLEFINS | | } 17 | <1 | 6 | 6 | } 26 | 2.5 | 11 |
| SATURATES | | | <1 | 6 | 6 | | 1.5 | 20 |
| SULFUR | | - | - | 0.47 | - | - | 0.68 | 0.40 |
| GUM | | 40 | 42 | 32 | 34 | 34 | - | - |
| RAFFINATE PRODUCT | | | | | | | | |
| VOL.% OF FEED | | 92 | 91.5 | 80 | 81 | 69 | 85 | 82 |
| REFRACTIVE INDEX, $N_D^{20}$ | | 1.4526 | 1.4489 | 1.4423 | 1.4413 | 1.4390 | 1.4472 | 1.4392 |
| ANALYSIS, VOL.% | | | | | | | | |
| AROMATICS | | 28 | 23 | 14 | 13 | 10 | 21 | 9 |
| OLEFINS | | - | - | - | - | } 90 | 8 | 8 |
| SATURATES | | - | - | - | - | | 71 | 83 |
| SULFUR | | - | - | 0.17 | - | - | 0.20 | 0.16 |
| GUM | | 30 | 30 | 37 | 49 | 47 | - | - |
| FEED | | | | | | | | |
| REFRACTIVE INDEX, $N_D^{20}$ | 1.4570 | 1.4560 | 1.4544 | 1.4532 | 1.4527 | 1.4544 | 1.4565 | 1.4470 |
| ANALYSIS, VOL.% | | | | | | | | |
| MONONUCLEAR AROMATICS | 30.5 | } 32 | 30 | 28 | 28 | 30 | 32 | 21 |
| POLYNUCLEAR AROMATICS* | 2.5 | | | | | | | 8 |
| OLEFINS | 8 | - | - | - | - | - | - | 71 |
| SATURATES | 59 | - | - | - | - | - | - | - |
| SULFUR | 0.29 | - | - | - | - | - | - | - |
| GUM | 45 | - | - | - | - | - | - | - |
| YIELDS | | | | | | | | |
| % OF FEED AROMATICS IN EXTRACT | | 20 | 29 | 60 | 61 | 77 | 45 | 53 |
| % OF FEED POLYNUCLEAR AROMS.* IN EXTRACT | | 25 | 30 | 55 | 45 | 60 | 50 | 60 |

* POLYNUCLEAR AROMATICS OF THE NAPHTHALENTIC TYPE.

(1) THE CHARGE FOR THIS EXTRACTION IS THE RAFFINATE FROM RUN 236, WHICH REPRESENTS 85 VOL.% OF THE "TOPPED" REFEREE FUEL.

Figure 33

EXTRACT AROMATIC CONTENT AND AROMATIC YIELD IN EXTRACT AS A FUNCTION OF VOL. % OF FEED TO EXTRACT

Topped Esso JP-4 Referee Fuel

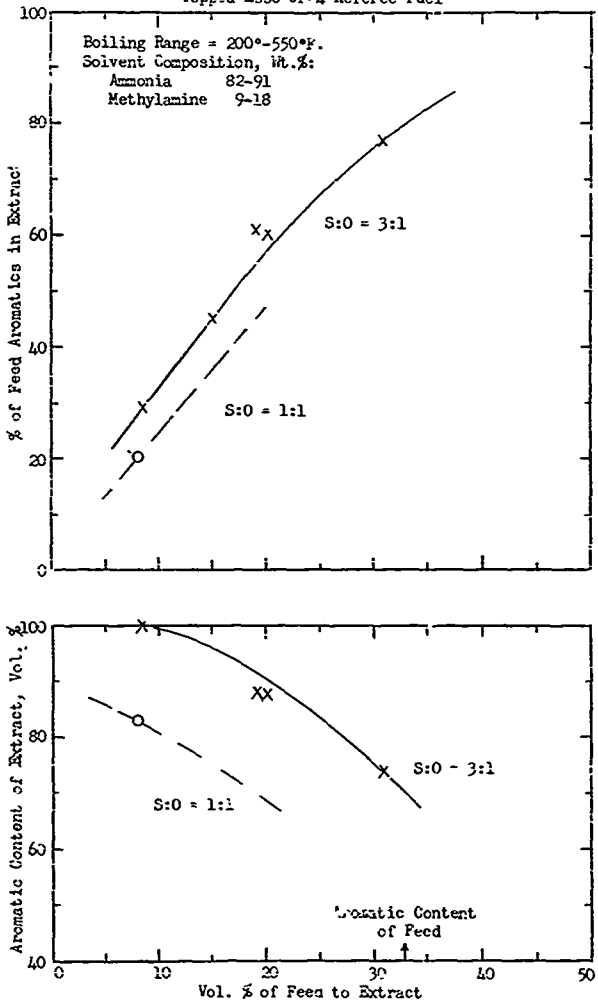
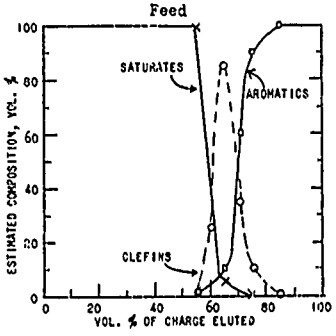


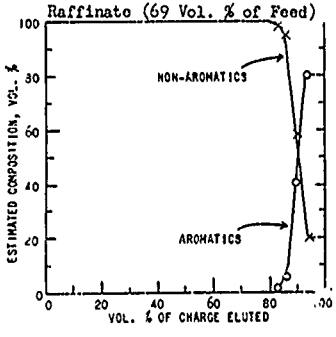
Figure 34
FRACTIONAL SILICA GEL ADSORPTION OF THE FEED AND THE PRODUCTS PREPARED BY LIQUID EXTRACTION OF TOPPED JP-4 REFEREE FUEL




(THE PRODUCTS ARE FROM EXTRACTION RUN 235 MADE IN THE 20-STAGE STACKED EXTRACTOR USING AMMONIA-AMINE SOLVENTS.)

DIAMETER OF TOWER = 0.39 INCH
HEIGHT OF GEL = 92 INCHES
WT. OF GEL USED = 130 GMS.
MESH OF GEL = 28-200
VOLUME OF CHARGE = 20-25 CC.
DESORBENT USED = 95% ETHYL ALCOHOL

| HYD. TYPE | EF FEED | TED ANALYSIS, VOL. % EXTRACT | RAFFINATE |
|---|---|---|---|
| AROMATICS | 33 | 74 | 10 |
| OLEFINS | 8 | } 26 | 90 |
| SATURATES | 59 | | |



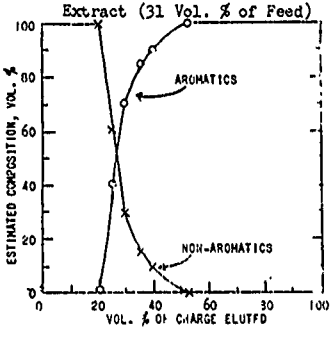
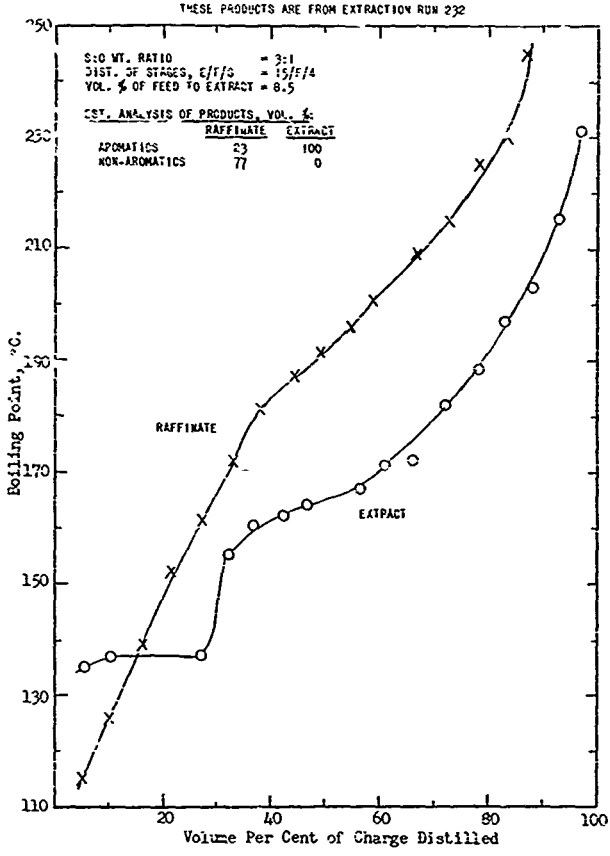



Figure 35
FRACTIONAL DISTILLATION OF THE END PRODUCTS FROM THE LIQUID EXTRACTION OF TOPPED JP-4 REFEREE FUEL

(FRACTIONATED IN 15 MM. I.D. GLASS COLUMNS HAVING 30 PLATES AT ABOUT 30:1 REFLUX RATIO)

THESE PRODUCTS ARE FROM EXTRACTION RUN 232



the bath can be controlled by the two Variacs shown in Figure 36. The temperature is controlled manually through the Variacs by regulating the heat input.

The well in the aluminum block is filled with low melting Cerrobase alloy. The Cerrobase alloy has a melting point of about 250°F. As indicated, a coil of 5/16 inch o.d. copper tubing five feet long is immersed in the Cerrobase alloy as an air preheater. Two forms, fashioned from steel tubing to fit snugly around a standard 100 milliliter beaker, are also immersed in the Cerrobase. The beakers used in the test could not be immersed directly in the Cerrobase because of the problem of cleaning solidified Cerrobase from the beakers after the test. The beaker weight must be repeatable to about ± 0.2 milligram to assure adequate precision for the measurement of small gum numbers. This apparatus has worked satisfactorily in the tests conducted to date.

The air jet method of conducting the ASTM gum test has been used throughout this study. It is believed that the air jet test method is somewhat more severe than the method involving superheated steam. It has been experimentally determined that the air jet method gives essentially no gum number for pure hydrocarbons up to at least a molecular size containing 16 carbon atoms. In general, this molecular weight range would include the highest boiling components of JP-4 fuel.

The gum number test procedure consists, briefly, of measuring a 50 milliliter sample of test fluid into a clean tared beaker of 100 milliliter capacity. The beaker is inserted in a 311 ± 9°F. constant temperature bath. A jet of dried air is blown over the surface of the liquid at a rate of 1000 ± 150 milliliters per second at a test temperature of 311 ± 9°F. The air flow is continued until the sample in the beaker reaches dryness plus an additional 15 minutes after dryness is reached. The beaker is removed from the bath at the end of the evaporation period and allowed to cool for two hours in a dessicator. The difference between the final weight and the tare weight is a measurement of the gum. The gum numbers used in this discussion are all expressed in terms of milligrams of gum per 100 milliliters of fuel sample.

In the test for potential gum, the same gum determination described above is applied to a sample of the fuel after subjection to an oxidation test. The oxidation tests utilized by this Laboratory in this study are modifications of the ASTM Test Method D873-49 for Oxidation Stability of Aviation Gasoline (Potential Gum Method). The apparatus consists of a modification of the Pyrex pipe oxidation apparatus developed for the PRL pressure oxidation and thin film oxidation tests.

The modified apparatus is shown on Figure 37. The apparatus consists of a 16-inch section of Pyrex pipe (1.5 inch i.d.) sealed off at one end and provided with a standard flanged fitting at the other. The oxidation heads are constructed from stainless steel and are sealed to the Pyrex pipe with a stainless steel flange using a Teflon gasket.

The construction of the oxidation head differs for a static test and pumping test as indicated in Figure 37. In the former case,

a 1/2-inch stainless steel cross is fastened to the stainless steel flange through a short nipple of 1/2-inch stainless steel pipe. The cross is provided with 2 stainless steel needle valves and a pressure gage. For the pumping test, the oxidation head has been enlarged to contain a water cooled condenser comprising a 16-inch length of 0.5 inch diameter stainless steel tubing. The 1/2-inch stainless steel pipe cross is mounted on top of the condenser. The vertical exit from the cross is flanged to a socket designed to accommodate a solenoid core for activating the bucket pump conventionally used in the PRL thin film oxidation test. The two other exits are connected to stainless steel needle valves. One of the arms contains a pressure gage between the cross and the needle valve. Pressure oxidation tests are conducted with both test systems. The total volume of the static system is 480 milliliters for the pumping test apparatus employing steel jack chain. When glass beads are used in the pumping procedure, the volume is 350 milliliters.

The oxidation tests have been conducted at a temperature of 250°F. and a pressure of 50 p.s.i. gage. The 50 p.s.i. gage is the maximum recommended working pressure for the Pyrex pipe. The 50 p.s.i. pressure is, therefore, the sum of the fluid vapor pressure and the oxygen pressure at the test temperature. The 250°F. temperature is a compromise between the increasing reaction rate with higher temperature and the decreasing amount of oxygen that can be charged.

These oxidation tests are all conducted with pure oxygen. In these exploratory oxidation tests primary emphasis has been placed on the amount of oxygen used. The time to obtain this degree of oxidation has been measured, but was not the factor used to determine the test severity. The amount of oxygen assimilated was measured as a pressure drop at room temperature rather than at the 250°F. test temperature. That is, the oxygen was charged to the tube, after adequate flushing with pure oxygen, at room temperature and the pressure recorded at this temperature.

Following the test, the apparatus was allowed to cool to room temperature again before the final reading was taken. This rules out errors in determining the amount of oxidation due to the formation of water or other products which are gaseous at 250°F. but liquid at 70°F. In essentially all cases where sufficient gas pressure remained, the exhaust gas was analyzed for carbon dioxide and oxygen. The tests conducted by the standard static test procedure resulted in an oxygen content of the gas in the system after the test of 90 to 100 per cent. The carbon dioxide content for the same samples runs from 0 to 2 per cent of the exhaust gas. These gas analyses after the standard oxidation test are about the same for all of the pure hydrocarbons and the JP-4 jet fuel tested. Measurement of gas pressure at room temperature following the oxidation test would be an adequate measure of the oxygen used during the standard static test without the additional gas analysis, since there is no indication of large quantities of gas other than oxygen in the test system.

In the thin film pumping procedure, gas analysis after oxidation tests with JP-4 and the pure hydrocarbons shows approximately 65 to 90 per cent oxygen in the gas. The carbon dioxide content of the gas following the thin film pumping tests varies from 5 to 10 per cent. No attempt has been made to identify the remaining gaseous products in the tests conducted, thus far. On the basis of exhaust gas analysis, the thin film pumping test appears to produce more severe oxidation and cleavage of the test fluid.

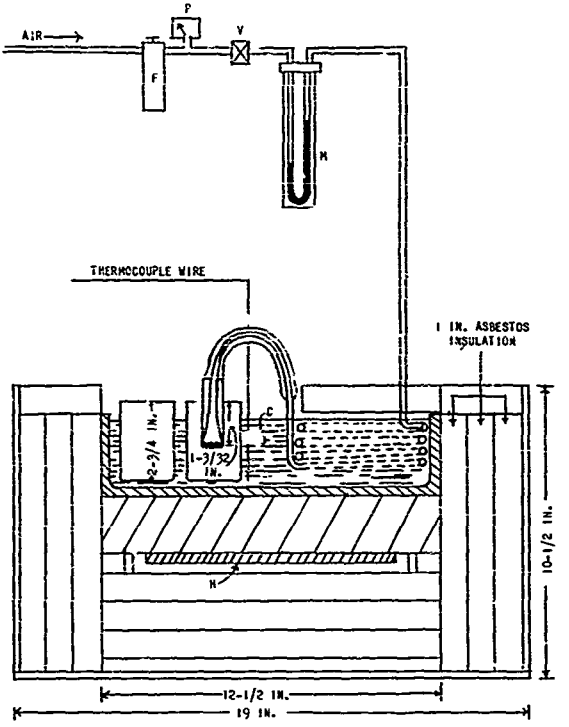
1. Existent Gum Studies. The effect both of hydrocarbon types and physical separation processes on existent and potential gum, or dirtiness in the JP-4 referee fuel has been determined. The procedures used to measure existent and potential gum have already been outlined. The existent gum determinations discussed here are concerned solely with gum or residue, which at the start of the gum test is in solution with the test fluid (i.e., one homogeneous liquid phase). In other words, this type of gum cannot be removed by a simple mechanical filtration process.

The effect of various physical separation processes on the gum content of topped JP-4 referee fuel is shown on Table 88. The gum value of JP-4 referee fuel and that of the topped JP-4 referee fuel are essentially identical (10 mg. per 100 ml. of fluid). It can be seen from the data on Table 87 that all of the products taken from the 20 stage liquid extractor show a larger gum number than the original JP-4 topped referee fuel used as the charge to the extractor. There is a difference in the physical appearance of the gum derived from the raffinate and extract samples of the topped JP-4 referee fuel. The gum or residue in the gum test from the raffinate products, in general, has a particulate appearance. There is some evidence that this material has progressively precipitated from the raffinate fraction during the course of the evaporation to dryness. The gum from the extract product is more typical of the soluble gum noted in the oxidation tests. This material forms a fairly even lacquer-like coating over the bottom of the test beaker.

The feed to the extractor, after contact with the ammonia-amine solvent, shows the same characteristic increase in gum value as the products (raffinate and extract) from the extractor. This increase in gum value could result from the reaction of ammonia as a base with materials present in the JP-4 to form a salt, such as the reaction with naphthenic acids, phenols, etc. Or it may result from the solution of small quantities of high molecular weight residues or dirt left in portions of the solvent recovery system from previous extractions. A sample of topped JP-4 referee fuel has been shaken with an equal volume of ammonia-amine solvent in a glass pressure flask and the referee fuel sample subjected to a gum test upon removal of the ammonia-amine liquid layer. A gum number has also been determined on a sample of JP-4 topped referee fuel following a wash with an equal volume of 5 weight per cent aqueous sodium hydroxide. Both of these alkaline washes in glass equipment cause an increase in the value of the gum number as shown on Table 88. This indicates that the chemical effect of the solvent on the JP-4 topped referee fuel caused at least a portion of the increased gum noted in the products from the extractor.

Figure 36

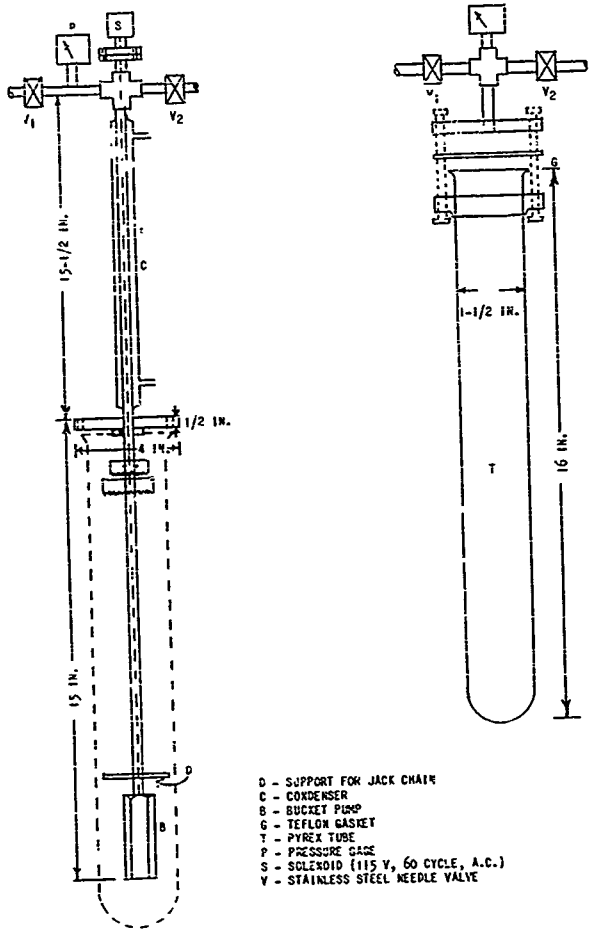
CONSTRUCTION DETAILS OF BATH USED TO CONDUCT A.S.T.M. TEST FOR EXISTENT GUM IN FUELS (D381-52T)




V - NEEDLE VALVE
F - AIR FILTER AND REDUCER
P - PRESSURE GAGE
M - MANOMETER
H - STRIP HEATER (250 WATT)
C - CERROBASE METAL

Figure 37

CONSTRUCTION DETAILS OF EQUIPMENT USED TO CONDUCT POTENTIAL JET FUEL DIRTINESS DETERMINATIONS




D - SUPPORT FOR JACK CHAIN
C - CONDENSER
B - BUCKET PUMP
G - TEFLON GASKET
T - PYREX TUBE
P - PRESSURE GAGE
S - SOLENOID (115 V, 60 CYCLE, A.C.)
V - STAINLESS STEEL NEEDLE VALVE

It is also known that high molecular weight impurities from previous extractions are present in portions of the liquid extractor apparatus. The effect of these impurities on the gum value, if any, would be difficult to determine. The extremely small quantities of gum necessary to cause a finite change in gum value emphasizes the need for special care in handling small samples, and illustrates the relatively large effect of minute contaminants.

The gum number of one (unity) means one milligram of gum per 100 ml. of sample. The magnitude of contamination necessary to cause an increase of one in the gum number is about 10 parts per million or 0.001 weight per cent. In general, the main object in extracting the topped JP-4 jet fuel was the separation of fractions showing different values for potential gum rather than large differences in existent gum. The potential gum values are discussed in a subsequent paragraph.

It is apparent from the extraction data that the ammonia-amine solvent will not improve existent gum values which are already in the low range. Two other physical separation processes have been applied to the topped JP-4 referee fuel and other fractions from this fuel to determine their effect on existent gum. Simple distillation and fractionation have been applied as physical separation processes for control of existent gum. In all cases tested, fractionation or simple distillation, where sufficient care is taken to prevent entrainment, removes essentially all existent gum. This effect is shown on Table 88 for simple distilled JP-4 topped referee fuel.

The effect of simple distillation on existent gum is shown in more striking fashion on Table 92 for several hydrocarbons. Tetralin, for example, shows an existent gum number of 1390 after storage in this laboratory for several years in a screw cap glass bottle. Simple distillation of the tetralin reduces this value to 0 for the gum number. Similar trends are shown for methyl naphthalene, dicyclohexyl, and diamyl benzene as indicated on Table 92. These data indicate that it is probably the high boiling polymer or condensation products of oxidation during storage that cause gum rather than the simple oxidation products themselves.

This is further borne out by a study of the gum value of a typical light petroleum naphtha fraction (112° to 260°F. boiling range) which has been subjected to vapor phase oxidation at elevated temperatures. The oxidized naphtha contained a total of 3 to 4 weight per cent oxygen following the oxidation. The oxidized product had an existent gum number of 208. The product, after simple distillation, had a gum number of 2.5. There was essentially no change in the oxygen content between the original oxidized product and the distillation product. The indications are that the gum found in all of these determinations represents high molecular weight products formed by polymerization or condensation, rather than being due to the simple or initial oxidation products.

Silica gel adsorption, or clay treatment, represents another physical separation process which may lend itself to reduction of existent gum. This treatment would probably be the most practical process to be applied to dirty fuels in the field. That is, filtration through clay or

silica gel requires the least complicated equipment. The silica gel treatments shown on Table 88 are mild treatments of the type that could be applied in the field, as opposed to the rigorous silica gel treatment which is normally used to achieve nearly quantitative hydrocarbon class separations in the laboratory. It can be seen that mild silica gel treatment, either batch or percolation, does result in a sizeable lowering of the existent gum value of the topped JP-4 referee fuel. The silica gel studies will be extended to include some of the more common clay types used in the petroleum industry. These studies will also be extended to include samples exhibiting considerably higher gum numbers than the JP-4 topped referee fuel used in this study.

2. Potential Gum Studies with JP-4 Referee Fuel. Studies of potential gum formation are of more interest in the investigation of fuel dirtiness than the study of existent gum. That is, the formation of potential gum is being examined in order to determine the hydrocarbon types, or impurities, in the fuel which contribute most to fuel dirtiness. There are several ways to survey potential dirtiness in fuels. These include a study of inhibitors and promoters, a comparison of dirtiness after a standard oxidation test, and a comparison of dirtiness at a given degree of oxygen assimilation.

The initial stages of this study have been made on the basis of dirtiness produced per unit of oxygen assimilated. Two general test procedures, as described previously, have been utilized in these tests. The standard test is conducted in the apparatus shown on Figure 37. The environment is glass with the exception of the stainless steel head. The fluid vapors and oxygen are in contact with the stainless steel oxidation head, but the liquid being tested is not normally in contact with the stainless steel. The thin film test is conducted in an environment which includes intimate mixing of the test fluid and oxygen on a metal (generally steel and stainless steel) surface.

In all of the accelerated oxidation tests, the gum or dirtiness noted is divided into two classes: insoluble material, which at the termination of the test is not in solution, and soluble gum which cannot be separated from the fluid by filtration or observed as a second separate phase in the fluid. The insoluble material in the thin film test is broken down into the material adhering to the steel jack chain and the insoluble material remaining in the test fluid. In all cases, the insoluble material is washed from the filter or test tube into a tared 100 ml. beaker with a volatile solvent such as acetone or low boiling petroleum naphtha. The insoluble material plus the volatile solvent is then subjected to an air jet evaporation test in accordance with the ASTM gum determination procedures and techniques. It has been determined that the acetone and low boiling petroleum naphtha solvents have no gum numbers as measured by this procedure.

3. Dirtiness Tests with JP-4 Topped Referee Fuel. Potential gum tests have been determined by both the standard and thin film procedures on the JP-4 topped referee fuel and various fractions resulting from the physical separation of this fuel by extraction, distillation, and silica gel adsorption. The results of these potential gum tests are

shown on Table 89. The first two tests shown on Table 89 illustrate the effect of degree of oxidation on dirtiness. The range in oxidative attack covered by the data on Table 89 ranges from about 15:1 to 100:1 in terms of moles of fuel per mole of oxygen. The rate of oxidation of the topped JP-4 referee fuel is not changed substantially over the range of oxidation noted in the first two tests. The total gum formed per unit of oxygen absorbed is not altered for the tests of differing severity. The primary difference noted between the two tests of differing severity is the amount of insolubles formed. For a 3.5 fold increase in oxygen assimilation, a 41 fold increase in insolubles is noted.

Standard oxidation tests on the products of extractions 231 and 235 are also shown on Table 89. These tests indicate that the extraction process eliminates much of the initial oxidation stability of the JP-4 topped referee fuel. That is, the time required to achieve a given degree of oxidation is much lower for all three extractor samples than for the topped JP-4 jet fuel. This same effect has been noted with JP-4 topped jet fuel that has been mixed with the ammonia-amine solvent and separated by evaporating off the ammonia-amine solvent. Thus, it would appear that mixing the topped JP-4 referee fuel with the ammonia-amine solvent reduces substantially the effectiveness of the oxidation inhibitor (natural or synthetic) present in the original fuel. The extract from run 231 shows a slightly higher ratio of total gum to oxygen assimilated than the two raffinate fractions. Of the total gum formed, however, the two raffinate fractions produce a larger portion of insolubles than does the extract. This has been a general trend with JP-4 extraction products. These studies will be pursued further to determine whether it is the poorer solvency of the raffinate fractions, or a basic difference in type of oxidized product formed, that causes this difference in the formation of insolubles.

The next series of tests shown on Table 89 attempt to show what, if any, are the effects of molecular weight on the sludge forming tendencies of the raffinate and extract fractions. The overall properties of extract and raffinate fractions from extractions 236 and 237 are shown on Table 87. Approximately one liter portions of each of the four products were simple distilled to yield the fractions indicated on Table 89. Following removal of the product from the extractor, all of these products were inhibited with 20 parts per million of U.O.P. Inhibitor No. 5, except a one gallon portion of the raffinate from extraction 237. The charge for the simple distillation of the raffinate from run 237 was taken from the gallon of uninhibited material. U.O.P. Inhibitor No. 5 is a volatile inhibitor and, therefore, would be carried along with the distilled product. This is indicated by the time required to achieve the desired degree of oxidation with some of the fractions from these simple distillations.

Little significance can be attached to the relative rates of oxidation noted in the various fractions of the products from runs 236 and 237 because of the lack of specific information on the inhibitor distribution in the distilled fractions. Some general trends have been noted from the dirtiness studies of these fractions. In terms of total gum, the raffinate appears to be cleaner than the extract, and the low

boiling materials of all of the products tend to be cleaner than the higher boiling material of the same products. The ratio of insoluble materials to total gum is higher for the raffinates than the extracts. This trend of increased dirtiness is more pronounced in the higher boiling fractions of the raffinates. There is some evidence to indicate that the amount of dirtiness is primarily dependent on the amount of oxygen assimilated, and practically independent of the rate of oxidation or the presence or absence of U.O.P. Inhibitor No. 5 in the standard oxidation tests.

A series of simple vacuum distillations have been run on about 10 gallon portions of the raffinate and extract fractions of extractor runs 236 and 237. These distillations were conducted to remove the existent gum and any insolubles present in the extractor products. The entire product from about 5 to 95 volume per cent distilled was blended as a single fraction for subsequent oxidation studies. In addition to these products, the raffinate from extractor run 237 has been vacuum fractionated in similar fashion to yield about 3 fractions between 5 and 95 volume per cent distilled. These seven products have been discussed previously in this section and are shown on Figure 32. All of these fractions, following the distillation, have been inhibited with 20 parts per million concentration of U.O.P. No. 5 gasoline inhibitor. These inhibited fractions have been evaluated in the oxidation test as shown on Table 89. These tests are essentially a check on the tests conducted with the preliminary fractions discussed above. It is interesting to note that there are still large differences in the rate of oxidation of these fractions in the presence of 20 p.p.m. of U.O.P. Inhibitor No. 5. The results of these tests are in good agreement with the corresponding fractions from the small scale preliminary distillations.

It is interesting to note that the extract is more stable than the corresponding raffinate and that the products from run 236 are more stable than the corresponding products from run 237. This is the expected trend since successive solvent treatment would be expected to remove preferentially the more polar compounds which in turn are generally associated more closely with the class of compounds that act as inhibitors. The total amount of gum formed per unit of oxygen absorbed increases with decreasing rate of oxidation. That is, the more polar fractions form more total gum than the less polar raffinates. The fractions of the raffinate from extractor run 237 show an increasing rate of gum formation with decreasing oxidation rate as the molecular weight or boiling range of the fraction increases. The stability or very slow rate of oxidation of fraction 3 from raffinate 237 stands out by comparison with the overall raffinate from run 237 and the general stability trend discussed above. This phenomenon of total gum formation and oxidation rate would be expected from analogy with extraction experience in the lube oil field. The item of dirtiness or insoluble gum, however, does not follow the trends of total gum and oxidation stability in the same manner. In general, the relative portion of the total gum that is insoluble gum increases with decreasing total gum formation.

One of the accepted fixes for reducing filter and nozzle plugging in domestic oil burner systems is the use of a dispersant or detergent in the fuel oil. This same approach has been discussed by Shell, Du Pont and others for jet fuels. Two typical dispersants have been added to topped JP-4 referee fuel and the resultant blend evaluated in the thin film fuel oxidation test. These data are shown on Table 89. Du Pont Additive No. 2 is believed to be a polymeric material of the type described by Biswell, C. B., Cathin, W. E., Forning, J. F., and Robbins, G. B., in Chemical and Engineering News, page 1447, Vol. 32, No. 15 (1954). The synthetic barium sulfonate additive has been obtained from the King Organic Chemicals Company. The use of these dispersants results in an increase in total and insoluble gum formation. There is no good method for determining the beneficial effects of a dispersant using the bench oxidation procedures described here. Thus, these dispersants will require testing in a fluid circulating test through a filter to determine any beneficial effects.

A sample of topped JP-4 referee fuel has been given a severe silica gel treatment to remove essentially all of the aromatics, olefins, and sulfur compounds. The product removed from the silica gel tower represents the first 50 per cent of the fuel to be pushed through the gel. The silica gel to fluid ratio by weight in this separation is 10:1. The results of a standard oxidation test with this sample are in Table 89. The total gum formation is substantially reduced from that of the original topped JP-4 referee fuel in a comparable test. The amount of the total gum made up by insolubles is again, as in the case of the raffinate fractions, relatively high.

A series of thin film pumping type oxidation tests have been conducted with the topped JP-4 referee fuel. This pumping test has been run under mild and severe conditions using three different procedures. In one case, the pump discharge is allowed to fall through the vapor space back into the reservoir. In another, the pump discharge flows over a 1500 sq. cm. surface area of 3 mm. diameter glass beads. In a third case, the pump discharge flows over a 2000 sq. cm. area of No. 20 steel jack chain, and in a fourth case, the pump discharge flows over a 2000 sq. cm. area of copper jack chain.

Under the mild conditions, these tests show that the large majority of total gum is soluble gum. These same trends were apparent in the mild tests conducted by the standard procedure with the topped JP-4 referee fuel. The amount of total gum per unit oxygen absorbed, and the ratio of insoluble material to soluble gum, are essentially the same for severe tests conducted in accordance with the standard and thin film tests. The most striking difference between the standard and thin film tests with topped JP-4 referee fuel is the time necessary to reach a given degree of oxidation. The pumping tests are more severe than the standard test. Of the pumping tests, the one containing the copper jack chain is by far the most severe in terms of oxidation rate. Both copper and steel jack chain cause a significant increase in oxidation rate over similar tests without the metal catalyst.

Thin film tests, in the presence of steel jack chain, are shown for the feed, extract, and raffinate from extraction 231. These tests show the same general trends as the standard tests. There is no large change in the amount of total gum formed per unit of oxygen absorbed in these thin film tests as compared with standard tests on the same stocks. The percentage of the total gum that is measured as insolubles is larger for the raffinate than for the extract in the thin film test.

Thin film tests using copper jack chain and no metal catalyst with topped JP-4 referee fuel are shown on Table 89. The test conducted without a large catalyst area shows a sharp drop in rate of oxidation. The total gum and insoluble gum values remain about the same, on the basis of the total oxygen absorbed, as for the thin film test containing the steel jack chain. The presence of copper jack chain in the thin film test with topped JP-4 effects a large rate increase in the oxidation. Very little insoluble gum was noted in this test in contrast to that normally encountered in the thin film tests containing steel jack chain.

4. Dirtiness Characteristics of High Paraffin JP-4 Fuel. A 5-gallon sample of a highly paraffinic JP-4 jet fuel has been obtained from the Phillips Petroleum Company. This material has been evaluated with and without anti-oxidant in the standard and thin film test procedures as shown on Table 90. The anti-oxidant used is 100 p.p.m. Paranox 441. This high paraffin JP-4 shows a very low rate of total gum formation in the standard test. It should be noted that despite the low value for total gum, approximately one third of this total gum is insoluble gum. The thin film tests with the high paraffin JP-4 give a high value of total gum and insoluble gum. It should be noted that the JP-4 referee fuel gives essentially the same test results in the thin film and standard tests in terms of total gum per unit of oxygen absorbed. Paraffinic hydrocarbons give a sharp rise in total gum and insoluble gum for the thin film test compared with the standard test. The high paraffin JP-4 shows a close resemblance to pure paraffinic hydrocarbons in the behavior toward the thin film and standard oxidation tests. The use of 100 p.p.m. of Paranox 441 has no appreciable effect on the stable life of the high paraffin JP-4 under either the standard or thin film conditions at 250°F. The apparent discrepancy in oxidation time in the thin film test results from the formation of gaseous products during the oxidation. That is, during the thin film test the pressure fell from 50 to 28 p.s.i. in 4.2 hours but did not fall appreciably below 28 p.s.i. for 172 hours total test time. The residual gas has been analyzed and found to contain no oxygen. Thus the subsequent thin film oxidation test was terminated after 4.2 hours.

5. Dirtiness Studies with Oxygenated Materials. It has been noted in the study of jet fuel dirtiness that the materials showing the highest portion of insoluble gum generally exhibit the poorest solvency characteristics. It has further been indicated that the insoluble gum is an oxidation product and as such should contain oxygenated groups. A preliminary study has been conducted on the gum forming tendencies of various oxygenated materials. The results of these gum tests are shown on Table 91. The oxygenated materials tested include n-hexyl ether,

octanone-2, capryl alcohol, n-decanol, and isoamyl acetate. These materials have been evaluated in the standard test. None of the oxygenated materials produced insoluble gum under these test conditions. The isoamyl acetate shows an extremely slow rate of oxidation in this test. The decanol gives about the same quantity of soluble gum per unit of oxygen absorbed as the total gum produced by the JP-4 referee fuel. The other oxygenated materials evaluated give very low gum values per unit of oxygen absorbed.

6. Effect of Oxygenated Compounds on JP-4 Dirtiness Characteristics. The lack of insoluble gum formation in the aliphatic oxygenated materials evaluated suggests good solvency for oxidation products. Blends of various oxygenated compounds and extractor run 237 raffinate fraction were prepared and evaluated in the standard oxidation test. Raffinate 237 from JP-4 referee fuel has been discussed previously. This fraction represents a concentration of the more paraffinic fractions with the removal of the more polar compounds (aromatics, oxygenated materials, sulfur-containing compounds, etc.) by two successive liquid extractions with liquid ammonia-methylamine. The gum formation for raffinate 237 fraction is shown on Table 91 as a basis of comparison for the blends with oxygenated materials. It can be seen that raffinate 237 fraction produces a very high insoluble gum value compared with the total gum value. Standard oxidation test results for blends of oxygenated materials in raffinate 237 fraction are shown in Table 91. Blends of raffinate 237 fraction with 25 weight per cent decanol or isoamyl acetate give no insoluble gum in the standard oxidation test. A raffinate 237 fraction blend containing [illegible] weight per cent 2-octanone gives a relatively small amount of insoluble gum in the standard test as compared to the raffinate 237 fraction alone.

In all cases where the oxygenated material is present in the blend, the rate of oxidation is considerably higher and/or the induction period is much shorter than for either the raffinate 237 fraction or the various oxygenated materials alone. The amount of sludge formed per unit oxygen absorbed appears to be influenced by the presence of the oxygenated material. Decanol and raffinate 237 fraction produce about the same quantity of gum per unit of oxygen absorbed when tested separately or in blends. The 2-octanone and isoamyl acetate form very little gum per unit of oxygen absorbed. Blends of raffinate 237 fraction with 2-octanone and isoamyl acetate produce less total gum than does the raffinate 237 fraction alone. This may be indicative of oxidation of the oxygenated material in the blend even though little or no oxidation of the oxygenated material alone would have taken place under similar test conditions.

Previous data have shown that JP-4 referee fuel and a high paraffin JP-4 show very little inhibitor effect with Paranox 441 or U.O.P. Inhibitor No. 5 in the 250°F. test procedures used in this study. This inhibitor study has been extended to include the blend of 25 weight per cent isoamyl acetate in raffinate 237 fraction. Concentrations of inhibitor of 20 and 100 p.p.m. have been used. The results are shown in Table 91. There is essentially no additional benefit from 100 p.p.m. of inhibitor over the initial 20 p.p.m concentration. The presence of

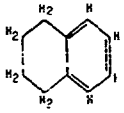
20 p.p.m. Paranox 441 extends the time required to absorb a given amount of oxygen by a factor of 2, while an equivalent concentration of U.O.P. Inhibitor No. 5 extends the time by a factor of 3. The inhibited blend still oxidizes in a fraction of the time required for either component. The addition of inhibitors to the blend results in all cases in the formation of a small quantity of insoluble gum.

The gum tests for blends of isoamyl acetate and raffinate 237 fraction discussed thus far are for blends containing 25 weight per cent isoamyl acetate. Additional tests have been conducted in which the concentration of isoamyl acetate has been reduced to [illegible] and 15 weight per cent. The incremental reduction in isoamyl acetate concentration causes a reduction in oxidation rate, an increase in the amount of total gum per unit of oxygen absorbed, and an increase in the amount of insoluble gum formed. In terms of insoluble gum formation the beneficial effects of 15 weight per cent isoamyl acetate are still apparent.

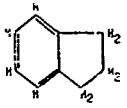
7. Potential Gum Studies with Pure Hydrocarbons. A number of pure hydrocarbons, representing the various classes of hydrocarbons, have been evaluated in the standard and thin film oxidation procedures for gum and dirtiness. It was indicated in the section on existent gum that the pure hydrocarbons in this molecular weight range have no existent gum. Any existent gum measured can be attributed to oxidative deterioration accompanied by polymerization or condensation reactions occurring during storage. This gum can be removed from the hydrocarbon by a simple distillation. The hydrocarbons studied are within the boiling range of JP-4 referee fuel. The hydrocarbon classes included in this study are paraffins, olefins, aromatics, condensed ring aromatics, and condensed ring compounds containing both aromatic and naphthenic rings.

These studies with the pure hydrocarbons show some interesting trends. In the standard oxidation test, no insoluble material was formed during the test with any of the pure hydrocarbons, with the exception of one hydrindene test. In this case, however, the hydrindene, as indicated, had a very high gum number from storage deterioration and, in addition, contained a substantial quantity of impurity in the form of a nitrogen-containing compound. This nitrogen-containing impurity and the oxidation products were removed by silica gel adsorption. The purified sample of hydrindene no longer shows the trace of insoluble material after the standard oxidation test.

The quantity of soluble gum formed in the standard oxidation test is very much smaller for a given amount of oxygen assimilated with the examples of pure hydrocarbons representing paraffins, olefins, naphthenes, aromatics, and condensed ring aromatics than with the topped JP-4 referee fuel. The only pure hydrocarbons which approach or exceed the JP-4 referee fuel in gum formation in the standard test are the condensed ring compounds containing a naphthenic and aromatic ring in the same molecule. These materials are tetralin and hydrindene. The structures indicating the aromatic and naphthenic rings are shown in the following illustration.



TETRALIN



HYDRINDENE

The times listed for the various oxidation tests are indicative of the relative oxidation stabilities of the hydrocarbon types. The rate of oxidation of methyl naphthalene is very slow. Thus, oxidation tests with methyl naphthalene have not been carried to the same degree of oxidation as with the other hydrocarbons.

It is apparent that the standard oxidation tests with the individual pure hydrocarbons shown on Table 92 do not predict the dirtiness or gum forming tendencies of the JP-4 referee fuel.

The JP-4 referee fuel contains some non-hydrocarbon impurities such as sulfur-containing compounds. Table 87 indicates that the overall concentration of sulfur in the JP-4 referee fuel is 0.29 weight per cent. Nitrogen impurities and others are also potentially present in hydrocarbon fractions in the JP-4 referee fuel range.

A mixture of pure hydrocarbons has been prepared to contain about the same overall percentage of pure hydrocarbons as are represented by the three or four hydrocarbon classes in the JP-4 fuel. These blends are shown on Table 92. The primary difference between blends I and II is the replacement of 10 weight per cent of the diethyl benzene of blend I with 10 weight per cent tetralin in blend II. Both synthetic hydrocarbon blends show the formation of a small amount of insolubles in the standard oxidation test. Blend II, as might be predicted from the presence of the 10 weight per cent of tetralin, shows an increase in the formation of insolubles and total gum over blend I. The total dirtiness of the synthetic blends I and II is only a small fraction of that encountered with topped JP-4 referee fuel and the best fractions separated from JP-4 referee fuel by distillation, extraction, and silica gel treatment.

One weight per cent of various non-hydrocarbons representing types encountered in petroleum have been added to synthetic blend I. These compounds include dibenzyl disulfide, methylbutyl sulfide, thiophene, and methyl quinoline. In general, the sulfides, thiophenes, and nitrogen compounds found as impurities in petroleum are more complicated in structure than those used in this study. The methyl quinoline does not change the gumming tendencies noted with blend I. The thiophene causes only a slight increase in dirtiness in blend I. The use of ditenzyl disulfide causes a large increase in insolubles and total gum in blend I. The blend containing ditenzyl disulfide causes more total

gum to be formed per unit oxygen absorbed than the topped JP-4 referee fuel in a similar oxidation test. The dibenzyl disulfide acts as a fairly effective oxidation inhibitor for blend I. Blend I containing one weight per cent methylbutyl sulfide shows the same general trends as the blend containing dibenzyl disulfide. The methylbutyl sulfide has a marked inhibitor effect on the oxidation causing a much lower oxidation rate than with blend I alone. The increased resistance to oxidation of blend I of pure hydrocarbons in the presence of an alkyl sulfide was accompanied by an increase in insoluble gum formation on oxidation to the same amount of oxygen assimilated. An additional test has been run on blend I containing 1.0 weight per cent methylbutyl sulfide. This second test has been run for the same time as the test on blend I alone. Under these conditions, it can be seen that blend I containing 1.0 weight per cent methylbutyl sulfide absorbs only about 10 per cent of the oxygen and forms 35 per cent of the gum formed by blend I alone. Both 4.3 hour tests form only soluble gum. In other words, the presence of the methylbutyl sulfide appears to be advantageous on the basis of these comparisons.

Some thin film tests have been conducted with pure hydrocarbons. The hydrocarbons evaluated in the thin film test include n-decane, 3,4-dimethyl hexane, 2,2,4-trimethyl pentane, diamylene, tetralin, and methyl naphthalene. The thin film test, in all cases except tetralin, results in an increase, over the standard test, in the total gum per unit of oxygen assimilated. This increment, in these cases, is significantly greater than any similar effect noted with the JP-4 referee fuel. All of the paraffins show an appreciable quantity of insolubles in the thin film test. The amounts of insolubles found in the decane test, for example, approach those found in a similar test with topped JP-4 referee fuel.

The two branched chain paraffins containing 8 carbon atoms (2,2,4-trimethyl pentane and 3,4-dimethylhexane) show the same trend in the thin film test as n-decane. It is interesting to note that 2,2,4-trimethyl pentane (isooctane) is a more stable configuration to oxidation in these tests than the other straight and branched chain paraffins tested. The 3,4-dimethyl hexane and 2,4,8-trimethyl nonane were chosen for study because of their tendency to form insoluble peroxides on storage in cork stoppered or screw cap glass bottles. These materials do not appear to be appreciably different from the other paraffins evaluated in the standard and thin film tests.

The thin film test with diamylenes does not produce insolubles. Thus, it would appear that the presence of a double bond results in significant behavior differences in the formation of gum and insolubles in this type of oxidation test. It may be that, in these relatively mild oxidation tests, the oxygen attack on the olefin is concentrated at the double bond, while in the case of decane the initial products of oxidation are more vulnerable to further attack than the decane, resulting in more complex oxidation products. That is, in the case of decane, additional oxygen attacks oxy-compounds, while with the olefin, the additional oxygen goes to the olefin.

n-Decane has been evaluated in various modifications of the thin film test procedure to determine the effect on insoluble gum formation. The steel jack chain was removed and copper jack chain substituted in a thin film test. In general, the copper results in a speeding up of the oxidation process with an overall reduction in both insoluble and soluble gum as compared with the steel jack chain. In a third thin film test with n-decane, glass beads were substituted for the metal jack chain. The oxidation rate in this test was slower than for the tests containing metals and much less total gum was formed with essentially no insoluble gum formation. A standard test was modified to contain the same amount of steel jack chain as the thin film test. The steel jack chain in this case was placed in the oil and there was no pumping. This modified standard test gave essentially the same amount of insoluble and soluble gum as the thin film test containing the steel jack chain. On the basis of this study it has been concluded that, in the case of the pure hydrocarbon, the effect of the metal catalyst was the predominant cause of variation in total gum formation and oxidation rate. The effect of pumping per se in the thin film test is a secondary effect.

E. DESIGN AND CONSTRUCTION OF THE HIGH TEMPERATURE DIRTINESS TEST UNIT. A schematic flow diagram of the high temperature dirtiness test unit is shown on Figure 38. The unit consists essentially of a pump, a fluidized bed heat exchanger, a filter holder, a pressure loading device and a reservoir. The piping between parts of the unit is primarily 3/16 inch stainless steel tubing. The total liquid holdup of the system is 150 milliliters. The unit is designed for both recycling and one pass tests.

A Zenith metering pump, size 1B, driven by a Vickers variable speed hydraulic transmission is used to circulate and to bring the fluid up to system pressure. This pump delivers 0.584 milliliter per revolution when the pressure load is 0 p.s.i. When pumping against a pressure of 250 p.s.i.g. from 0 p.s.i.g. using the JP-4 referee fuel at room temperature as the test fluid, the pump delivers about 0.35 milliliter per revolution. The slip of this pump will vary with the viscosity of the fluid and the pressure load.

The heat exchanger used to bring the test fluid up to test temperature utilizes a bed of fluidized solids. The test fluid is pumped through six feet of 3/16 inch i.d. stainless steel tubing wound in the form of a helix with a 2-1/4 inch i.d. and a pitch of 5/8 inch per turn which is immersed in a fluidized solids bed. The housing for the fluidized bed is 5 by 4 by 15 inches and is filled to a height of approximately 10 inches with fused alumina of 100 to 150 micron size. Four 350 watt heaters are clamped directly to the outer shell and are controlled by variable heat switches and variacs. The bottom of the fluidized solids section consists of a porous brass plate to distribute the fluidizing air. The exhaust air from the fluidized section passes through a cyclone precipitator to remove any entrained particles. The heat exchanger is insulated with 1 inch thick laminated asbestos paper. Tests indicate that there is essentially constant temperature throughout

Table 88

EXISTENT GUM STUDIES ON JP-4 REFEREE FUEL

Gum determinations have been conducted in accordance with the air jet procedure of ASTM Test Method D381-52T. In accordance with this procedure a 50 ml. sample of test fluid is evaporated at a test temperature of 311 ± 9°F. by an air stream of 1000 ± 150 ml. per sec. at the test temperature. The test is continued for a period of 15 minutes after dryness is reached.

| Test Fluid(1) | Preliminary Treatment | Existent Gum mg./100 ml. |
|---|---|---|
| "Topped" JP-4 referee fuel | None | 10 |
| "Topped" JP-4 referee fuel | Feed taken from extractor(2) | 43 |
| "Topped" JP-4 referee fuel | Treated with liquid $NH_3$ in glass(3) | 17 |
| "Topped" JP-4 referee fuel | Washed with 5% NaOH (aqueous) | 20 |
| "Topped" JP-4 referee fuel | Simple distilled | 2.4 |
| "Topped" JP-4 referee fuel | 10:1 weight ratio oil to gel silica gel percolation(4) | 1.8 |
| "Topped" JP-4 referee fuel | 10:1 weight ratio oil to gel silica gel batch contact(5) | 2.4 |
| "Topped" JP-4 referee fuel | 30:1 weight ratio oil to gel silica gel batch contact(5) | 3.6 |

(1) JP-4 referee fuel topped in fractionating column (75 theoretical plates) to remove material boiling below 200°F. This low boiling material comprises approximately 15 volume per cent of the JP-4 referee fuel.

(2) This sample was removed from the feed tank of the extractor during run 231. The feed had been contacted with ammonia-amine solvent for about 40 hours prior to the sampling.

(3) This sample was shaken with an equal part by weight of ammonia-amine solvent for one hour in a glass pressure flask.

(4) This sample was percolated through a 0.39" i.d. column packed with 28-200 mesh silica gel for a height of 21". The sample used represents about 90% of the "topped" JP-4 fuel. The other 10% remained adsorbed on the gel.

(5) This sample was shaken with the silica gel for 1/2 hour and then filtered.

Table 89

## EXISTENT AND POTENTIAL GUM STUDIES WITH JP4 FUEL FRACTIONS FROM EXTRACTION, DISTILLATION, AND SILICA GEL TREATMENT

GUM DETERMINATIONS HAVE BEEN CONDUCTED IN ACCORDANCE WITH THE AIR JET PROCEDURE OF ASTM TEST METHOD D381-52T

IN ACCORDANCE WITH THIS PROCEDURE A 50 ML. SAMPLE OF TEST FLUID IS EVAPORATED AT A TEST TEMPERATURE OF 311 ± 9°F. BY AN AIR STREAM OF 1000 ± 150 ML. PER SEC. AT THE TEST TEMPERATURE. THE TEST SAMPLE IS EVAPORATED TO DRYNESS. THE TEST IS CONTINUED FOR A PERIOD OF 15 MINUTES AFTER DRYNESS IS REACHED.

| DESCRIPTION OF SAMPLE | EXISTENT GUM, MG./100 ML. | POTENTIAL GUM DETERMINATION: TYPE OXIDATION TEST(1) | OXIDATION TEST TIME, HRS. | OXYGEN ABSORBED, ML./100 ML. SAMPLE | GUM DETERMINATION AFTER OXID., MG./100 ML.: DEPOSIT ON THIN FILM CATALYST | INSOLUBLES IN FLUID(2) | SOLUBLE GUM | TOTAL GUM | MG. GUM/ML. OXYGEN ABSORBED |
|---|---|---|---|---|---|---|---|---|---|
| JP4 "TOPPED" FEED STOCK(3) | 10 | STANDARD | 48 | 192 | - | 16 | 235 | 251 | 1.31 |
| | | STANDARD | 142 | 685 | - | 659 | 243 | 902 | 1.32 |
| EXTRACTOR RUN 231 RAFFINATE(4) | 30 | STANDARD | 17.5 | 500 | - | 352 | 355 | 707 | 1.41 |
| EXTRACTOR RUN 231 EXTRACT(4) | 40 | STANDARD | 17.5 | 308 | - | 103 | 439 | 542 | 1.76 |
| EXTRACTOR RUN 235 RAFFINATE(4) | 47 | STANDARD | 15.3 | 484 | - | 273 | 316 | 589 | 1.22 |
| EXTRACTOR RUN 236(4) RAFFINATE FRACTIONS(5) FROM SIMPLE DISTILLATION | | | | | | | | | |
| FRACT. 1 (41.5 VOL.%, 170°C. MAX. B.P.) | 0 | STANDARD | 2 | 925 | - | 100 | 520 | 620 | 0.67 |
| FRACT. 2 (39.5 VOL.%, 200°C. MAX. B.P.) | 2.6 | STANDARD | 77.8 | 587 | - | 495 | 241 | 736 | 1.25 |
| FRACT. 3 (14 VOL.%, >200°C. MAX. B.P.) | 25 | STANDARD | 85 | 527 | - | 527 | 616 | 1143 | 1.82 |
| RESIDUE (5 VOL.%) | 850 | - | - | - | - | - | - | - | - |
| EXTRACTOR RUN 236(4) EXTRACT FRACTIONS(5) FROM SIMPLE DISTILLATION | | | | | | | | | |
| FRACT. 1 (31.5 VOL.%, 152°C. MAX. B.P.) | 0.0 | STANDARD | 5 | 893 | - | 213 | 993 | 1211 | 1.36 |
| FRACT. 2 (37.5 VOL.%, 175°C. MAX. B.P.) | 0.2 | STANDARD | 142 | 760 | - | 607 | 848 | 1455 | 1.91 |
| FRACT. 3 (31.0 VOL.%, >175°C. MAX. B.P.) | 22.4 | STANDARD | 28 | 1560 | - | 439 | 1745 | 2244 | 1.44 |
| RESIDUE (1.0 VOL.%) | - | - | - | - | - | - | - | - | - |
| EXTRACTOR RUN 237(4) RAFFINATE FRACTIONS(6) FROM SIMPLE DISTILLATION | | | | | | | | | |
| FRACT. 1 (29.5 VOL.%, 170°C. MAX. B.P.) | 0.0 | STANDARD | 2.5 | 1000 | - | 195 | 441 | 636 | 0.64 |
| FRACT. 2 (35.0 VOL.%, 200°C. MAX. B.P.) | 1.0 | STANDARD | 4.8 | 690 | - | 269 | 323 | 592 | 0.86 |
| FRACT. 3 (30 VOL.%, 252°C. MAX. B.P.) | 6.8 | STANDARD | 141.5 | 725 | - | 749 | 342 | 1091 | 1.52 |
| RESIDUE (5.5 VOL.%) | 1420 | - | - | - | - | - | - | - | - |

(CONTINUED ON NEXT PAGE)

Table 89 (Continued)

| DESCRIPTION OF SAMPLE | EXISTENT GUM, MG./100 ML. | POTENTIAL GUM DETERMINATION: TYPE OXIDATION TEST(1) | OXIDATION TEST TIME, HRS. | OXYGEN ABSORBED, ML./100 ML. SAMPLE | GUM DETERMINATION AFTER OXID., MG./100 ML.: DEPOSIT ON THIN FILM CATALYST | INSOLUBLES IN FLUID(2) | SOLUBLE GUM | TOTAL GUM | MG. GUM/ML. OXYGEN ABSORBED |
|---|---|---|---|---|---|---|---|---|---|
| EXTRACTOR RUN 237(4) EXTRACT FRACTIONS(5) FROM SIMPLE DISTILLATION | | | | | | | | | |
| FRACT. 1 (27.7 VOL.%, 150°C. MAX. B.P.) | 0.0 | STANDARD | 2.2 | 1050 | - | 64 | 1050 | 1114 | 1.06 |
| FRACT. 2 (26.7 VOL.%, 175°C. MAX. B.P.) | 0.0 | STANDARD | 4.8 | 795 | - | 109 | 925 | 1034 | 1.30 |
| FRACT. 3 (27.6 VOL.%, 196°C. MAX. B.P.) | 4.2 | STANDARD | 51.3 | 676 | - | 276 | 821 | 1097 | 1.62 |
| FRACT. 4 (16.5 VOL.%, 252°C. MAX. B.P.) | 73 | STANDARD | 58 | 750 | - | 228 | 1333 | 1511 | 2.15 |
| RESIDUE (1.5 VOL.%) | - | - | - | - | - | - | - | - | - |
| EXTRACTOR RUN 236 EXTRACT(5) (SIMPLE DISTILLED) | - | STANDARD | 127.5 | 1000 | - | 1160 | 1226 | 2386 | 2.39 |
| EXTRACTOR RUN 237 EXTRACT(5) (SIMPLE DISTILLED) | - | STANDARD | 27.5 | 1050 | - | 506 | 804 | 1310 | 1.25 |
| EXTRACTOR RUN 236 RAFFINATE(5) (SIMPLE DISTILLED) | - | STANDARD | 17 | 980 | - | 481 | 448 | 929 | 0.95 |
| EXTRACTOR RUN 237 RAFFINATE(5) FRACTIONS FROM SIMPLE DISTILLATION | | | | | | | | | |
| FRACT. 1 (20.0 VOL.%, 177°C. MAX. B.P.) | - | STANDARD | 12.5 | 1470 | - | 416 | 570 | 986 | 0.67 |
| FRACT. 2 (28.0 VOL.%, 232°C. MAX. B.P.) | - | STANDARD | 17.9 | 1030 | - | 569 | 283 | 852 | 0.83 |
| FRACT. 3 (8.5 VOL.%, 288°C. MAX. B.P.) | - | STANDARD | 262 | 770 | - | 924 | 608 | 1532 | 1.99 |
| JP4 "TOPPED" FEED STOCK (SILICA GEL TREATED)(7) | 0 | STANDARD | 15 | 895 | - | 485 | 217 | 702 | 0.78 |
| JP4 "TOPPED" FEED STOCK(3) | 11.6 | THIN FILM (STEEL CHAIN) | 15.8 | 1390 | 242 | 972 | 655 | 1869 | 1.34 |
| + 0.01 WT.% SYNTHETIC BARIUM SULFONATE | - | THIN FILM (STEEL CHAIN) | 17.5 | 1590 | 452 | 1890 | 1010 | 3352 | 2.10 |
| + 0.01 WT.% DUPONT ADDITIVE NO. 2 | - | THIN FILM (STEEL CHAIN) | 17.5 | 1540 | 292 | 1308 | 855 | 2455 | 1.59 |
| JP4 "TOPPED" FEED STOCK(3) | 10 | THIN FILM (NO CATALYST) | 3 | 143 | - | NONE | 104 | 104 | 0.73 |
| | | | 88(9) | 1400 | - | 1857 | 650 | 2517 | 1.80 |
| | | | 116 | 1080 | - | 1140 | 316 | 1456 | 1.35 |

(CONCLUDED ON NEXT PAGE)

Table 89 (Concluded)

| DESCRIPTION OF SAMPLE | EXISTENT GUM, MG./100 ML. | POTENTIAL GUM DETERMINATION: TYPE OXIDATION TEST(1) | OXIDATION TEST TIME, HRS. | OXYGEN ABSORBED, ML./100 ML. SAMPLE | GUM DETERMINATION AFTER OXID., MG./100 ML.: DEPOSIT ON THIN FILM CATALYST | INSOLUBLES IN FLUID(2) | SOLUBLE GUM | TOTAL GUM | MG. GUM/ML. OXYGEN ABSORBED |
|---|---|---|---|---|---|---|---|---|---|
| JP4 "TOPPED" FEED STOCK(3) | 10 | THIN FILM (GLASS BEADS) | 3 | 72 | 0.8 | NONE | 80 | 80.8 | 1.12 |
| | | | 88 | 1450 | 18 | 901 | 394 | 1413 | 0.97 |
| JP4 "TOPPED" FEED STOCK(3) | 10 | THIN FILM (STEEL CHAIN) | 3 | 98 | 20 | NONE | 61 | 81 | 0.83 |
| | | | 5 | 145 | 24 | NONE | 173 | 207 | 1.43 |
| | | | 9.5 | 1460 | 372 | 701 | 661 | 1734 | 1.19 |
| | | | 9.5 | 1475 | 248 | 875 | 730 | 1873 | 1.27 |
| JP4 "TOPPED" FEED STOCK(3) | 10 | THIN FILM (COPPER CHAIN) | 1 | 1790 | 242 | - | 1203 | 1445 | 0.81 |
| | | | 1.9 | 1600 | 145 | NONE | 1514 | 1659 | 1.03 |
| JP4 "TOPPED" FEED STOCK FROM EXTRACTOR RUN 231(8) | 43 | THIN FILM (STEEL CHAIN) | 5 | 850 | 264 | 460 | 706 | 1430 | 1.62 |
| | 43 | | 5 | 1300 | 310 | 722 | 911 | 1951 | 1.50 |
| JP4 "TOPPED" FEED STOCK FROM EXTRACTOR RUN 231 RAFFINATE(4) | 30 | THIN FILM (STEEL CHAIN) | 5 | 1540 | 494 | 922 | 896 | 2312 | 1.50 |
| | 30 | | 5 | 1320 | 268 | 671 | 954 | 1693 | 1.43 |
| JP4 "TOPPED" FEED STOCK FROM EXTRACTOR RUN 231 EXTRACT(4) | 40 | THIN FILM (STEEL CHAIN) | 2 | 1600 | 278 | 690 | 2008 | 3046 | 1.92 |

(1) THE OXIDATION TESTS ARE MODIFICATIONS OF THE PRESSURE OXIDATION TEST SPECIFIED BY ASTM METHOD D873-49. THESE TESTS WERE CONDUCTED IN A 1-1/2 INCH DIAMETER SECTION OF PYREX PIPE SEALED OFF AT THE TOP BY A STAINLESS STEEL FLANGE AND TEFLON GASKET. THE STANDARD OXIDATION TEST IS CONDUCTED WITH A 50 ML. CHARGE OF TEST FLUID AT 250°F. THE TUBE VOLUME IS 480 ML. A TOTAL OF 32 P.S.I. GAGE OXYGEN PRESSURE IS IMPOSED AT ROOM TEMPERATURE AT THE START OF THE TEST YIELDING A TOTAL PRESSURE OF ABOUT 50 P.S.I. GAGE AT 250°F. THE COURSE OF THE REACTION IS FOLLOWED BY CHANGES IN SYSTEM PRESSURE. THE AMOUNT OF OXYGEN ASSIMILATED IS DETERMINED BY COOLING TO ROOM TEMPERATURE AND AGAIN MEASURING THE OXYGEN PRESSURE. THE THIN FILM TEST IS CONDUCTED IN THE SAME GENERAL FASHION WITH ONE EXCEPTION. DURING THE THIN FILM TEST THE FLUID IS CIRCULATED OVER A LARGE CATALYST AREA CONSISTING OF JACK CHAIN OR GLASS BEADS. THE CIRCULATION IS ACCOMPLISHED BY MEANS OF A STAINLESS STEEL BUCKET PUMP WHICH LIFTS THE FLUID APPROXIMATELY 7 INCHES FROM THE BOTTOM OF THE TUBE AND DISTRIBUTES THE FLUID OVER THE CATALYST AREA OF THE PACKING MATERIAL SUPPORTED IN THE TUBE BETWEEN THE RESERVOIR AND THE PUMP DISTRIBUTING HEAD. THIS PUMP IS SOLENOID OPERATED.

(2) OIL INSOLUBLES PRESENT IN THE FLUID AFTER THE OXIDATION TEST ARE REMOVED BY FILTRATION THROUGH A SINTERED GLASS FILTER AND THE QUANTITY OF THESE INSOLUBLES MEASURED SEPARATELY BY THE AIR JET METHOD FROM A VOLATILE SOLVENT.

(3) JP4 REFEREE FUEL TOPPED IN FRACTIONATION COLUMN (75 THEORETICAL PLATES) TO REMOVE MATERIAL BOILING BELOW 200°F. THIS LOW BOILING MATERIAL COMPRISES APPROXIMATELY 15 VOLUME PER CENT OF THE JP4 REFEREE FUEL.

(4) CONDITIONS FOR LIQUID-LIQUID EXTRACTION AND PROPERTIES OF THE RESULTANT FRACTIONS ARE SHOWN ON TABLE 87.

(5) CHARGE FOR THE SIMPLE DISTILLATION CONTAINED 20 PARTS PER MILLION OF U.O.P. INHIBITOR #5.

(6) CHARGE FOR THE SIMPLE DISTILLATION, IN THIS CASE, CONTAINED NO INHIBITOR.

(7) FLUID USED IN THIS TEST COMPRISES ABOUT THE FIRST 50 VOLUME PER CENT OF JP4 TOPPED FEED STOCK PERCOLATED THROUGH A SILICA GEL ADSORPTION TOWER. THE SILICA GEL FLUID RATIO IN THIS CASE WAS 10:1.

(8) FLUID FOR THIS TEST IS JP4 TOPPED FEED STOCK REMOVED FROM THE EXTRACTOR AFTER CONTACT WITH THE LIQUID AMMONIA-AMINE SOLVENT.

(9) EXTENSIVE PITTING OF THE STEEL FLANGE WAS NOTED IN THIS TEST.

## Table 90

## EXISTENT AND POTENTIAL GUM STUDIES WITH HIGH PARAFFIN JP-4 FUEL

GUM DETERMINATIONS HAVE BEEN CONDUCTED IN ACCORDANCE WITH THE AIR JET PROCEDURE OF ASTM TEST METHOD D381-52T. IN ACCORDANCE WITH THIS PROCEDURE A 50 ML. SAMPLE OF TEST FLUID IS EVAPORATED AT A TEST TEMPERATURE OF 311 ± 9°F. BY AN AIR STREAM OF 1000 ± 110 ML. PER SEC. AT THE TEST TEMPERATURE. THE TEST SAMPLE IS EVAPORATED TO DRYNESS. THE TEST IS CONTINUED FOR A PERIOD OF 15 MINUTES AFTER DRYNESS IS REACHED.

| COMPOUND | EXISTENT GUM, MG./100 ML. | POTENTIAL GUM DETERMINATION | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | TYPE OXIDATION TEST(1) | OXIDATION TEST TIME, HRS. | OXYGEN ABSORBED, ML./100 ML. SAMPLE | GUM DETERMINATION AFTER OXIDATION, MG./100 ML. — DEPOSIT ON THIN FILM CATALYST (STEEL JACK CHAIN) | INSOLUBLES IN FLUID(2) | SOLUBLE GUM | TOTAL GUM | MG. GUM/ML. OXYGEN ABSORBED |
| HIGH PARAFFIN JP-4 | 28.2 | STANDARD | 7 | 1590 | - | 44 | 108 | 152 | 0.095 |
| | 28.2 | THIN FILM (STEEL CHAIN) | 172(3) | 2260 | 84 | 1281 | 439 | 1604 | 0.80 |
| HIGH PARAFFIN JP-4 + 100 P.P.M. PARANOX 441 | 28.2 | STANDARD | 7.8 | 162 | - | 42 | 117 | 159 | 0.099 |
| | 28.2 | THIN FILM (STEEL CHAIN) | 4.2 | 1760 | 344 | 309 | 219 | 872 | 0.50 |

(1) THE OXIDATION TESTS ARE MODIFICATIONS OF THE PRESSURE OXIDATION TEST SPECIFIED BY ASTM METHOD D873-49. THESE TESTS WERE CONDUCTED IN A 1-1/2 INCH DIAMETER SECTION OF PYREX PIPE SEALED OFF AT THE TOP BY A STAINLESS STEEL FLANGE AND TEFLON GASKET. THE STANDARD OXIDATION TEST IS CONDUCTED WITH A 50 ML. CHARGE OF TEST FLUID AT 250°F. THE TUBE VOLUME IS 480 ML. A TOTAL OF 22 P.S.I. GAGE OXYGEN PRESSURE IS IMPOSED AT ROOM TEMPERATURE AT THE START OF THE TEST YIELDING A TOTAL PRESSURE OF ABOUT 50 P.S.I. GAGE AT 250°F. THE COURSE OF THE REACTION IS FOLLOWED BY CHANGES IN SYSTEM PRESSURE. THE AMOUNT OF OXYGEN ASSIMILATED IS DETERMINED BY COOLING TO ROOM TEMPERATURE AND AGAIN MEASURING THE OXYGEN PRESSURE. THE THIN FILM TEST IS CONDUCTED IN THE SAME GENERAL FASHION WITH ONE EXCEPTION. DURING THE THIN FILM TEST THE FLUID IS CIRCULATED OVER A LARGE CATALYST AREA CONSISTING OF JACK CHAIN OR GLASS BEADS. THE CIRCULATION IS ACCOMPLISHED BY MEANS OF A STAINLESS STEEL BUCKET PUMP WHICH LIFTS THE FLUID APPROXIMATELY 7 INCHES FROM THE BOTTOM OF THE TUBE AND DISTRIBUTES THE FLUID OVER THE CATALYST AREA OF THE PACKING MATERIAL SUPPORTED IN THE TUBE BETWEEN THE RESERVOIR AND THE PUMP DISTRIBUTING HEAD. THIS PUMP IS SOLENOID OPERATED.

(2) OIL INSOLUBLES PRESENT IN THE FLUID AFTER THE OXIDATION TEST ARE MEASURED BY FILTRATION THROUGH A SINTERED GLASS FILTER AND THE QUANTITY OF THESE INSOLUBLES MEASURED SEPARATELY BY THE AIR JET METHOD FROM A VOLATILE SOLVENT.

(3) PRESSURE FELL TO 20 P.S.I.G. AFTER 4.2 HOURS. NO APPRECIABLE CHANGE IN REMAINDER OF TEST TIME.

## Table 91

## EXISTENT AND POTENTIAL GUM STUDIES WITH OXYGENATED COMPOUNDS

OXIDATION TESTS CONDUCTED IN ACCORDANCE WITH A MODIFICATION OF ASTM METHOD D873-49[1]

GUM DETERMINATIONS HAVE BEEN CONDUCTED IN ACCORDANCE WITH THE AIR JET PROCEDURE OF ASTM TEST METHOD D381-52T, IN ACCORDANCE WITH THIS PROCEDURE A 50 ML. SAMPLE OF TEST FLUID IS EVAPORATED AT A TEST TEMPERATURE OF 311 ± 9°F. BY AN AIR STREAM OF 1000 ± 150 ML. PER SEC. AT THE TEST TEMPERATURE. THE TEST SAMPLE IS EVAPORATED TO DRYNESS. THE TEST IS CONTINUED FOR A PERIOD OF 15 MINUTES AFTER DRYNESS IS REACHED.

| DESCRIPTION OF SAMPLE | EXISTENT GUM, MG./100 ML. | POTENTIAL GUM DETERMINATION: OXIDATION TEST TIME, HRS. | OXYGEN ABSORBED, ML. PER 100 ML. SAMPLE | GUM DETERMINATION AFTER OXIDATION, MG./100 ML.: INSOLUBLES IN FLUID[2] | SOLUBLE GUM | TOTAL GUM | MG. GUM/ML. OXYGEN ABSORBED |
|---|---|---|---|---|---|---|---|
| N-HEXYL ETHER | 8.4 | 2.3 | 1100 | 0 | 21.6 | 21.6 | 0.020 |
| DECANOL | 10.8 | 39 | 640 | 0 | 943 | 943 | 1.57 |
| 2-OCTANONE | 0.7 | 9 | 770 | 0 | 40 | 40 | 0.052 |
| CAPRYL ALCOHOL | 0 | 8.3 | 770 | 0 | 11 | 11 | 0.014 |
| ISOAMYL ACETATE | 2.8 | 184 | 30 | 0 | 6.8 | 6.8 | 0.23 |
| JP-4 "STOPPED" FEED STOCK, EXTRACTOR RUN 237 RAFFINATE (SIMPLE DISTILLED) | - | 73.5 | 800 | 769 | 196 | 965 | 1.21 |
| + 25 WT.% DECANOL | - | 10.5 | 1150 | 0 | 1366 | 1366 | 1.19 |
| + 25 WT.% 2-OCTANONE | - | 9 | 1035 | 108 | 786 | 894 | 0.76 |
| + 25 WT.% ISOAMYL ACETATE | - | 4.5 | 1080 | 0 | 769 | 769 | 0.71 |
| + 20 WT.% ISOAMYL ACETATE | - | 8.5 | 1125 | 84 | 806 | 890 | 0.77 |
| + 15 WT.% ISOAMYL ACETATE | - | 11.5 | 1150 | 208 | 828 | 1036 | 0.91 |
| JP-4 "STOPPED" FEED STOCK, EXTRACTOR RUN 237 RAFFINATE (SIMPLE DISTILLED) + 25 WT.% ISOAMYL ACETATE | | | | | | | |
| + 20 P.P.M. PARANOX 441 | - | 7.5 | 1175 | 50 | 829 | 897 | 0.76 |
| + 100 P.P.M. PARANOX 441 | - | 8 | 1330 | 75 | 895 | 971 | 0.73 |
| + 20 P.P.M. U.O.P. INHIB. NO. 5 | - | 15.5 | 1170 | 90 | 843 | 933 | 0.80 |
| + 100 P.P.M. U.O.P. INHIB. NO. 5 | - | 17.3 | 1410 | 157 | 1021 | 1178 | 0.83 |

(1) THE OXIDATION TESTS ARE MODIFICATIONS OF THE PRESSURE OXIDATION TEST SPECIFIED BY ASTM METHOD D873-49. THESE TESTS WERE CONDUCTED IN A 1-1/2 INCH DIAMETER SECTION OF PYREX PIPE SEALED OFF AT THE TOP BY A STAINLESS STEEL FLANGE AND TEFLON GASKET. THE STANDARD OXIDATION TEST IS CONDUCTED WITH A 50 ML. CHARGE OF TEST FLUID AT 250°F. THE TUBE VOLUME IS 480 ML. A TOTAL OF 32 P.S.I. GAGE OXYGEN PRESSURE IS IMPOSED AT ROOM TEMPERATURE AT THE START OF THE TEST YIELDING A TOTAL PRESSURE OF ABOUT 50 P.S.I. GAGE AT 250°F. THE COURSE OF THE REACTION IS FOLLOWED BY CHANGES IN SYSTEM PRESSURE. THE AMOUNT OF OXYGEN ASSIMILATED IS DETERMINED BY COOLING TO ROOM TEMPERATURE AND AGAIN MEASURING THE OXYGEN PRESSURE.

(2) OIL INSOLUBLES PRESENT IN THE FLUID AFTER THE OXIDATION TEST ARE MEASURED BY FILTRATION THROUGH A SINTERED GLASS FILTER AND THE QUANTITY OF THESE INSOLUBLES MEASURED SEPARATELY BY THE AIR JET METHOD FROM A VOLATILE SOLVENT.

Table 92

## EXISTENT AND POTENTIAL GUM STUDIES WITH PURE HYDROCARBONS

GUM DETERMINATIONS HAVE BEEN CONDUCTED IN ACCORDANCE WITH THE AIR JET PROCEDURE OF ASTM TEST METHOD D381-52T. IN ACCORDANCE WITH THIS PROCEDURE A 50 ML. SAMPLE OF TEST FLUID IS EVAPORATED AT A TEST TEMPERATURE OF 311 ± 9°F. BY AN AIR STREAM OF 1000 ± 150 ML. PER SEC. AT THE TEST TEMPERATURE. THE TEST SAMPLE IS EVAPORATED TO DRYNESS. THE TEST IS CONTINUED FOR A PERIOD OF 15 MINUTES AFTER DRYNESS IS REACHED.

| COMPOUND | EXISTENT GUM, MG./100 ML. | <----POTENTIAL GUM DETERMINATION---- TYPE OXIDATION TEST[2] | OXIDATION TEST TIME, HRS. | OXYGEN ABSORBED, ML./100 ML. SAMPLE | GUM DETERMINATION AFTER OXIDATION, MG./100 ML.---> DEPOSIT ON THIN FILM CATALYST | INSOLUBLES IN FLUID[3] | SOLUBLE GUM | TOTAL GUM | MG. GUM/ML. OXYGEN ABSORBED |
|---|---|---|---|---|---|---|---|---|---|
| n-DECANE | 0.8 | STANDARD | 15.5 | 412 | - | NONE | 5.2 | 5.2 | 0.013 |
| | 0.8 | STANDARD | 23 | 1430 | - | NONE | 48 | 48 | 0.034 |
| | 0.8 | STANDARD (STEEL CHAIN) | 42 | 1360 | 61 | 899 | 154 | 1114 | 0.82 |
| | 0.8 | THIN FILM (STEEL CHAIN) | 11 | 1590 | 515 | 517 | 117 | 1243 | 0.78 |
| | 0.8 | THIN FILM (STEEL CHAIN) | 22 | 1580 | 453 | 945 | 37 | 1490 | 0.94 |
| | 0.8 | THIN FILM (COPPER CHAIN) | 6.8 | 1215 | 441 | 61 | 265 | 766 | 0.48 |
| | 0.8 | THIN FILM (GLASS BEADS) | 20.3 | 1850 | 12 | NONE | 200 | 212 | 0.12 |
| n-HEPTANE | - | STANDARD | 43 | 870 | - | NONE | 2 | 2 | 0.002 |
| 2,4-DIMETHYL HEXANE | 0 | STANDARD | 6.5 | 1080 | - | NONE | 0 | 0 | 0 |
| | 0 | THIN FILM (STEEL CHAIN) | 3.6 | 1790 | 285 | 191 | 1.2 | 447 | 0.25 |
| 2,2,4-TRIMETHYL PENTANE (ISOOCTANE) (SILICA GEL TREATED) | 0 | STANDARD | 72 | 405 | - | NONE | 0 | 0 | 0 |
| 2,2,4-TRIMETHYL PENTANE (ISOOCTANE) | 0 | THIN FILM (STEEL CHAIN) | 72 | 170 | 52 | NONE | 13 | 65 | 0.38 |
| 2,4,6-TRIMETHYL NONANE | - | STANDARD | 3.5 | 895 | - | 12 | 2 | 14 | 0.016 |
| DIAMYLENES | 3.4 | STANDARD | 2 | 583 | - | NONE | 66 | 66 | 0.11 |
| | 3.4 | THIN FILM (STEEL CHAIN) | 1.3 | 1610 | 158 | NONE | 213 | 371 | 0.23 |
| TRANS DECALIN | 1.2 | STANDARD | 30.5 | 466 | - | NONE | 50 | 50 | 0.10 |

(CONTINUED ON NEXT PAGE)

Table 92 (Continued)

| COMPOUND | EXISTENT GUM, MG./100 ML. | POTENTIAL GUM DETERMINATION | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | TYPE OXIDATION TEST(2) | OXIDATION TEST TIME, HRS. | OXYGEN ABSORBED, ML./100 ML. SAMPLE | GUM DETERMINATION AFTER OXIDATION, MG./100 ML. | | | | MG. GUM/ML. OXYGEN ABSORBED |
| | | | | | DEPOSIT ON THIN FILM CATALYST | INSOLUBLE IN FLUID(3) | SOLUBLE GUM | TOTAL GUM | |
| DICYCLOHEXYL | 20 | - | - | - | - | - | - | - | - |
| DICYCLOHEXYL (SIMPLE DISTILLED) | 6 | - | - | - | - | - | - | - | - |
| 1,3-DIETHYL BENZENE | 0 | STANDARD | 9.5 | 483 | - | NONE | 29 | 29 | 0.060 |
| DIAMYL BENZENE | 19 | - | - | - | - | - | | - | - |
| DIAMYL BENZENE (SIMPLE DISTILLED) | 2.8 | - | - | - | - | - | - | - | - |
| METHYL NAPHTHALENE | 50 | - | - | - | - | - | - | - | - |
| METHYL NAPHTHALENE (SIMPLE DISTILLED) | 0<br>0 | STANDARD<br>THIN FILM (STEEL CHAIN) | 22.5<br>67 | 143<br>260 | -<br>35 | NONE<br>NONE | 40<br>336 | 40<br>371 | 0.28<br>1.4 |
| TETRALIN | 1390 | - | - | - | - | - | - | - | - |
| TETRALIN (SIMPLE DISTILLED) | 0<br>0 | STANDARD<br>THIN FILM (STEEL CHAIN) | 8<br>0.5 | 510<br>1830 | -<br>9 | NONE<br>NONE | 1000<br>2390 | 1000<br>2399 | 2.0<br>1.3 |
| HYDRINDENE | 927 | STANDARD | 1.5 | 645 | - | 8.0 | 2084 | 2092 | 3.2 |
| HYDRINDENE (SILICA GEL TREATED) | - | STANDARD | 8.5 | 615 | - | NONE | 510 | 510 | 0.83 |
| SYNTHETIC BLEND I(4) | - | STANDARD | 4.3 | 720 | - | 1.4 | 125 | 126.4 | 0.17 |
| SYNTHETIC BLEND II(5) | - | STANDARD | 3.2 | 675 | - | 29 | 188 | 217 | 0.32 |
| BLEND #1 + 1.0 WT.% DIBENZYL DISULFIDE | - | STANDARD | 38 | 130 | - | 174 | 240 | 414 | 3.2 |
| BLEND #1 + 1.0 WT.% THIOPHENE | - | STANDARD | 8.5 | 765 | - | 18 | 178 | 196 | 0.26 |

(CONCLUDED ON NEXT PAGE)

Table 92 (Concluded)

| COMPOUND | EXISTENT GUM, MG./100 ML. | POTENTIAL GUM DETERMINATION | | | GUM DETERMINATION AFTER OXIDATION, MG./100 ML. | | | | MG. GUM/ML. OXYGEN ABSORBED |
|---|---|---|---|---|---|---|---|---|---|
| | | TYPE OXIDATION TEST(2) | OXIDATION TEST TIME, HRS. | OXYGEN ABSORBED, ML./100 ML. SAMPLE | DEPOSIT ON THIN FILM CATALYST | INSOLUBLES IN FLUID(3) | SOLUBLE GUM | TOTAL GUM | |
| BLEND #1 + 1.0 WT.% METHYL QUINOLINE | - | STANDARD | 10 | 780 | - | NONE | 156 | 156 | 0.20 |
| BLEND #1 + 1.0 WT.% METHYLBUTYL SULFIDE | - | STANDARD | 4.3 | 75 | - | NONE | 41 | 41 | 0.55 |
| | - | STANDARD | 159 | 615 | - | 212 | 115 | 327 | 0.53 |

(1) THE SAMPLES USED FOR THIS STUDY WERE TAKEN FROM STORAGE IN SEALED SCREW CAP BOTTLES. THE TIME IN STORAGE VARIES FROM ABOUT 2 TO 6 YEARS. THE SAMPLES LISTED AS SIMPLE DISTILLED HAVE BEEN DISTILLED WITHIN A DAY OF THE GUM DETERMINATION.

(2) THE OXIDATION TESTS ARE MODIFICATIONS OF THE PRESSURE OXIDATION TEST SPECIFIED BY ASTM METHOD D873-49. THESE TESTS WERE CONDUCTED IN A 1-1/2 INCH DIAMETER SECTION OF PYREX PIPE SEALED OFF AT THE TOP BY A STAINLESS STEEL FLANGE AND TEFLON GASKET. THE STANDARD OXIDATION TEST IS CONDUCTED WITH A 50 ML. CHARGE OF TEST FLUID AT 250°F. THE TUBE VOLUME IS 480 ML. A TOTAL C 32 P.S.I. GAGE OXYGEN PRESSURE IS IMPOSED AT ROOM TEMPERATURE AT THE START OF THE TEST YIELDING A TOTAL PRESSURE OF ABOUT 50 P.S.I. GAGE AT 250°F. THE COURSE OF THE REACTION IS FOLLOWED BY CHANGES IN SYSTEM PRESSURE. THE AMOUNT OF OXYGEN ASSIMILATED IS DETERMINED BY COOLING TO ROOM TEMPERATURE AND AGAIN MEASURING THE OXYGEN PRESSURE. THE THIN FILM TEST IS CONDUCTED IN THE SAME GENERAL FASHION WITH ONE EXCEPTION. DURING THE THIN FILM TEST THE FLUID IS CIRCULATED OVER A LARGE CATALYST AREA CONSISTING OF JACK CHAIN OR GLASS BEADS. THE CIRCULATION IS ACCOMPLISHED BY MEANS OF A STAINLESS STEEL BUCKET PUMP WHICH LIFTS THE FLUID APPROXIMATELY 7 INCHES FROM THE BOTTOM OF THE TUBE AND DISTRIBUTES THE FLUID OVER THE CATALYST AREA OF THE PACKING MATERIAL SUPPORTED IN THE TUBE BETWEEN THE RESERVOIR AND THE PUMP DISTRIBUTING HEAD. THIS PUMP IS SOLENOID OPERATED.

(3) OIL INSOLUBLES PRESENT IN THE FLUID AFTER THE OXIDATION TEST ARE MEASURED BY FILTRATION THROUGH A SINTERED GLASS FILTER AND THE QUANTITY OF THESE INSOLUBLES MEASURED SEPARATELY BY THE AIR JET METHOD FROM A VOLATILE SOLVENT.

(4) BLEND PREPARED FROM 20 WT.% DIETHYL BENZENE, 10 WT.% DIAMYL BENZENE, 3 WT.% METHYL NAPHTHALENE, 7 WT.% DIAMYLENES, 30 WT.% DECANE, AND 30 WT.% DECALIN.

(5) BLEND PREPARED FROM 10 WT.% DIETHYL BENZENE, 10 WT.% DIAMYL BENZENE, 3 WT.% METHYL NAPHTHALENE, 7 WT.% DIAMYLENES, 30 WT.% DECANE, 30 WT.% DECALIN, AND 10 WT.% TETRALIN.

the fluidized bed. This fluidized solids bed is of the same general construction, but smaller in capacity, as the heater for the high temperature hydraulic pump system described in section I of this report.

The filter holder consists essentially of a high pressure 3/4 inch steel pipe union fitted on both ends with 1-3/8 inch steel bar stock and a holding nut machined to screw into the inside of the male part of the union. A simplified cross section is shown on Figure 39. The filter disc and its gasket is held between the holding nut and the squared shoulder of the bar stock in the male part of the union. A 7/16 inch diameter hole is drilled through the two pieces of bar stock and the holding nut to give a filter area equal to one square centimeter. The pressure taps on each side of the filter disc are connected by 1/8 inch o.d. stainless steel tubing to two calibrated pressure gauges. Two thermocouples, protected by stainless steel hypodermic tubing, are fitted to the holder to measure the temperature of the test fluid before and after passing through the filter disc.

The filter holder is equipped with a heating jacket. This jacket consists of a 9-1/2 inch length of 3 inch o.d. Shelby tubing slotted to fit over the filter holder. Two pieces of 1/2 inch o.d. steel tubing act as holders for two 150 watt heaters wired in parallel and controlled by a variac. This equipment is designed to keep the test fluid at test temperature as it passes through the filter. The 3/16 inch o.d. stainless steel line from the fluidized bed heat exchanger is insulated with asbestos cloth to minimize the heat loss.

The hot test fluid is cooled by water in a countercurrent heat exchanger before it enters the pressure loading capillary. The heat exchanger consists of eight feet of 3/16 inch o.d. stainless steel tubing inside a similar length of 1/2 o.d. copper tubing.

The pressure loading device consists of a 5-1/2 inch length of 0.008 i.d. stainless steel capillary tubing supported in a 1/8 inch pipe 5-1/2 inches long. The exit of the pressure loading device is teed and fitted with two stainless steel needle valves. One line goes to the feed reservoir and the other line is used as a sampler. By proper setting of the valve, the circulation rate of the test fluid may be measured.

F. PROCEDURE FOR HIGH TEMPERATURE DIRTINESS TEST. The unit is washed with benzene, dismantled, and air dried after each run. The high temperature dirtiness test procedure consists of circulating a 250 milliliter charge of test fluid through a 5 micron stainless steel porous plate filter at room temperature to remove any suspended material in the test fluid. The 5 micron filter disc is then removed and the test filter is mounted in its place. The test fluid is circulated at room temperature at a rate of about 20 to 25 milliliters per minute under approximately 250 p.s.i.g. pressure for one hour. The pressure drop across the filter at the end of this time is taken as the starting pressure drop for this test.

The heat is turned on the fluidized bed heat exchanger, and the fluid is brought to test temperature as rapidly as possible. During the heating period (approximately 1-1.5 hours) the fluid is continually recycled. The heat is stopped when either the pressure drop across the test filter exceeds 100 p.s.i. or the test fluid is recycled through the filter at test temperature for one hour. The pressure drop at the end of the test is an indication of the high temperature dirtiness of the test fluid.

1. Preliminary Test Results. The results of high temperature dirtiness tests in the filter test unit are given in Table 93. A total of 23 runs were made. Some runs were discarded, primarily because of operational difficulties.

The pressure drop across the filter is indicative of the dirtiness of the test fluid. It is believed that this is not a linear function of the amount of insolubles. At the flow rates used, 10 p.s.i. pressure drop indicates essentially a plugged filter. Present knowledge of filtration suggests that there is no simple relationship between plugging of filters and amounts of insolubles, since particle size plays an important part in closing off pore openings in a filter. Past experience shows that, for equal quantities, insoluble materials with particle sizes approximately equal to the mean pore openings of a filter disc will cause much higher pressure drops than insolubles with fairly large particle sizes. It is also known that filters will remove much smaller particle sizes than the mean pore opening.

The data on Table 93 can be taken as indicative of general trends. The extraction products evaluated all appear to cause more severe filter clogging than the starting material for the extraction (topped JP-4 referee fuel). This is consistent with the sharp increase in existent gum for the extractor products over the topped JP-4 referee fuel as shown on Table 88. The high paraffin JP-4, topped JP-4 referee fuel, and the original JP-4 referee fuel all show some increase in pressure drop across the filter under these test conditions. High paraffin JP-4 is generally considered to be a clean fuel and JP-4 referee fuel a relatively dirty fuel in the various oxidation tests. This trend is not as pronounced in these filter tests.

The last three tests on Table 93 show the results of an oxygenated solvent (isoamyl acetate) on raffinate 237 fraction. This blend exhibits excellent cleanliness in the severe oxidation tests. It has been suggested that the improved cleanliness of this blend over the raffinate 237 fraction may be due in part to the solvent powers of the isoamyl acetate. It is evident from an evaluation of the filtration unit after the tests with the raffinate 237 fraction containing 25 weight per cent isoamyl acetate, that the improved solvent powers of the blend have cleaned deposits from previous tests from the walls of the heat exchanger, filter case, and cooler. This cleaning effect of the blend contributed substantially to the filter plugging noted in tests 19, 21 and 23.

This last series of tests points up some of the problems inherent with a recycling test following the current design. Using 3/16 inch stainless steel tubing for the heater and cooler makes adequate cleaning between tests impossible. In recycling tests, not only the system ahead of the filter but the entire system must be adequately cleaned between tests. The test system is currently being revised to minimize some of the problems encountered in these preliminary tests.

G. CONCLUSIONS. The problem of preventing gum formation in jet fuels does not appear to have a simple solution which can be obtained by minor changes in refining processes. The various hydrocarbon classes in JP-4 referee fuel have been successfully concentrated by means of liquid extraction with an ammonia-amine solvent. The products of this liquid extraction, as well as other products of JP-4 referee fuel separated by silica gel adsorption and distillation, show major changes in composition over the original JP-4 referee fuel, but only minor differences in potential dirtiness and gum forming tendencies.

In general, the total gum formation appears to be a linear function of the oxygen assimilated for the JP-4 fuel and JP-4 fuel fractions in the standard oxidation test. The dirtiness or insolubles formed exhibit a typical induction period phenomenon. That is, the insolubles do not form until after some oxidation has occurred. From this point on, however, the formation of insolubles appears to be essentially linear with further oxidation.

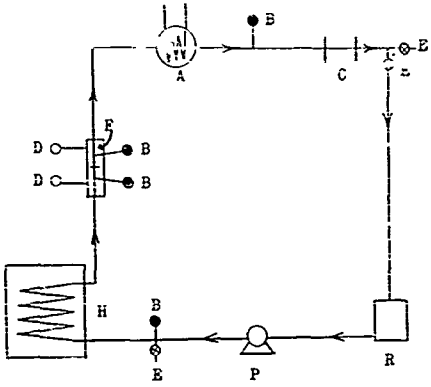
In the standard oxidation tests, the formation of total gum is generally very much lower for the various pure hydrocarbons tested than for any of the fractions separated from the JP-4 referee fuel. Condensed ring compounds containing both aromatic and naphthenic rings show by far the most gum forming tendencies among the pure hydrocarbons tested. Simple mixtures of pure hydrocarbons, blended to give roughly the same ratios of the various classes of hydrocarbons found in JP-4 fuel, give only a fraction of the dirtiness and gum formation of the JP-4 fuel after oxidation tests of equal severity. The addition of about one weight per cent of a sulfide or disulfide to the blend of pure hydrocarbons tends to increase the insoluble and gum forming tendencies of the blend under oxidation. The presence of these sulfur compounds slows down the rate of oxidation, however.

It has been noted that fractions of JP-4 referee fuel from which substantial portions of the aromatic and olefin hydrocarbons have been removed show an appreciable increase in insoluble formation upon oxidation over that of the fractions of the JP-4 referee fuel in which the aromatic portion is concentrated.

Existent gum and/or insolubles appear to be relatively complex oxidation and condensation products of the original hydrocarbon. Existent gum can be removed from JP-4 referee fuel and all of the other hydrocarbons tested by distillation. Silica gel adsorption is also effective in removing, or lowering the gum content of hydrocarbon mixtures. Ammonia-amine extraction of JP-4 referee fuel was not effective in reducing existent

Figure 38

FLOW DIAGRAM FOR HIGH TEMPERATURE DIRTINESS TESTS WITH JET FUELS



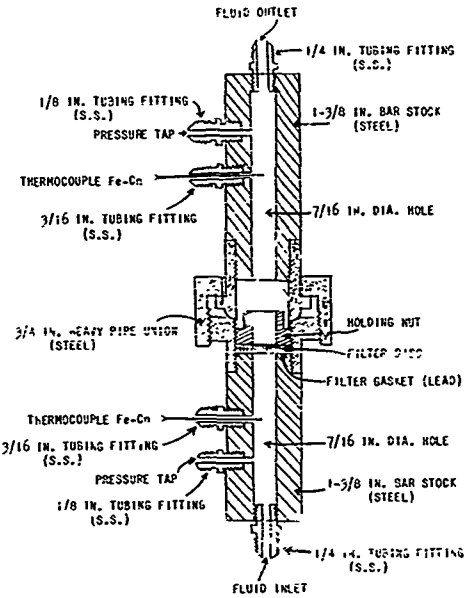

Legend

A - Cooler
B - Thermocouple
C - Pressure loading capillary
D - Pressure gauge
E - Needle valve
F - Filter holder
H - Fluidized bed heat exchanger
P - Pump
R - Fluid reservoir

Figure 39

FILTER HOLDER FOR HIGH TEMPERATURE JET FUEL INSOLUBLES EVALUATIONS

SCALE: 0.5 IN. = 1 IN.




S.S. - STAINLESS STEEL

Table 93

EVALUATION OF HIGH TEMPERATURE DIRTINESS IN JET FUELS

NOTE: TESTS WERE TERMINATED AFTER 1 HOUR AT TEST TEMPERATURE OR WHEN 100 P.S.I. PRESSURE DROP OBTAINED ACROSS THE TEST FILTER. ALL TESTS WERE CONDUCTED USING A STAINLESS STEEL FILTER.

FLOW RATE = 20 TO 25 ML. PER MINUTE — AREA OF FILTER DISC = 1 SQUARE CENTIMETER

| RUN NO. | TEST FLUID | MEAN PORE OPENING OF FILTER, MICRONS | PRESSURE DROP ACROSS FILTER, P.S.I. | MAXIMUM TEST TEMPERATURE AT FILTER, °F. |
|---|---|---|---|---|
| 3 | RAFFINATE 237 (DISTILLED)(1) | 5 | 13 | 295 |
| 5 | RAFFINATE 237 (DISTILLED)(1) | 5 | 16 | 450 |
| 6 | "TOPPED" JP-4(2) | 5 | 7 | 455 |
| 7 | RAFFINATE 237 (DISTILLED)(1) | 5 | 18 | 450 |
| 9 | RAFFINATE 237 (DISTILLED)(1) | 5 | 98 | 310 |
| 10 | RAFFINATE 237 (DISTILLED)(1) | 20 | 110 | 305 |
| 12 | RAFFINATE 237 (DISTILLED)(1) | 20 | 25 | 460 |
| 13 | HIGH PARAFFIN JP-4 | 20 | 2 | 460 |
| 14 | "TOPPED" JP-4(2) | 20 | 1 | 460 |
| 15 | ORIGINAL JP-4 | 20 | 6 | 460 |
| 16 | ORIGINAL JP-4 | 20 | 3 | 455 |
| 17 | RAFFINATE 237 (DISTILLED)(1) | 20 | 20 | 455 |
| 18 | EXTRACT 236 (DISTILLED)(1) | 20 | 15 | 460 |
| 19 | RAFFINATE 237 (DISTILLED)(1) + 25 WT.% ISOAMYL ACETATE | 20 | 99 | 450 |
| 21 | RAFFINATE 237 (DISTILLED)(1) + 25 WT.% ISOAMYL ACETATE | 5 | 52 | 450 |
| 23 | RAFFINATE 237 (DISTILLED)(1) + 25 WT.% ISOAMYL ACETATE | 20 | 39 | 450 |

(1) PROPERTIES OF EXTRACT RUN 236 AND RAFFINATE RUN 237 ARE SHOWN ON TABLE 87.
(2) JP-4 REFEREE FUEL WAS TOPPED IN A FRACTIONATION COLUMN (75 THEORETICAL PLATES) TO REMOVE MATERIAL BOILING BELOW 200°F. THIS TOPPED FUEL COMPRISES APPROXIMATELY 85 VOLUME % OF THE ORIGINAL JP-4 REFEREE FUEL.

gum. This may be due in part to a chemical action of the ammonia-amine solvent on the JP-4 reference fuel.

A high paraffin JP-4 fuel sample from Phillips Petroleum Corp. has been evaluated in standard oxidation tests. The oxidation characteristics of this fuel resemble those of paraffin hydrocarbons. That is, little soluble gum and no insoluble gum is formed in the standard oxidation test with the high paraffin JP-4.

The pure hydrocarbons and JP-4 fuels have also been evaluated in a thin film type test involving the use of large metal catalytic surfaces. The metals used as catalysts are steel and copper. The use of large catalytic surfaces appears to have little effect on the formation of overall gum or insolubles with JP-4 referee fuel and its fractions. The rate of oxygen assimilation is increased, however. The paraffin hydrocarbons and high paraffin JP-4 which produce no insoluble gum in the standard oxidation test produce large quantities of insoluble gum in the thin film test with steel catalyst. Additional studies show that the presence of the metal catalyst area is the most important factor in the gum formation. Copper as well as steel shows a marked catalytic effect on the thin film oxidation test. Copper, in general, tends to increase the oxidation rate and in some cases may lower gum formation as compared to steel.

None of the simple oxygenated materials evaluated in the standard oxidation test produced insoluble gum. The addition of oxygenated materials to a "dirty" fuel (raffinate 237 fraction of JP-4 referee fuel) does, in all cases, substantially reduce the dirtiness formed per unit of oxygen absorbed. Mixtures of oxygenated materials and raffinate 237 fraction give, in all cases, a higher rate of oxidation or less induction period than either of the components tested alone.

Inhibitor studies with Paranox 441 and U.O.P. Inhibitor No. 5 indicate that these materials are not particularly effective in the JP-4 fuels evaluated in the 250°F. oxidation tests. In all cases, U.O.P. Inhibitor No. 5 is more effective than Paranox 441 in the same test fluid.

The pumping test rig for jet fuel dirtiness evaluation shows general correlation with the relatively severe standard oxidation tests. Some redesign of the pumping apparatus appears necessary to aid in system cleaning between tests.

H. FUTURE WORK. The test unit designed to simulate the thermal history of jet fuel flow from the tank through the heat exchanger to the burner nozzle is now being modified to facilitate cleaning and to allow for the observation of the deposits formed on the heat exchanger as well as measurement of the pressure buildup across a sintered metal filter. This unit will be employed in the cooperative study of 10 jet fuels sponsored by the Power Plant Laboratory of the Wright Air Development Center.

An attempt will be made to develop a thin film type test in which the deposits adhering to the metal catalyst can be better observed and measured. The temperature of such a test will be increased to the range of 300° to 400°F. The extent of oxidation will be limited by the amount of oxygen or air charged to the test tube. The oxidation range studied will be much less severe than those of the standard and thin film tests discussed in this report. A mild thin film test of this type will also be included in the cooperative jet fuel testing program. The charge for the larger jet fuel test unit discussed above is on the order of 2 to 5 gallons compared with 50 to 100 ml. for the thin film test unit. It is apparent that this latter unit is more desirable for conducting tests on materials of limited quantity, such as pure hydrocarbons or trace components separated from actual jet fuels.

The effectiveness of oxygenated compounds as solubilizers for insoluble gum in JP-4 referee fuel will be evaluated further. The fractions of JP-4 referee fuel which are described in this report will be used as test fluids for the proposed test techniques.

## IV. MISCELLANEOUS STUDIES

A. DEVELOPMENT AND EVALUATION OF THIN FILM RUST PREVENTIVE COMPOSITIONS. This Laboratory is conducting research and development work on a thin film rust preventive and preservative oil which is designed to be compatible with both mineral oil and synthetic hydraulic fluids. This work is being conducted for the Navy Bureau of Ordnance under Supplemental Agreement No. S4(53-1095) of Contract AF33(038)18193. A progress report on this development work covering the period of October 1953 through January 1954 has been issued as report PRL 7.1-Jan54 and is included here as Appendix B. It is believed that these data may have application in some Air Force problems. The mineral oil and synthetic fluids that this thin protective film is designed to be compatible with include fluid types such as Spec. MIL-O-5606, MIL-L-6387, and MIL-L-7808 which are widely used by the Air Force.

B. USED SAMPLES OF SPEC. MIL-L-6387 HYDRAULIC FLUID. This Laboratory has received from the Wright Air Development Center, three samples of used Spec. MIL-L-6387 hydraulic fluid. It is indicated that these fluids were removed from Sundstrand constant speed alternator drives during a Technical Order Compliance overhaul. It is further indicated that the brass and bronze parts of the drive showed some brown discoloration. It was requested that these fluids be evaluated with respect to fluid stability. The designations of these fluids are shown in Table 94.

Table 94

HISTORY OF USED SPEC. MIL-L-6387 HYDRAULIC FLUIDS

| Design. | Taken from Drive Serial No. | Engine Time, Hrs. |
|---|---|---|
| PRL 3319 | Unused Commercial Batch of Spec. MIL-L-6387 Fluid | |
| PRL 3482-1 | 707 | - |
| PRL 3482-2 | 747 | 465:00 |
| PRL 3482-3 | 750 | - |

These samples were clear and free from sediment as they were received by this Laboratory. The properties of the original fluid charged to the alternator drives are not known to this laboratory. Comparative properties have, therefore, been obtained for a commercial batch of Spec. MIL-L-6387 hydraulic fluid (PRL 3319) available at this Laboratory.

The viscosity properties, neutralization number, and wear behavior determined for these samples, along with similar properties for PRL 3319, are given in Table 95.

Table 95

PROPERTIES OF USED SPEC. MIL-L-6387 HYDRAULIC FLUIDS

| Test Fluid | PRL 3319 | PRL 3482-1 | PRL 3482-2 | PRL 3482-3 |
|---|---|---|---|---|
| Centistoke Viscosity at 210°F. | 4.57 | 3.80 | 4.20 | 3.68 |
| 100°F. | 15.5 | 13.3 | 14.6 | 12.9 |
| ASTM Slope (210° to 100°F.) | 0.580 | 0.634 | 0.608 | 0.643 |
| Per Cent Viscosity Decrease at 100°F. | - | 14 | 6 | 17 |
| Neut. No. (Mg. KOH/Gm. Oil) | 0.5 | 0.2 | 0.4 | 0.5 |
| Wear Characteristics | | | | |
| Average Wear Scar Diam., mm. | | | | |
| 1 Kg. | 0.35 | 0.36 | 0.43 | 0.43 |
| 10 Kg. | 0.37 | 0.35 | 0.36 | 0.50 |
| 40 Kg. | 0.78 | 0.56 | 0.91 | 0.84 |

Aside from the viscosity decrease and the accompanying change in ASTM slope, there does not appear to be any appreciable fluid deterioration. A viscosity decrease due to shear of this magnitude would be expected with a fluid of the Spec. MIL-L-6387 type. As indicated previously, these viscosity changes are only approximate in that they are based on an unused fluid available at this Laboratory.

Stable life type oxidation and corrosion tests have been carried out on these samples as well as on PRL 3319. In these tests, the fluids are subjected to the conditions of the 347°F. Spec. MIL-L-6387 procedure except that the test time is extended to the point at which there is a rapid increase in neutralization number with test time. Only one of the used fluids (PRL 3482-1) shows a characteristic break in the plot of neutralization number versus test time. PRL 3482-1 has an oxidation stability of the same order of magnitude as that shown by a Spec. MIL-L-6387 fluid prepared at this Laboratory with distilled base stock (PRL 3039).

PRL 3482-2 and PRL 3482-3, along with the unused fluid (PRL 3319), do not give the characteristic break in the plot of neutralization number versus test time. Rather, these three fluids show a steady increase in neutralization number with test time to a value of approximately 11 mg. potassium hydroxide per gram of fluid after a test time of 300 hours at 347°F.

These data indicate that the oxidation stability of the three used fluids is not appreciably changed from that shown by typical unused fluids of the Spec. MIL-L-6387 type.

C. SHEAR STABILITY REFERENCE POLYMER. A sample of Acryloid HFS-4 has been received from the Rohm and Haas Company. This polymer has been prepared for use in the formulation of Spec. MIL-F-5602 shear stability reference fluid. Spec. MIL-F-5602 shear stability reference



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fluid is used to control permanent viscosity decrease due to shear in the procurement of Spec. MIL-O-5606 hydraulic fluid. This sample has been submitted in accordance with the Specification requirement that each new lot of reference polymer be approved by the Wright Air Development Center before it can be accepted for use in Spec. MIL-F-5602 shear stability reference fluid.

An experimental blend (PRL 3492) containing Acryloid HFS-4 has been prepared to meet the viscosity requirements of Spec. MIL-F-5602. The viscosity-shear stability of PRL 3492 has been determined in this Laboratory's Hycon pump test stand. The values obtained for PRL 3492 have been compared directly with those obtained for blend PRL 3060 containing Acryloid HFS-3 under the same test conditions. The test conditions for the evaluation of the two fluids are listed below.

| | |
|---|---|
| Pump | Hycon model 67-A-050 |
| Temperature (Pump inlet temp.) | 100°F. |
| System pressure | 1250 to 1300 p.s.i. |
| Loading device | 0.030 inch orifice |
| Pressure across orifice | 1225 to 1250 p.s.i. |
| Test time | 5000 cycles |

The data obtained for PRL 3492 shows that it incurs essentially the same permanent viscosity decrease with pumping time as that determined for PRL 3060 containing Acryloid HFS-3. On the basis of these data, Acryloid HFS-4 is considered to be satisfactory for the preparation of Spec. MIL-F-5602 shear stability reference fluid.

D. ASTM REFERENCE FLUID EVALUATION FOR PERMANENT SHEAR EFFECTS. Section B, Research Division VII, ASTM Committee D-2 has undertaken a cooperative test program for evaluating the permanent viscosity loss due to shear of two non-Newtonian test oils. This Laboratory is cooperating in this evaluation. The two ASTM reference oils 10761 and 11081 have been evaluated in the PRL Hycon pump test stand and the results compared with those of ASTM oils 103 and 104 previously described in report P.R.L.-9-49 to the American Petroleum Institute entitled THE PREPARATION, PROPERTIES AND VISCOSITY-SHEAR BEHAVIOR OF A.P.I. TEST OILS NOS. 103 AND 104, dated October 24, 1949. These results are also compared with similar tests for Spec. MIL-F-5602 shear stability reference fluid and Spec. MIL-O-5606 mineral oil-base hydraulic fluid. The composition and properties of the two ASTM reference fluids, as supplied by the ASTM D-2 Committee, are shown on Table 96.

All of the permanent shear data for the ASTM reference fluids have been obtained in our PRL Hycon pump test stand using an orifice loading device. Figure 40 shows a comparison of the permanent viscosity decrease as a function of time on shear for the two ASTM reference fluids and Spec. MIL-O-5606 hydraulic fluid. These shear tests were conducted at a pressure of 1325 ± 25 p.s.i. for a duration of 5000 cycles through the orifice. These data show that Spec. MIL-O-5606 hydraulic fluid is about midway between the two ASTM reference fluids in severity and appears

to belong to the same family of curves for permanent shear versus oil cycles through the shearing device. Data have been obtained for the two ASTM reference oils at a pressure drop of 3025 ± 50 p.s.i. for a test duration of 5000 cycles. These tests indicate that ASTM oil 10761 shows less permanent viscosity decrease due to shear than does ASTM oil 11081.

Figures 40 and 41 show the permanent viscosity decrease as a function of oil cycles through the orifice at two pressure loadings. Sufficient data are available to show the ASTM reference oils in comparison with similar reference and hydraulic fluids in permanent viscosity decrease due to shear versus pressure drop across the orifice after 5000 oil cycles. The data on Figure 42 show a comparison between the current ASTM reference oils 10761 and 11081 and ASTM reference oils 103 and 104 reported in P.R.L.-9-49. The indications are that the same type and concentration of polymer was used in ASTM oils 103 and 10761. The same relationship is apparent for ASTM oils 104 and 11081. The major difference between these two sets of reference oils is the base stock viscosity in which the polymer is dissolved. ASTM oils 103 and 104 were prepared in a naphthenic gas oil of 8.8 centistokes at 100°F. while the base stock for ASTM oils 10761 and 11081 is indicated to be a naphthenic gas oil of about 3.5 to 4 centistokes at 100°F. Thus, it is believed that the extrapolation of the data for ASTM reference oils below pressures of 1325 p.s.i. is valid.

Figure 43 shows the comparison of Spec. MIL-O-5606 hydraulic fluid and Spec. MIL-F-5602 shear stability reference fluid with the two ASTM reference oils. The Spec. MIL-O-5606 and MIL-F-5602 fluids again appear to be midway between the two ASTM reference oils over the entire pressure range evaluated.

These data have been transmitted to Section B, Research Division VII of Committee D-2.

E. TEMPORARY VISCOSITY DECREASE DUE TO SHEAR. This Laboratory has evaluated the non-Newtonian behavior of polymer-containing fluids in several mechanical devices. These methods include (a) leakage at high shear rates past pintles, seals, and pistons in hydraulic units, (b) leakage through the piston-cylinder small clearance of a Bosch Diesel-type piston pump where the pistons are lapped into the cylinders, (c) flow at shear rates in the range of 0.1 to 300 reciprocal seconds (sec.$^{-1}$) using glass capillaries as viscometers, and (d) flow through calibrated metal capillaries using a hydraulic pump to attain extremely high shear rates while maintaining streamline flow. This latter device is designated as the PRL high shear viscometer. These testers are all based on oil flow through a capillary tube and it is the viscosity as such that has been measured.

There is a dearth of information in the literature on the application of these non-Newtonian liquids to conventionally loaded journal bearings for the evaluation of friction and oil film thickness. Through the NACA subcommittee on wear and lubrication, this Laboratory



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Table 96

COMPOSITION AND PHYSICAL PROPERTIES OF ASTM REFERENCE FLUIDS

| REFERENCE FLUID DESIG. | NO. 10761 | NO. 11081 |
|---|---|---|
| POLYMER | | |
| SAMPLE NO | R3850X | SVB 3043 |
| APPARENT MOLECULAR WT.(1) | 26 | 96 |
| SOLIDS, WT.% | 52.0 | 50.3 |
| BASE OIL | APPROXIMATES THAT SPECIFIED IN MIL-F-5602 | APPROXIMATES THAT SPECIFIED IN MIL-F-5602 |
| REFERENCE FLUID | | |
| CONC. POLYMER, WT.% (AS RECEIVED) | 20.0 | 11.2 |
| VIS. AT 210°F., CS. | 5.30 | 5.66 |
| AT 130°F., CS.(2) | 11.10 | 11.45 |
| AT 100°F., CS. | 16.03 | 16.23 |
| AT -40°F., CS. | 780 | 680 |
| VIS. AT 210°F., SUS | 43.6 | 44.8 |
| AT 130°F., SUS(2) | 62.9 | 64.2 |
| AT 100°F., SUS | 81.4 | 82.2 |
| AT -40°F., SUS | 3560 | 3120 |
| VISCOSITY INDEX | 212 | 212 |
| ASTM SLOPE, 210°F. TO 100°F. | 0.509 | 0.538 |
| POUR POINT, °F. | BELOW -75 | BELOW -75 |
| FLASH POINT, °F. (COC) | 220 | 205 |
| TAN-F, MG. KOH/G. | 0.3 | 0.3 |
| TBN-E, MG. KOH/G. | 0.2 | 0.1 |
| VOLATILE MATTER, WT.% (CRC L-25-745, 23 HRS. AT 210°F.) | 50.3 | 55.1 |
| ANILINE POINT, °C. | 68.6 | 69.4 |
| SPECIFIC GRAVITY, 60°F./60°F. | 0.876 | 0.970 |
| COLOR, NPA | 1-1/2- | 1-1/2- |

(1) VISCOSITY IN CS. AT 210°F. OF 30% SOLIDS IN REFERENCE GAS OIL: ON SAME SCALE REFERENCE POLYMER, ACRYLOID KFS-3 HAS AN APPARENT MOLECULAR WEIGHT OF 62.
(2) INTERPOLATED VALUES.

Figure 40

PERMANENT VISCOSITY DECREASE DUE TO SHEAR FOR SEVERAL FLUIDS IN PRL HYCON PUMP TEST STAND

TEST CONDITIONS: ALL TESTS CONDUCTED AT 100°F. (PUMP INLET TEMPERATURE). PRESSURE LEAKING DEVICE = 0.030 IN. ORIFICE. PRESSURE DROP ACROSS ORIFICE IN ALL CASES = 1325 ± 25 P.S.I. FLOW RATE IN ALL CASES = 2650 ± 25 ML./MIN.

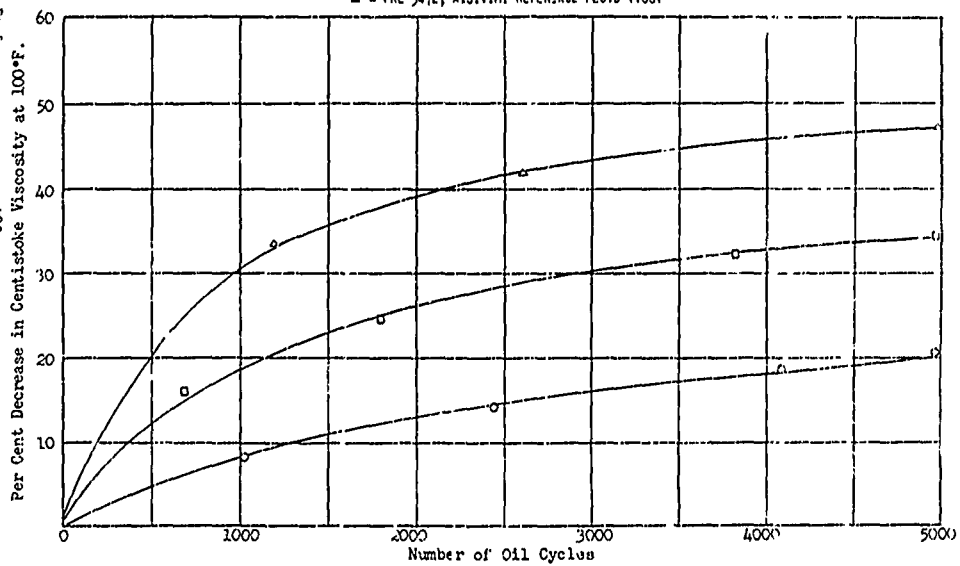


Figure 41

PERMANENT VISCOSITY DECREASE DUE TO SHEAR FOR SEVERAL FLUIDS IN PRL HYCON PUMP TEST STAND

TEST CONDITIONS: ALL TESTS CONDUCTED AT 100°F. (PUMP INLET TEMPERATURE). PRESSURE LOADING DEVICE = 0.024 IN. ORIFICE. PRESSURE DROP ACROSS ORIFICE IN ALL CASES = 3025 ± [illegible] P.S.I. FLOW RATE = 2425 ± 25 GAL./MIN.

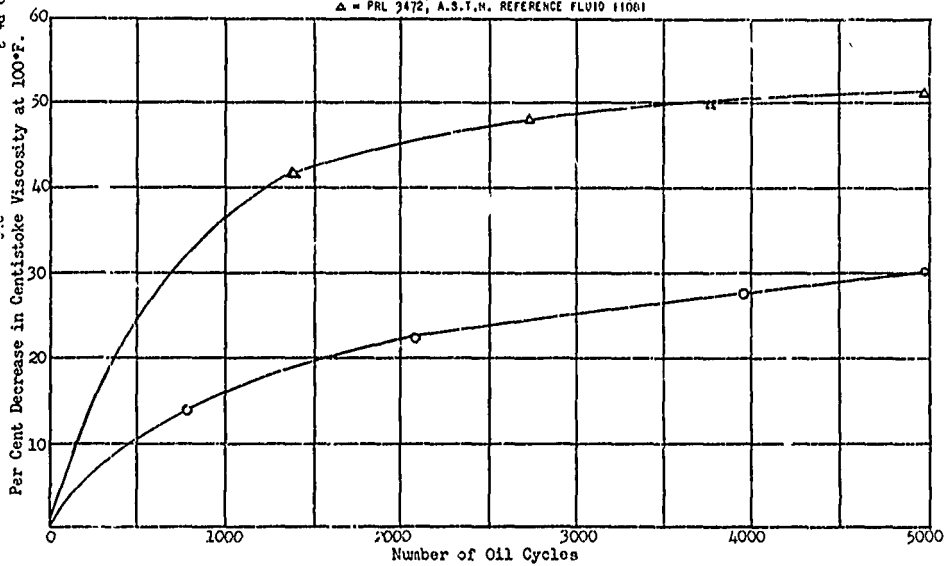


Figure 42

PERMANENT VISCOSITY DECREASE DUE TO SHEAR AT VARIOUS PRESSURE DROP

TESTS CONDUCTED IN HYCON PUMP TEST STAND AT 100°F. (PUMP INLET TEMPERATURE) USING AN ORIFICE AS THE PRESSURE LOADING DEVICE. FLUIDS CIRCULATED IN PUMP TEST STAND FOR 5000 CYCLES.

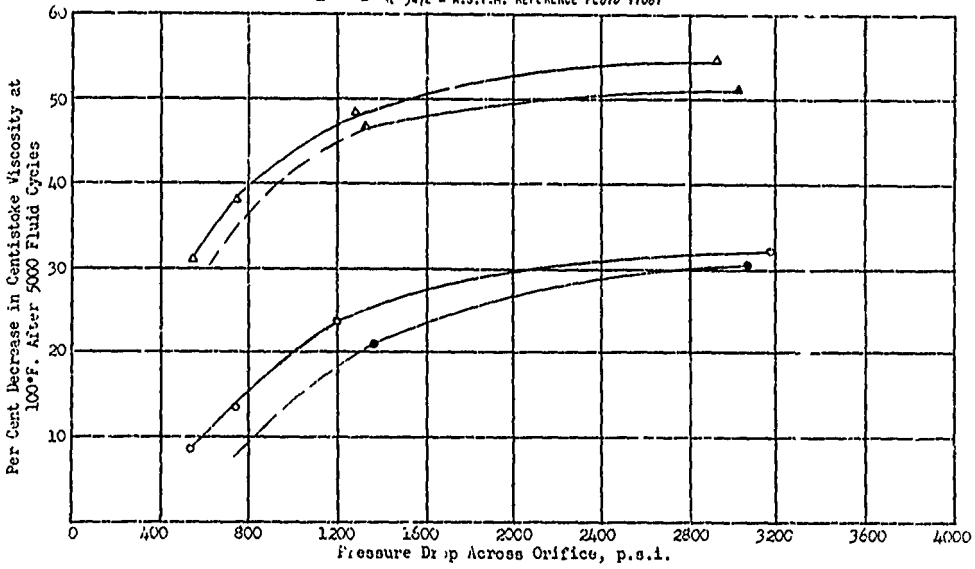
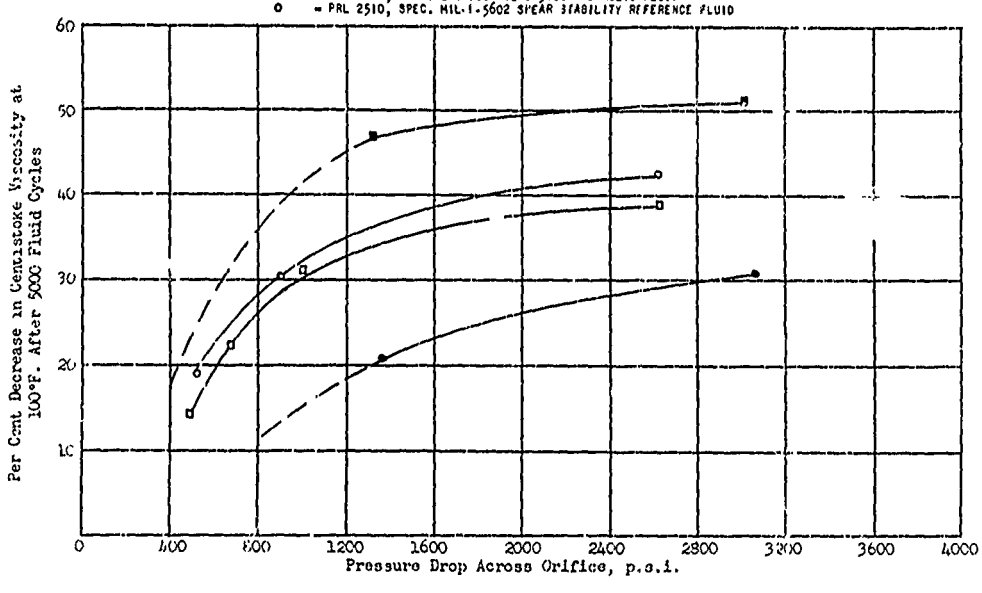


Figure 43

PERMANENT VISCOSITY DECREASE DUE TO SHEAR AT VARIOUS PRESSURE DROPS

ALL TESTS CONDUCTED IN HYCON PUMP TEST STAND AT 100°F. (PUMP INLET TEMPERATURE) USING AN ORIFICE AS THE PRESSURE LOADING DEVICE FLUIDS CIRCULATED IN PUMP TEST STAND FOR 5000 CYCLES.



has submitted five gallon samples of each of two non-Newtonian and one Newtonian oil to the NACA journal bearing lubrication project at Cornell University. These three fluids have been designated as PRL 3375, PRL 3374, and PRL 3373 and were formulated to match the properties of ASTM oils 101, 104 and 103, respectively. These ASTM oils are described in detail in report P.R.L.-9-49 mentioned previously in this section. The viscosity properties of these oils are summarized in Table 97.

Table 97

PROPERTIES OF NON-NEWTONIAN TEST FLUIDS FOR NACA JOURNAL BEARING TESTS

| PRL Designation | PRL 3375 | PRL 3374 | PRL 3373 |
|---|---|---|---|
| Polymer Conc., Wt.% | - | 5.1 | 11.1 |
| Polymer Mol. Wt. | - | 160 | 25 |
| Centistoke Viscosity | | | |
| at 210°F. | 5.24 | 9.14 | 8.39 |
| at 100°F. | 33.1 | 33.2 | 33.4 |
| ASTM Slope (210° to 100°F.) | 0.762 | 0.480 | 0.521 |
| Centistoke Visc. at 100°F. and | | | |
| 0 sec.$^{-1}$ shear | 33.1 | 33.2 | 33.4 |
| 100,000 sec.$^{-1}$ shear | 33.1 | 25.7 | 29.6 |
| 250,000 sec.$^{-1}$ shear | 33.1 | 22.7 | 27.2 |
| 500,000 sec.$^{-1}$ shear | 33.1 | 20.5 | 25.3 |
| 1,000,000 sec.$^{-1}$ shear | 33.1 | 18.3 | 23.4 |

These fluids have now been evaluated by the NACA project at Cornell University in a journal bearing tester. The evaluation includes friction studies and film thickness, or eccentricity ratio. Eccentricity ratio refers to the displacement of the journal from the center of the bearing by increasing the load or by using a lower viscosity lubricant. The used samples of PRL 3373, PRL 3374 and PRL 3375 have been returned to this Laboratory for tests to determine any significant property changes such as contamination or permanent viscosity decrease due to shear. The used samples have been evaluated and show essentially no signs of contamination, oxidative deterioration, or permanent viscosity decrease due to shear.

The test results reported by Cornell University are very interesting. It can be noted from the viscosity data on Table 97 that all three fluids are matched in viscosity at 100°F. The major difference between the fluids is the effective viscosity under high rates of shear. Test results are reported in Progress Report No. 9 (Revised) on Bearing Friction and Eccentricity Tests of Non-Newtonian Oil by R. B. DuBois, F. W. Ocvirk, and R. L. Wehe under NACA Contract NAw-6197. These results show that friction values are reduced as much as 40 per cent for PRL 3374 as compared with PRL 3375. Similarly, friction values for PRL 3373 are as much as 25 to 30 per cent lower than for PRL 3375. These results are



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in agreement with the effective viscosity values at high shear rates.

The study of film thickness in the bearing, or the eccentricity ratio, revealed that the eccentricity ratio is essentially the same within the limits of error for all three oils tested. Since film thickness is also a function of viscosity, these results are not predicted by effective viscosities at high rates of shear. These film thickness results appear to follow the low shear viscosity values. In other words, the use of a non Newtonian oil such as PRL 3374 appears to provide a substantial reduction in friction for no sacrifice in load carrying capacity over a Newtonian oil of the same viscosity value. This aspect of non-Newtonian oils deserves further consideration and study.

F. LOW TEMPERATURE VISCOSITY STANDARD. This Laboratory has distributed a four-ounce sample of PRL 2815 low temperature viscosity standard to each of the following organizations. PRL 2815 is calibrated as a standard for viscosity determinations at -40°F. and -65°F. The primary purpose of this standard is the establishment of a common temperature scale for viscosity determinations at these low temperatures.

Mr. L. Van Volkinburg
Dow-Corning Corporation
Midland, Michigan

Mr. E. L. Wood
Department of the Army, Springfield Armory
Springfield 1, Massachusetts

Dr. A. J. Barry
Research Department, Dow-Corning Corporation
Midland, Michigan

Dr. T. W. Mastin
Research Department, The Lubrizol Corporation
Cleveland 17, Ohio

Mr. H. P. Demerjian
Baker Castor Oil Company
35 Avenue "A"
Bayonne, New Jersey

Mr. W. D. Thomas (2 samples)
Southwest Research Institute
San Antonio 6, Texas

Deecy Products Co.
Cambridge, Massachusetts

Mr. W. W. LeRoy
Vickers Inc.
1400 Oakman Blvd.
Detroit 32, Mich.

Ford Motor Co.
Quality Laboratory
Production Offices
Gate 4, Rouge Plant
Dearborn, Mich.

G. SAMPLES DISTRIBUTED AT THE REQUEST OF WADC. The Wright Air Development Center (WADC) has requested that this Laboratory furnish the following materials to the organizations indicated.

A one-ounce sample of calcium cetyl phenate was sent to Dr. A. J. Barry, Research Department, Dow-Corning Corporation, Midland, Michigan. This is the material used as a metal deactivator in PRL 3209 type non-inflammable fluid.

A one-ounce sample of Hercoflex 600 (a pentaerythritol type ester) was sent to Mr. Robert Paige, Boeing Aircraft Company, Seattle, Washington.

A 200 ml. sample of tetralin has been sent to the Wright Air Development Center, Materials Laboratory, WCRTR-1, addressed to the attention of Capt. J. O'Brien.

One gallon each of fluids MLO 7008 and MLO 7009 has been furnished to the Wright Air Development Center (WADC). MLO 7008 is a PRL 3209 type non-inflammable fluid prepared without the polymer-thickening agent. MLO 7009 is the ethyldibromobenzene base stock used in the formulation of PRL 3209 non-inflammable fluid.

A two-gallon sample of MLO 7010 synthetic jet engine oil containing diisopropyl acid phosphite has been sent to the Wright Air Development Center for evaluation.

The following quantities of experimental jet engine oils were sent to Mr. A. Hundere, Southwest Research Institute, 8500 Culebra Road, San Antonio, Texas.

| | |
|---|---|
| 10 gal. | PRL 3161 |
| 2 gal. | GTO 16 |
| 2 gal. | GTO 17 |
| 2 gal. | PRL 3313 |

One gallon of an ethyldibromobenzene-base hydraulic fluid (PRL 3209) was sent to Capt. Bradley F. Bennett, Bureau of Ships, Navy Department, Washington 25, D. C.

A one-pint sample of each of two fluids suitable for inter-laboratory calibration of the Shell four-ball wear tester has been sent to Mr. D. H. Moreton, Douglas Aircraft Company, Santa Monica, California. These fluids are designated as PRL 3207 and PRL 3462. They represent a good non-additive lubricant and a lubricant with a good anti-wear additive, respectively. The compositions and properties of these fluids are given

in report PRL 5.8-Sep53.

H. DISTRIBUTION OF REPORTS. The following reports have been distributed to the organizations indicated during the period covered by this report. The distribution of these reports has been at the request of either the Materials Laboratory, Wright Air Development Center or the Chief of Bureau of Ordnance, Department of the Navy.

One copy of report PRL 106.8 entitled "Apparatus and Procedure for the Determination of Low-Temperature Viscosities" dated February 6, 1945 has been sent to each of the following organizations.

Mr. John Mathe
Celanese Product Development Laboratory
Summit, New Jersey

Mr. G. C. Vickery
Baker Castor Oil Company
40 Avenue "A"
Bayonne, New Jersey

Mr. W. D. Thomas
Southwest Research Institute
8500 Culebra Road
San Antonio, Texas

Emery Industries, Inc.
Control Laboratories
Cincinnati 2, Ohio
Attn: Mr. R. H. Dreyer

One copy of report P.R.L.-4-52 entitled "Wear and Lubrication Characteristics of Some Mineral Oil and Synthetic Lubricants" has been loaned to Mr. C. W. Sauter, Western Gear Works, Lynwood, California. It was indicated that this report was to be used in connection with a Wright Air Development Center contract. Report P.R.L.-4-52 is a thesis prepared by Dr. E. E. Klaus apart from the work carried out under Contract AF33(038)18193.

Four copies of report P.R.L.-2-53 entitled "The Interrelation of Lubricants and Metals of Construction" and dated February 27, 1953 have been sent to the Library of Congress, ASTIA Reference Center, Washington 25, D. C.

One copy of report PRL 3.46-Apr49 entitled "Viscous Damping Fluids" and dated April 14, 1949 has been sent to the Bell Aircraft Corporation, Buffalo 5, New York.

One copy of report P.R.L.-3-53 entitled "Liquid Phase Oxidation of Dibasic Acid Esters" has been sent to each of the following Service organizations. Report P.R.L.-3-53 is a thesis prepared by Mr. N. E. Shirk apart from work carried out under Contract AF33(038)18193.

Mr. J. C. Mosteller
Wright Air Development Center
Materials Laboratory, WCRTR-3
Wright-Patterson Air Force Base, Ohio

Chief of Bureau of Aeronautics
Department of the Navy
Equipment and Materials Branch
Engineering Division
Washington 25, D. C.

Chief of Bureau of Ordnance
Department of the Navy
Washington 25, D. C.

One copy of report PRL 6.3-Dec53 entitled "Some Properties of Spec. MIL-O-5606 Hydraulic Fluid at Elevated Temperatures" has been sent to Bendix Products Division, Bendix Aviation Corporation, South Bend 20, Ind.

PETROLEUM REFINING

LABORATORY

APPENDIX A
WADC TR 55-30 PT 3

REPORT

ON

# SOME PROPERTIES OF SPEC MIL-O-5606 HYDRAULIC FLUID AT ELEVATED TEMPERATURES

CONTRACT NO. AF33(038)18193

REPORT NO. PRL 6.3-DEC53

DATE: 30 DECEMBER 1953

THE PENNSYLVANIA STATE UNIVERSITY
*College of Chemistry and Physics*
STATE COLLEGE, PENNSYLVANIA

APPENDIX A
WADC TR 55-30 PT 3

PETROLEUM REFINING LABORATORY
MERRELL R. FENSKE, DIRECTOR

COLLEGE OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE UNIVERSITY
STATE COLLEGE, PENNSYLVANIA

REPORT TO

MATERIALS LABORATORY WCRTR3, ENGINEERING DIVISION
WRIGHT AIR DEVELOPMENT CENTER

ON

# SOME PROPERTIES OF SPEC. MIL-O-5606 HYDRAULIC FLUID AT ELEVATED TEMPERATURES

CONTRACT NO. AF33(038)18193

REPORT NO. PRL 6.3-DEC53

30 DECEMBER 1953

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## FOREWORD

This report has been prepared by the Petroleum Refining Laboratory of the College of Chemistry and Physics at the Pennsylvania State University under Air Force Contract AF33(038)18193. Mr. J. C. Mosteller, Materials Laboratory, WCRTR3, Engineering Division, Wright Air Development Center is the Acting Project Engineer for this work.

Research work for the Air Force on Fluids, Lubricants, Fuels and Re ted Materials by this Laboratory has been a continuous project since March 1941. The work from March 1941 to July 1945 was conducte under National Defense Research Committee Contract OEMsr408. Work from July 1945 to October 1951 was conducted under Navy Contract NOrd 7958(B).

# SOME PROPERTIES OF SPEC. MIL-O-5606 HYDRAULIC FLUID AT ELEVATED TEMPERATURES

Summary. At the request of the Materials Laboratory, WCRTR-3 of the Wright Air Development Center, this Laboratory has assayed in the laboratory some of the more important properties of Spec. MIL-O-5606 hydraulic fluids at elevated temperatures. These properties are summarized as a function of temperature on Table 1

Volatility is an important property in high temperature applications of Spec. MIL-O-5606 fluids. Three characteristics in hydraulic system applications, directly related to the fluid's volatility, are: (1) vapor pressure, (2) inflammability, and (3) residual film formation due to evaporation. The upper limit of usefulness in a hydraulic system pressurized to one atmosphere would be of the order of 500°F., which is the initial boiling point of a typical Spec. MIL-O-5606 fluid at one atmosphere pressure. The flash point of a typical Spec. MIL-O-5606 fluid is about 220°F., which is approximately equal to the boiling point of the fluid at 10 mm. Hg. The spontaneous ignition temperature of the fluid is of the order of 500°F. Problems of tacky films arising from the extensive evaporation of exposed thin films of Spec. MIL-O-5606 fluids are related both to time and temperature. Undesirable tacky films appear after about 4 to 6 hours exposure at 200°F. without fluid scavenging. Control of tacky films is primarily a function of system design.

The viscosity-temperature characteristics of Spec. MIL-O-5606 fluid are good. Pump tests in commercial Vickers 3,000 p.s.i. piston pumps indicate that the viscosity level is adequate for successful operation over the entire range of -65° to +500°F. Lubricity studies show that the fluid has adequate lubricating properties for hydraulic pumps over this same temperature range. Volatility is probably the limiting factor in high temperature pump operation. It appears that fluid volatility may increase wear in pumps operating at temperatures above 400°F.

The thermal stability of typical Spec. MIL-O-5606 hydraulic fluids is excellent up to 500°F. In the temperature range of 450° to 500°F. there is some viscosity decrease due to thermal depolymerization of the polymeric thickener. There is, however, no evidence of volatile product formation, or of thermal decomposition products which are deleterious to the fluid's use or to overall fluid stability.

The oxidation behavior and stability are among the most important items in appraising the high temperature characteristics of Spec. MIL-O-5606 hydraulic fluid. The decrease with temperature in the fluid's induction period, or stable life during oxidation, is illustrated in Table 1. At elevated temperatures where the stable life of the fluid is very short and at lower temperatures when the stable life is exceeded, the oxidative deterioration becomes a function of the amount

of oxygen or air in contact with the fluid and on the intimacy of this air-oil contact. The data indicate that a Spec. MIL-O-5606 fluid can tolerate the assimilation of moderate quantities of oxygen at elevated temperatures without excessive deterioration of the fluid or troublesome corrosion of metals. It may be desirable, therefore, to pressurize with nitrogen, or seal with a diaphragm, hydraulic systems designed to have a bulk oil temperature in excess of about 200°F.

Oil change intervals in a closed system of this type could be scheduled to approximate the stable life of the fluid plus the time of operation during which the air leakage or entrainment into the fluid is estimated to be 100 to 200 cubic feet (at 32°F. and 760 mm. Hg) per five gallons of oil. It is believed that the assimilation by the fluid of the oxygen in 600 to 1,000 cubic feet of air per five gallons of fluid can be tolerated without causing the average hydraulic system to become inoperative from the standpoint of oxidative deterioration.

In accelerated laboratory tests copper, copper alloys, and silver cause a reduction of about 50 per cent in the stable life of a typical Spec. MIL-O-5606 fluid at 300°F. These metals are the most effective of those evaluated in this study in causing a decrease in the fluid's stable life. The fluid's stable life is the time interval (hours) during which oxygen is not significantly absorbed, or assimilated, by the fluid even though there is available ample oxygen and oxygen-oil contact. It is believed that one of the metals evaluated in this study should be excluded from aircraft hydraulic systems using Spec. MIL-O-5606 fluid solely on the basis of their catalytic effects in accelerating oxidation.

A high quality Spec. MIL-O-5606 hydraulic fluid does not corrode metals normally used in hydraulic systems. It has been established that a typical Spec. MIL-O-5606 fluid in a state of incipient oxidation does not corrode copper, aluminum, and steel at 500°F. On the basis of low temperature (250°F.) tests it is suggested that cadmium plate be eliminated from hydraulic systems. High temperature oxidation and corrosion tests indicate that it would be desirable to eliminate magnesium from hydraulic systems where temperatures of 250°F. or greater exist or are predicted, or where the fluid will be used to the point of incipient oxidation. This applies primarily to closed hydraulic systems where oxidized products including water will be in intimate contact with the metals of construction.

A number of miscellaneous physical properties have been included in this report primarily for use in design and engineering calculations. These properties include: specific heat, thermal conductivity, bulk modulus of elasticity as a function of temperature, density as a function of temperature, cubical coefficient of expansion, and viscosity as a function of temperature and pressure.

In general, these studies show that a high quality Spec. MIL-O-5606 fluid exhibits good overall stability at temperatures up to

500°F. under a variety of conditions. It should be emphasized that the quality of the Spec. MIL-O-5606 fluid used in this study in terms of oxidation and corrosion stability, in particular, is better by at least a factor of two than the minimum quality fluid guaranteed by the Specification. The formulation of more specific limitations will require the testing of actual hydraulic system components and current Spec. MIL-O-5606 fluids.

Table 1

SUMMARY OF THE PROPERTIES OF A TYPICAL SPEC. MIL-O-5606 FLUID

| TEMPERATURE, °F. | -65 | -40 | 0 | 100 | 200 | 300 | 400 | 500 |
|---|---|---|---|---|---|---|---|---|
| KINEMATIC VISCOSITY, CS. | 2,000 | 487 | 103 | 14.2 | 5.3 | 2.9 | 1.9 | 1.4 |
| VAPOR PRESSURE, MM. HG | - | - | <0.01 | 0.1 | 3.0 | 38 | 210 | 600 |
| TACKINESS PROPERTIES OF EVAPORATED FLUID FILM AFTER 20 HOURS | O.K. | O.K. | O.K. | O.K. | BORDERLINE | POOR | POOR | POOR |
| THERMAL STABILITY | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. | FAIR |
| OXIDATION AND CORROSION STABLE LIFE (SPEC. MIL-O-5606 CONDITIONS), HOURS | - | - | - | >10,000 | 3,000 | 60 | <2(3) | <1(3) |
| LUBRICITY IN SHELL FOUR-BALL WEAR TESTER | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. | - |
| ESTIMATED LUBRICITY FOR PISTON TYPE HYDRAULIC PUMP(1) | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. | - |
| ESTIMATED PUMP DELIVERY (% OF RATED CAPACITY) FOR PISTON TYPE PUMP(1) | 100 | 100 | 100 | 100 | 100 | 98 | 96 | 93 |
| ESTIMATED PUMP PERFORMANCE BASED ON FLUID VOLATILITY(2) | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. | POOR |
| CORROSION PROPERTIES WITHIN THE OXIDATION STABLE LIFE OF THE SPEC. MIL-O-5606 FLUID FOR: | | | | | | | | |
| STEEL | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. |
| ALUMINUM | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. |
| COPPER | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. | O.K. |
| BRONZE | - | - | - | - | O.K. | O.K. | - | - |
| MAGNESIUM | O.K. | O.K. | O.K. | O.K. | O.K. | BORDERLINE | POOR | POOR |
| SILVER-PLATED STEEL | - | - | - | - | O.K. | O.K. | - | - |
| LEAD | - | - | - | - | O.K. | O.K. | - | - |
| LEAD-INDIUM COATED SILVER-PLATED STEEL | - | - | - | - | O.K. | O.K. | - | - |
| DENSITY, GMS./CC. | 0.89 | 0.88 | 0.86 | 0.83 | 0.79 | 0.75 | 0.71 | - |
| BULK MODULUS OF ELASTICITY, P.S.I. X $10^{-5}$ (AVERAGE FOR 0 TO 10,000 P.S.I.) | 3.6 | 3.4 | 3.2 | 2.7 | 2.2 | 1.7 | 1.2 | 0.7 |
| SPECIFIC HEAT, B.T.U./LB./°F. | - | - | 0.45 | 0.50 | 0.55 | 0.60 | 0.65 | - |
| THERMAL CONDUCTIVITY, B.T.U./SQ. FT./HR./°F./FT. | - | - | 0.081 | 0.079 | 0.076 | 0.074 | 0.071 | - |

(1) THESE DATA ARE BASED ON STUDIES IN A VICKERS MODEL PF-17-3911-10ZEL PISTON PUMP MADE WITH MINERAL OILS PREPARED TO EXHIBIT THE SAME VISCOSITY AND LUBRICITY LEVEL AT 100° TO 200°F. THAT IS CHARACTERISTIC OF SPEC. MIL-O-5606 IN THE 300° TO 500°F. TEMPERATURE RANGE.

(2) THESE DATA ARE BASED ON WEAR STUDIES CONDUCTED IN PISTON AND GEAR TYPE HYDRAULIC PUMPS USING LARGE CONCENTRATIONS OF VOLATILE HYDROCARBONS IN SPEC. MIL-O-5606 TYPE FLUIDS.

(3) THESE VALUES REFER TO THE INDUCTION PERIOD OR STABLE LIFE. THE ACTUAL USEFUL LIFE OF THE FLUID AT THIS TEMPERATURE IS A DIRECT FUNCTION OF THE RATE OF OXYGEN OR AIR LEAKAGE INTO THE FLUID OR HYDRAULIC SYSTEM. AS INDICATED IN TABLE 12 OF THIS REPORT, USEFUL LIVES OF 20 TO 40 HOURS CAN BE ACHIEVED IN THE TEMPERATURE RANGE OF 400° TO 500°F. AT MODERATE RATES OF AIR CIRCULATION OR AVAILABILITY.

# SOME PROPERTIES OF SPEC. MIL-O-5606 HYDRAULIC FLUID AT ELEVATED TEMPERATURES

Introduction. The Wright Air Development Center requested that this Laboratory evaluate the properties of Spec. MIL-O-5606 hydraulic fluid at elevated temperatures. Spec. MIL-O-5606 hydraulic fluid has been used over the past 10 years as the aircraft hydraulic fluid by the U.S. Air Force and the British and Canadian Air Forces. Indications are that Spec. MIL-O-5606 hydrocarbon-base hydraulic fluids have performed satisfactorily in a wide variety of uses over this period. The bulk of the data on the behavior of this hydraulic fluid has been obtained from use in conventional World War II piston engine aircraft.

Current developments in aircraft place emphasis on higher speeds and, therefore, higher ambient temperatures which result in higher hydraulic system temperatures. The hydraulic system temperature problem is intensified in some cases by the proximity of hydraulic lines to the combustion chamber and to the exhaust of turbine engines. With current emphasis on higher hydraulic system temperatures, a study of some of the practical limitations, temperature-wise, of Spec. MIL-O-5606 hydraulic fluid is of particular interest. Many of the data pertinent to a high temperature study of Spec. MIL-O-5606 hydraulic fluid had been obtained and discussed in reports contracts prior to Contract AF33(038)18193. These data along with current data are presented in this report.

Spec. MIL-O-5606, and earlier editions of this same specification (Spec. AN-O-366 and Spec. AN-VV-O-366b), are used interchangeably in this report except in discussions on wear and lubrication. Spec. MIL-O-5606 and Spec. AN-O-366 fluids contain tricresyl phosphate as the anti-wear additive while Spec. AN-VV-O-366b fluid does not contain a lubricity additive. For this reason any lubrication studies discussed are for the fluid containing the tricresyl phosphate.

Volatility. The volatility of Spec. MIL-O-5606 hydraulic fluid is one of the important properties determining its high temperature behavior. Three items in hydraulic system applications, related directly to volatility, are (1) vapor pressure, (2) inflammability, and (3) residual film formation due to evaporation.

A typical Spec. MIL-O-5606 hydraulic fluid is a blend comprising a mineral oil base stock, a less volatile mineral oil as the anti-tack component, a polymeric additive (viscosity index improver), an oxidation and corrosion inhibitor, and an anti-wear or lubricity additive. The mineral oil base stock constitutes the major portion of the hydraulic fluid. This mineral oil base stock is also the most volatile component of the fluid. Accordingly, it determines the general volatility level of the fluid. The Spec. MIL-O-5606 requirements place considerable restrictions on the volatility of the mineral oil base stock.

Thus, the volatility characteristics of a typical commercially-prepared fluid meeting the specification can be considered to be of the same order of magnitude for any commercial Spec. MIL-O-5606 fluid.

The vapor pressure-temperature relationship for a typical Spec. MIL-O-5606 type fluid is shown on Table 2 and Figure 1. These data show that this fluid has a vapor pressure of approximately 3 mm. Hg at 200°F. and 38 mm. Hg at 300°F. Expressing these vapor pressure data in another way, the fluid would begin to boil at about 500°F. and atmospheric pressure at sea level. Boiling would begin in an unpressurized system at 375°F. and at an altitude of 40,000 ft. (140 mm. Hg absolute pressure). Currently, pressurized hydraulic systems are being considered. On the basis of vapor pressure, a maximum temperature of about 500°F. could be tolerated in a hydraulic system pressured to 760 mm. The data shown on Table 1 indicate about a 20°F. spread between the initial boiling point and the 20 per cent distillation point. This is typical of the narrow boiling fractions commonly used as a base stock for Spec. MIL-O-5606 hydraulic fluid. Values of vapor pressure, or boiling point, intermediate to those shown on Table 1 can be obtained from the graph of the logarithm of absolute pressure versus the logarithm of the temperature as shown on Figure 1.

The volatility of mineral oils and most synthetic lubricants is closely related to inflammability properties as revealed by the open cup flash and fire points. The Spec. MIL-O-5606 limit on flash point is 200°F. The flash point for the sample used to obtain the vapor pressure data shown on Table 2 is 230°F.

The relationship between flash point, fire point, and vapor pressure is shown on Figure 2. These data include narrow boiling mineral oil fractions and some dibasic acid esters. There is relatively good correlation between the Cleveland open cup fire point and the initial Cottrell boiling point, or the 10 per cent distillation point when converted to 10 mm. Hg absolute pressure. The fire point is slightly lower than the 10 mm. Hg boiling point for values above 400°F. The correlation is good in the 200° to 400°F. region which includes the volatility range of Spec. MIL-O-5606 hydraulic fluid. The data on Figure 2 also show, for these narrow boiling mineral oil fractions and esters, that the spread between the open cup flash point and the fire point is about 10°F. per 100°F.

<u>Thin Film Evaporation</u>. Evaporation of the base stock from thin films of Spec. MIL-O-5606 fluid results in concentrating the polymeric additive in the residual film. Excessive base stock evaporation gives a tacky or sticky film. A high boiling component is added to the bulk of the mineral oil base stock as an anti-tack component to control the properties of the films left after extensive evaporation. Problems in the hydraulic system due to excessive evaporation could exist in portions of the system which are wetted with oil during operation, but which are not filled with oil during shut down periods and are open, or have access to substantial amounts of circulating air. Severe film

Table 2

VAPOR PRESSURE - TEMPERATURE RELATIONSHIPS FOR SPECIFICATION AN-VV-O-366b HYDRAULIC FLUID

Test Fluid = PRL 1912 = Typical Commercially-Prepared Specification AN-VV-O-366b Fluid

INITIAL BOILING POINT data obtained on new sample of Specification AN-VV-O-366b Fluid

20% DISTILLATION POINT data obtained on sample of Specification AN-VV-O-366b fluid after distilling off 20 volume per cent of the fluid.

| ABSOLUTE PRESSURE, mm. Hg | TEMPERATURE, °F. Initial Boiling Point | 20% Distillation Point |
|---|---|---|
| 700 | 494 | - |
| 600 | 481 | 499 |
| 500 | 466 | 484 |
| 400 | 448 | 465 |
| 300 | 426 | 442 |
| 200 | 397 | 414 |
| 100 | 353 | 372 |
| 50 | 315 | 336 |
| 10 | 246 | 273 |
| 1 | - | 213 |

| TEMPERATURE, °F. | ABSOLUTE PRESSURE, mm. Hg Initial Boiling Point | 20% Distillation Point |
|---|---|---|
| 475 | 558 | 450 |
| 450 | 405 | 330 |
| 425 | 297 | 237 |
| 400 | 210 | 162 |
| 375 | 146 | 107 |
| 350 | 97.5 | 67.0 |
| 325 | 63.0 | 40.0 |
| 300 | 38.2 | 21.5 |
| 275 | 21.9 | 11.9 |
| 250 | 11.3 | 4.6 |
| 225 | 5.3 | 1.7 |
| 200 | 3.0 | - |

Figure 1

VAPOR PRESSURE-TEMPERATURE RELATIONSHIPS FOR SPEC. AN-VV-O-366b HYDRAULIC FLUID

TEST FLUID: PRL 1912 = TYPICAL COMMERCIALLY-PREPARED SPEC. MIL-O-5606 TYPE FLUID.

△ = INITIAL BOILING POINT DATA OBTAINED ON A NEW SAMPLE.
○ = 20% DISTILLATION POINT DATA OBTAINED ON SAMPLE AFTER DISTILLING OFF 20 VOLUME PER CENT OF THE FLUID.

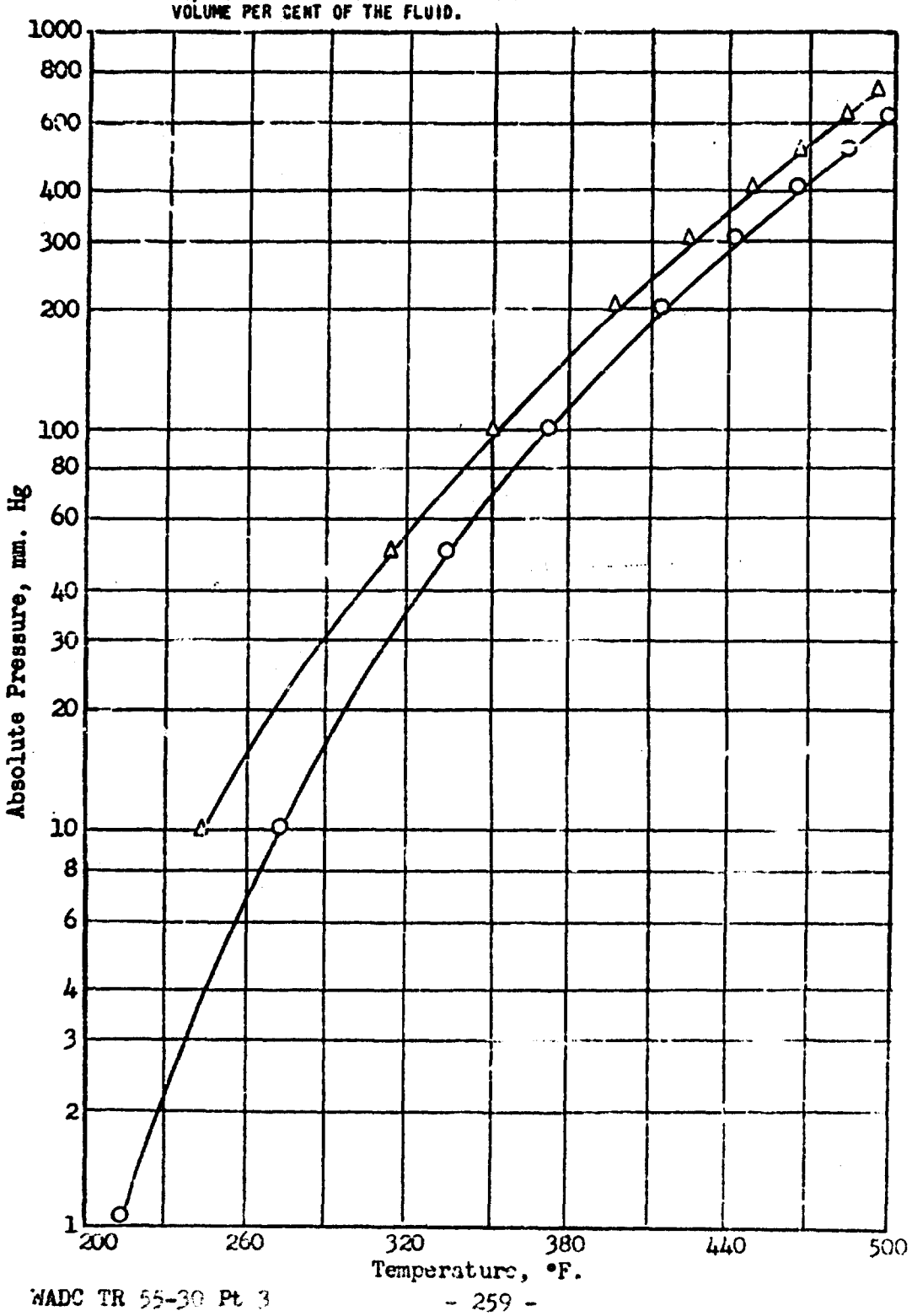
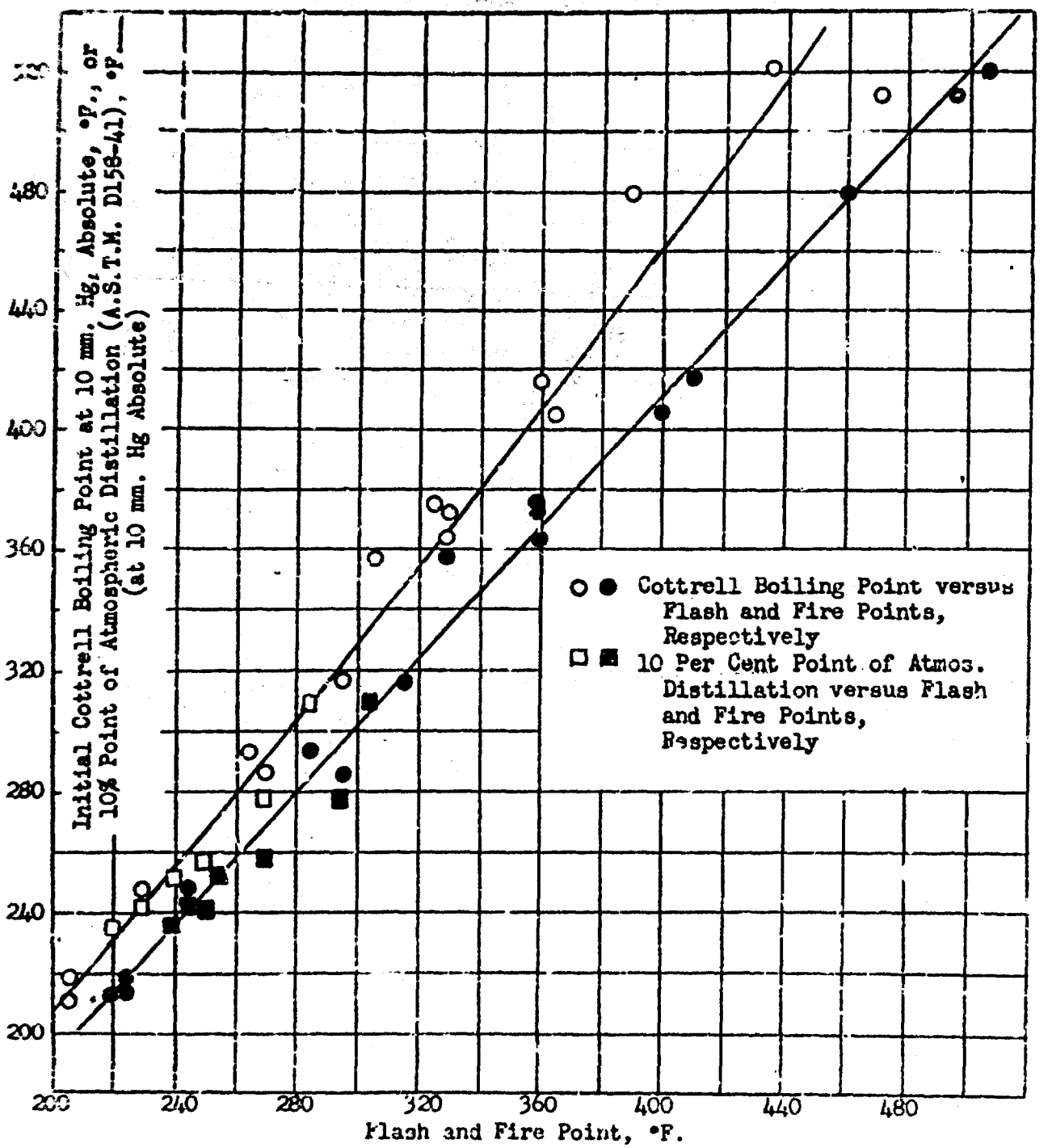


Figure 2

CORRELATION OF COTTRELL BOILING POINT, FLASH AND FIRE POINTS, AND DISTILLATION TEMPERATURE OF VARIOUS LIQUIDS



tackiness in these portions of a hydraulic system could lead to malfunctioning of close clearance parts such as valves. This is strictly an evaporation phenomenon, and if the system is closed, or otherwise arranged so that evaporation is minimized, then these problems of thin film tackiness do not arise.

This Laboratory developed a quantitative measure of evaporation and tackiness of thin films of hydraulic fluid. This technique has been applied to both Spec MIL-O-5606 and Spec. 51-F-21 (Navy) hydraulic fluids. Two distinct operations are involved in the evaporation test. These techniques are described briefly in the following paragraphs. A more complete description of these tests is given in Formal Report No. 11 to the National Defense Research Committee dated March 1, 1946, pages 41 to 67.

The first portion of the test comprises evaporating a thin film. A one millimeter thick fluid film is evaporated for 80 hours in a flat steel cup at an oil film temperature of 190°F. The evaporation cup rests on the bottom of a glass beaker which is immersed in a constant temperature oil bath. Dry air at the rate of 5 liters per hour is passed over the surface of the oil film. At regular intervals the steel cups are removed from the bath and weighed on an analytical balance. The weight per cent oil evaporated can be determined from the weight change. The evaporation characteristics of each oil can then be represented by a curve of total weight per cent evaporation versus time.

An 80 hour test period is employed as a reference point. At the end of this period most of the more volatile components of the base stock of a typical Spec. MIL-O-5606 fluid have evaporated, and the rate of evaporation has reached a slow or negligible rate. This appears to be a desirable point at which to compare weight per cent evaporated and film tackiness.

The second portion of the evaporation test comprises a simple vacuum distillation of a portion of test fluid. The vacuum distillation is carried to the same value of weight per cent distilled as the value of weight per cent evaporation noted in the first portion of the test. The temperature of the vacuum distillation is kept below 400°F. to prevent any viscosity changes due to thermal decomposition or cracking. The properties of the residue from the distillation are then considered to represent or typify the residue from the 80 hour evaporation test. The 100°F. viscosity of the distillation residue is determined. This viscosity is considered to be approximately equal to the viscosity of the oil film after 80 hours' evaporation in the steel cup. It is believed that viscosity is the property that relates most closely to film tackiness.

A complete discussion of the above test techniques for measuring tackiness on a quantitative basis is in Report PRL 3.4-Sep45 entitled "PREPARATION OF SPECIFICATION O.S. 2943 HYDRAULIC FLUIDS WITH

IMPROVED TACKINESS CHARACTERISTICS" and dated September 27, 1945. Report PRL 106.11, June 1945 entitled "SPECIFICATION AN-VV-O-366b HYDRAULIC FLUIDS WITH IMPROVED TACKINESS CHARACTERISTICS" describes the improvements that can be made in the tackiness, or residual film viscosity, by using more effective anti-tack components of the dibasic acid ester type. The improvements discussed in these previous reports have been achieved without altering the overall specification limits on fluid properties with the possible exception of slight increases in rubber swelling.

Evaporation characteristics for typical Spec. MIL-O-5606 base stock components are shown on Figure 3. These data clearly indicate that the thin film evaporation rates at temperatures of 190°F. and higher are rapid for the bulk base stock (Winkler base oil) and still appreciable for the anti-tack component (Voltesso 36) of a good quality Spec. MIL-O-5606 fluid. Evaporation data for a typical dibasic acid ester (di-2-ethylhexyl sebacate) in the same viscosity grade as the mineral oil anti-tack component (Voltesso 36) are shown as a basis of comparison.

Evaporation data for four commercial Spec. AN-VV-O-366b fluids are shown on Figure 4. Composition, evaporation, and film viscosity data for the fluids shown on Figure 4 are tabulated on Table 3. The film viscosity illustrates the relative tackiness of the residual films after evaporation much more effectively than data showing simply weight per cent evaporation. These data indicate that there was considerable variation in the evaporation and tackiness characteristics of commercial Spec. AN-VV-O-366b hydraulic fluids. These fluids were formulated in 1944. It is of interest to note, however, that the requirements on evaporation and tackiness in the current Spec. MIL-O-5606 are the same as those in Spec. AN-VV-O-366b. A range in film viscosity similar to that illustrated on Table 3 would be anticipated from current commercial Spec. MIL-O-5606 fluids.

As hydraulic system temperatures increase, it may be desirable to consider placing more restrictive limits on evaporation and tackiness. Current limits in the specification are based on a touch test.

<u>Viscosity-Temperature Characteristics.</u> A complete viscosity-temperature curve for a typical Spec. MIL-O-5606 hydraulic fluid (PRL 2883) for the range of -65°F. to +300°F. has been experimentally determined and is shown in Figure 5. PRL 2883 is a typical commercial Spec. MIL-O-5606 hydraulic fluid prepared by the Standard Oil Company of New Jersey. The fluid has a viscosity of 2.98 centistokes at 298°F. and 2,000 centistokes at -65°F. Mineral oils, in general, appear as straight lines on the ASTM viscosity-temperature chart. However, fluids of the Spec. MIL-O-5606 type exhibit a slight curvature at temperatures below about 0°F. which leads to higher values than predicted from a straight line extrapolation in this low temperature region. The high temperature viscosity values have been predicted to 450°F. by a straight line extrapolation from the 210° and 298°F. measured values.

Figure 3
EVAPORATION CHARACTERISTICS OF SPEC. MIL-O-5606 TYPE COMPOSITIONS AT A TEMPERATURE OF 190°F. AND AN INITIAL FILM THICKNESS OF 1.00 MM.

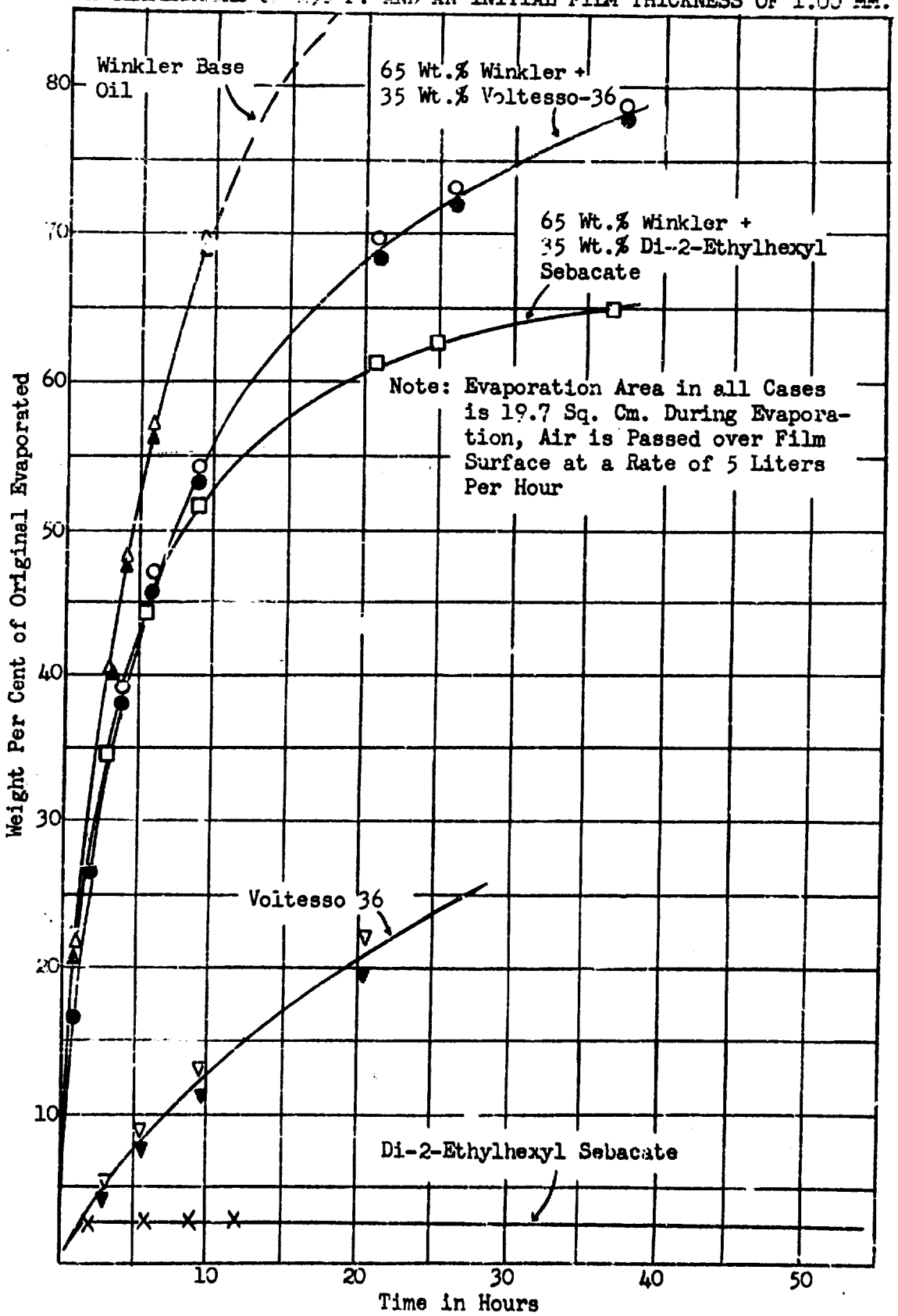


Figure 4

THIN FILM EVAPORATION CHARACTERISTICS OF SEVERAL SPECIFICATION AN-VV-O-366b FLUIDS FROM VARIOUS COMMERCIAL SOURCES

ALL TESTS CARRIED OUT AT AN INITIAL FILM THICKNESS OF 1.0 MM. AND AN AREA OF 19.7 SQUARE CM. THE OIL IS MAINTAINED AT A TEMPERATURE OF 190 ± 1°F., AND DURING EVAPORATION DRY AIR IS PASSED OVER THE FILM AT A RATE OF APPROXIMATELY 5 LITERS PER HOUR.

VISCOSITY AND EVAPORATION PROPERTIES ARE SHOWN ON TABLE 3.

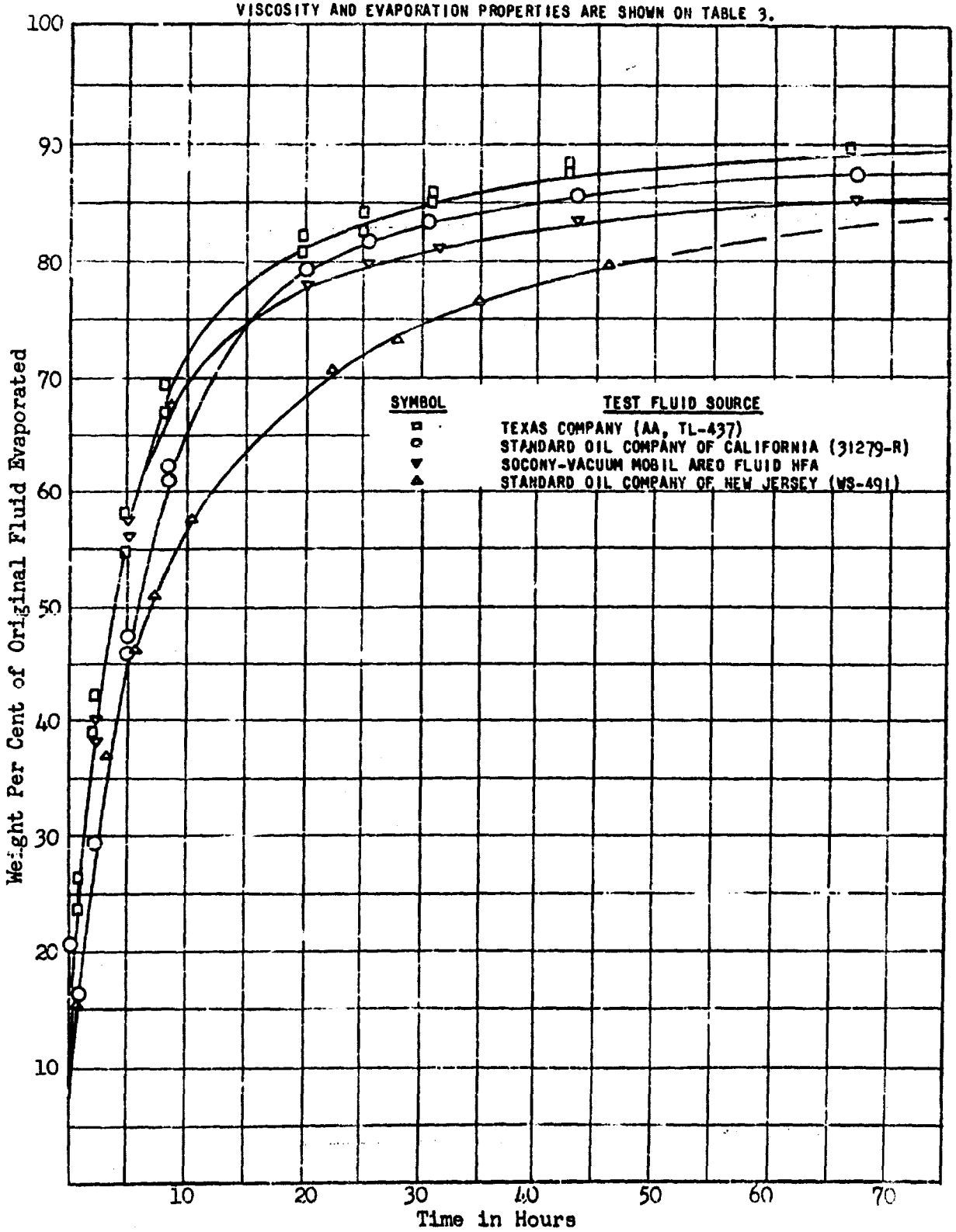


Table 3

TACKINESS EVALUATION OF SEVERAL IMPROVED AND COMMERCIAL AN-VV-O-366b FLUIDS

ALL TESTS CARRIED OUT AT AN INITIAL FILM THICKNESS OF 1.00 MM. AND AN AREA OF 19.7 SQUARE CM. THE OIL IS MAINTAINED AT A TEMPERATURE OF 190 ± 1°F., AND DURING EVAPORATION DRY AIR IS PASSED OVER THE OIL FILM AT A RATE OF APPROXIMATELY 5 LITERS PER HOUR.

| PRL NO. | - - - COMPOSITION OF FLUID, WT.% - - - ACRYLOID 858 | VOLTESSO 36 | WINKLER | CENTISTOKE VISCOSITY +130°F. | -40°F. | FILM PROPERTIES AFTER EVAPORATION OF A 1 MM. FILM AT 190 ± 1°F. FOR 80 HOURS WT.% EVAPORATED | POLYMER CONC., WT.%(2) | FILM VISCOSITY AT 100°F., CS. |
|---|---|---|---|---|---|---|---|---|
| | | | | PRESENT BASE STOCKS OR EQUIVALENT | | | | |
| (1) | 7.0 | 18.6 | 74.4 | 10.0 | 480 | 84.0 | 43.7 | 3621 |
| 2229 | 6.1 | 32.9 | 61.0 | 9.7 | 603 | 79.5 | 29.7 | 885 |
| | | | | COMMERCIAL SAMPLES FROM VARIOUS SOURCES | | | | |
| 2119 | SOCONY-VACUUM, MOBIL AERO FLUID HFA | | | 10.0 | 435 | 85.5 | 53.8 | 8025 |
| 1848 | STANDARD OIL COMPANY OF CAL. - NO. 31279-R | | | 10.2 | 469 | 87.5 | 62.4 | 48000 |
| 1928 | TEXAS COMPANY - NO. AA, TL-437 | | | 10.3 | 383 | 90.0 | 78.3 | 308000 |
| 1912 | STANDARD OIL COMPANY OF N. J. - WS-491 | | | 10.1 | 454 | 84.0 | 48.8 | 3800 |

(1) FLUID COMPOSITION TYPICAL OF SPECIFICATION AN-VV-O-366B FLUIDS NOW BEING PREPARED.
(2) FINAL POLYMER CONCENTRATION FOR COMMERCIAL SAMPLES CALCULATED BY ASSUMING EACH FLUID TO HAVE AN INITIAL POLYMER CONCENTRATION OF 7.8 WEIGHT PER CENT.

Improved evaporation characteristics are obtained, in general, at the expense of viscosity-temperature characteristics and low temperature viscosity. That is, the inclusion of higher concentrations of the same anti-tack component results in poorer viscosity-temperature characteristics. Blending curves showing the effects of increasing the anti-tack component concentration in typical Spec. MIL-O-5606 and Spec. 51-F-21 (Navy) hydraulic fluids are shown on Figure 6. These data are for Voltesso 36 as the anti-tack component. Voltesso 36 is a typical naphthenic mineral oil suitable as an anti-tack component.

It should be emphasized that the low temperature viscosity scales on Figure 6 are accurate for only the compositions having an 80:20 base stock ratio of Winkler base oil to anti-tack component. There are reasonable deviations in the viscosity-temperature characteristics for blends having other ratios of base oil to anti-tack component. This deviation is illustrated in Table 4.

Table 4

VISCOSITY CHARACTERISTICS OF FLUIDS CONTAINING VARIOUS CONCENTRATIONS OF ANTI-TACK COMPONENT

| Test Fluid Composition, Wt.% | | | Measured Visc., cs. at | | Predicted -40°F. Visc. from Figure 6, cs. |
|---|---|---|---|---|---|
| Light Base Oil | Anti-Tack (Voltesso 36) | Acryloid Polymer | 130°F. | -40°F. | |
| 92.0 | 0 | 8.0 | 10 | 330 | 460 |
| 83.2 | 9.3 | 7.5 | 10 | 395 | 490 |
| 74.6 | 18.6 | 6.8 | 10 | 500 | 500 |
| 65.6 | 28.1 | 6.3 | 10 | 605 | 590 |
| 55.5 | 38.7 | 5.8 | 10 | 750 | 640 |
| 47.4 | 47.4 | 5.2 | 10 | 970 | 690 |

Table 4 also illustrates the advantages in terms of the concentration of anti-tack component that can be gained by allowing a -40°F. viscosity of 750 centistokes instead of 500 centistokes.

High Temperature Pump Operation. Lubrication and volumetric efficiency are two important items in the operation of hydraulic pumps at high temperatures. Direct measurement of these properties is very difficult because of the lack of proven high temperature pumps. There have been indications that in the temperature range above 300°F. certain

Figure 5

VISCOSITY-TEMPERATURE CURVE FOR A TYPICAL SPEC. MIL-O-5606 HYDRAULIC FLUID FOR THE TEMPERATURE RANGE OF -65°F. TO +300°F.
Test Fluid = PRL 2883, a typical commercial Spec. MIL-O-5606 prepared by the Standard Oil Company of New Jersey

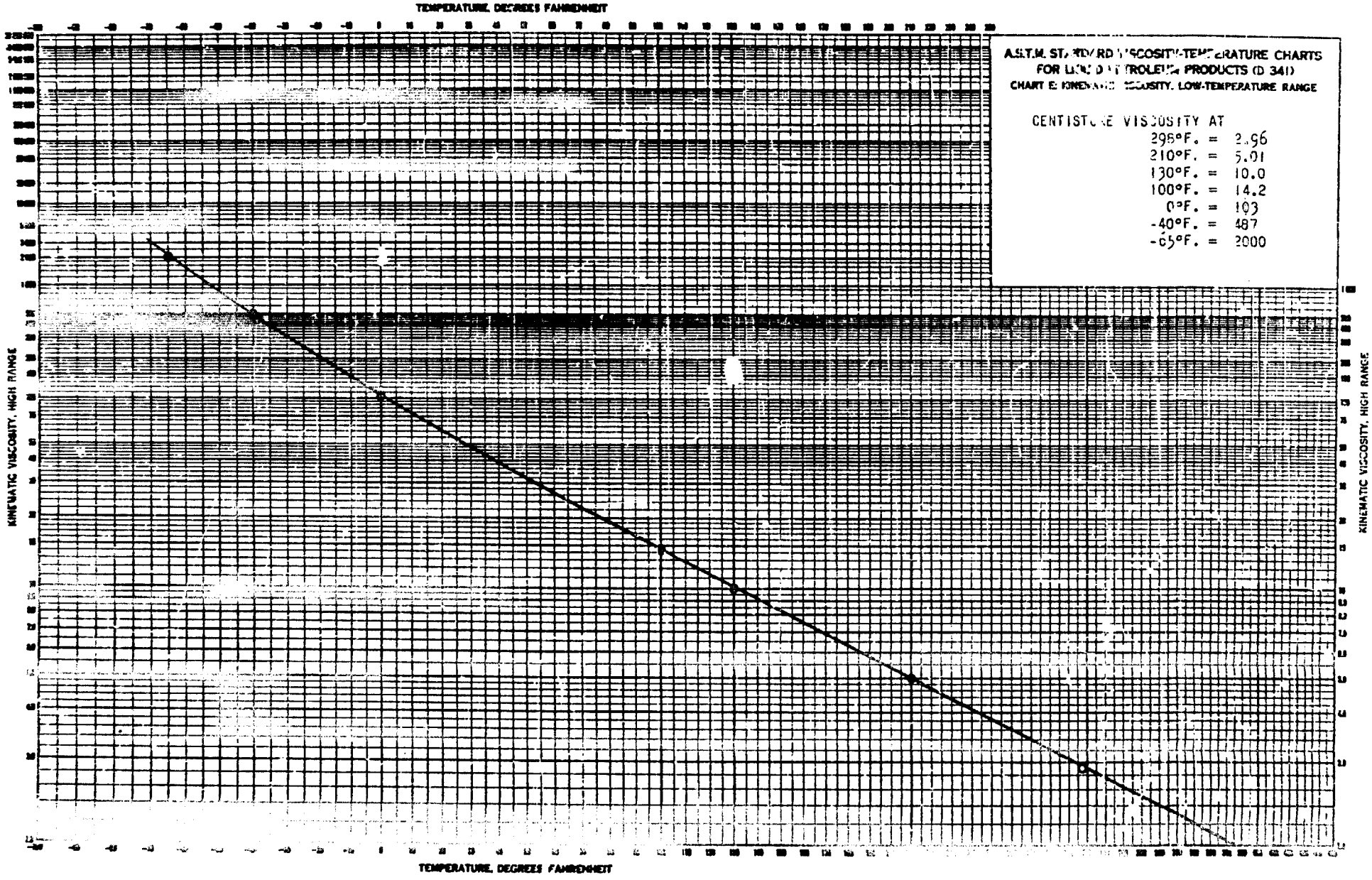
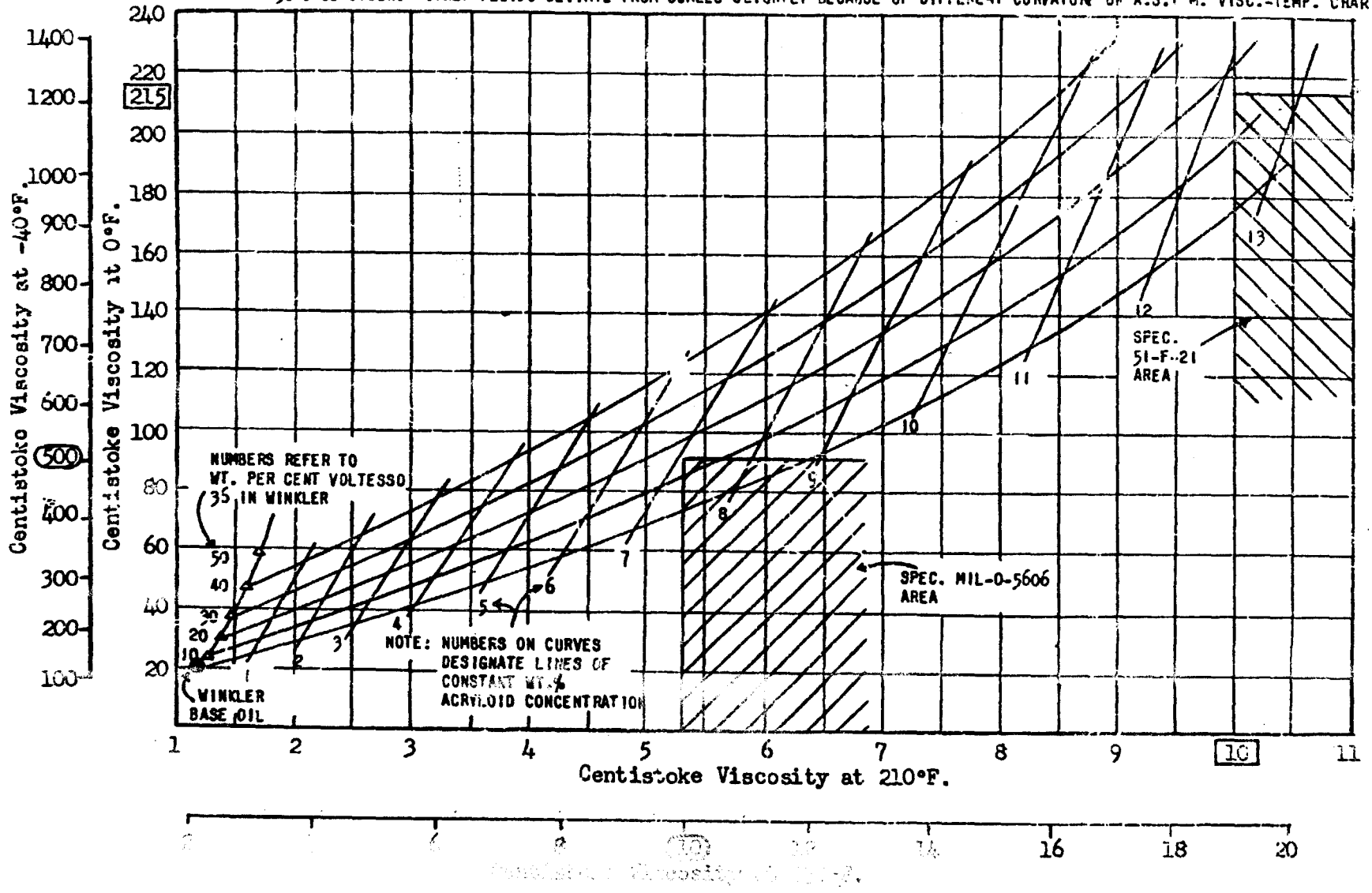


Figure 6

BLENDING CHARACTERISTICS OF ACRYLOID 858 IN WINKLER BASE OIL
EMPLOYING VOLTESSO 36 AS AN ANTI-TACK COMPONENT

NOTE: VISCOSITY SCALES FOR 130°F. AND -40°F. VALUES APPLY ONLY TO THOSE BLENDS CONTAINING AN 82:18 RATIO WINKLER-VOLTESSO 36 BASE STOCK. OTHER FLUIDS DEVIATE FROM SCALES SLIGHTLY BECAUSE OF DIFFERENT CURVATURE ON A.S.T.M. VISC.-TEMP. CHART.



mechanical problems with currently available pumps retard or prohibit fluid testing. Therefore, another approach to lubrication and volumetric efficiency tests has been used. Lubricity and viscosity of high temperature hydraulic fluids can be measured in laboratory equipment. These measured properties at the desired temperatures can then be built into experimental fluids in the range of 100° to 200°F. These experimental fluids can then be tested in a pump under lower temperature conditions where no mechanical problems are anticipated. Tests reported in previous Formal Reports to the National Defense Research Committee indicate that Spec. AN-VV-O-366b hydraulic fluids (without an anti-wear additive) operate satisfactorily in a Pesco 349 gear type pump at a viscosity level of 3.5 centistokes. The current study has emphasized viscosities below 3.5 centistokes at the test temperature.

The test fluids used in this study are mineral oil fractions containing an anti-wear additive and an oxidation inhibitor. The compositions of these test fluids, PRL 3414 and PRL 3415, are in Table 6. A comparison of the viscosities and volatilities of the mineral oil compositions and a typical commercial Spec. MIL-O-5606 hydraulic fluid are shown on Table 5.

Table 5

VISCOSITY AND VOLATILITY PROPERTIES OF SEVERAL MINERAL OIL COMPOSITIONS

| Test Fluid | C.O.C. Fire Point, °F. | Temperature, °F. at Which Indicated Viscosity Value is Obtained | | | |
|---|---|---|---|---|---|
| | | 3.0 cs. | 2.0 cs. | 1.5 cs. | 1.0 cs. |
| Commercial Spec. MIL-O-5606 | 235 | 295 | 390 | 485 | - |
| PRL 3414 | 230 | 107 | 145 | 178 | 240 |
| PRL 3415 | 235 | 72 | 109 | 142 | 203 |

The mineral oil fractions, PRL 3414 and PRL 3415, have viscosities of 1.0 to 3.0 centistokes in the range of 100° to 200°F. The commercial Spec. MIL-O-5606 hydraulic fluid has viscosities of 3.0 to 1.0 centistokes between 290°F. and the initial boiling point of the fluid (approx. 500°F.). The mineral oil fractions and the Spec. MIL-O-5606 fluid have about the same volatility properties.

The effect of bulk oil temperature on the wear characteristics measured by the Shell four-ball wear tester, of a typical Spec. 51-F-21 fluid and a Spec. 51-F-21 type hydraulic fluid without tricresyl phosphate, are shown on Table 9. This series of tests has not been conducted

with a Spec. MIL-O-5606 hydraulic fluid. It should be noted that the ingredients of Spec. 51-F-21 and Spec. MIL-O-5606 fluids are essentially the same except that the Spec. MIL-O-5606 does not contain a rust inhibitor. Spec. MIL-O-5606 also contains less polymeric additive and a lower anti-wear additive concentration. It is noteworthy that there is no appreciable increase in wear with temperature for either blend. The data for a Spec. MIL-O-5606 fluid would be expected to follow quite closely the data for the Spec. 51-F-21 fluid. Thus, the wear properties of Spec. MIL-O-5606 type fluids at temperatures up to at least 400°F. would be expected to parallel the wear properties of PRL 3414 and PRL 3415 in the 100° to 200°F. test region. Wear data for these test fluids at 167°F. in the Shell four-ball wear testing machine are shown on Table 6.

Table 6

WEAR CHARACTERISTICS OF SOME LOW VISCOSITY HYDRAULIC FLUIDS

Tests Conducted in the Shell Four-Ball Wear Tester.

Test Conditions Include: Test Time = 1 Hr.; Test Temp. = 75°C. (167°F.); Test Speed = 850 r.p.m.; Steel Balls = SKF Industries Grade #1 (0.5 inch Diameter) Steel Ball Bearings, PRL Batch #10.

| PRL No. | Test Fluid Composition in Wt.% | Visc. at 100°F. cs. | Average Wear Scar Diameter, mm. Steel-on-Steel Bearing Surfaces 1 kg. | 10 kg. | 40 kg. |
|---|---|---|---|---|---|
| 3115 | Commercial Spec. MIL-O-5606 Hydraulic Fluid | 14.2 | 0.16 | 0.22 | 0.62 |
| 3414 | 0.4 Paranox 441 + 5.0 Tricresyl Phosphate in XCT White Oil(1) | 3.27 | 0.14 | 0.20 | 0.44 |
| 3415 | 0.4 Paranox 441 + 5.0 Tricresyl Phosphate in Kendall C-13(2) | 2.18 | 0.15 | 0.48 | C.45 |

(1) Narrow boiling fraction of highly refined naphthenic gas oil obtained from the Standard Oil Company of New Jersey.
(2) Narrow boiling fraction of Pennsylvania gas oil obtained from the Kendall Refining Company.

The behavior of PRL 3414 and PRL 3415 in the Vickers piston pump is shown on Table 8. The pump operated satisfactorily throughout this series of tests. The pump used for this series of tests is a standard production model. A typical Spec. MIL-O-5606 fluid was used to establish a basis for volumetric efficiency at 100°F. The volumetric efficiency as a function of viscosity is shown on Table 7.

Table 7

VOLUMETRIC EFFICIENCY VERSUS FLUID VISCOSITY IN A VICKERS PF-17-3911-10ZEL PISTON PUMP

| Fluid Viscosity, Centistokes | Volumetric Delivery, g.p.m. | Per Cent of Maximum Delivery(1) |
|---|---|---|
| 14.2 | 3.10 | 100 |
| 3.3 | 3.04 | 98 |
| 2.2 | 3.00 | 97 |
| 1.4 | 2.89 | 93 |
| 1.1 | 2.76 | 89 |

(1) Volumetric delivery with typical Spec. MIL-O-5606 fluid at 100°F. test temperature is considered 100% of maximum delivery.

These data indicate that currently available standard hydraulic pumps can be operated successfully with relatively low viscosity fluids having good lubricity.

The limitation in high temperature operation with Spec. MIL-O-5606 fluid may stem from volatility. That is, the lubricity and viscosity properties of Spec MIL-O-5606 fluid are adequate up to the 400° to 500°F. temperature range. The initial atmospheric boiling point of a typical Spec. MIL-O-5606 is about 500°F. Some problems, such as high wear and cavitation, might be anticipated in the 400° to 500°F° region.

This Laboratory has conducted Pesco gear pump and wear studies with typical hydrocarbon-base fluids containing 30 weight per cent of a low boiling hydrocarbon such as hexane or isooctane. These studies are described in report PRL 3.35-May47. They were conducted at temperatures approximately 30° to 40°F. below the normal boiling point of the volatile constituent without difficulty. Moderately high wear was noted in both the Pesco gear pump and the Shell four-ball wear testing machine under these conditions. The determination of the actual high temperature limit of operability of Spec. MIL-O-5606 fluid, therefore, awaits the development of adequate high temperature pumps.

Thermal Stability. Thermal stability tests have been conducted at 500°F. on various components of, as well as a complete, Spec. MIL-O-5606 hydraulic fluid. These thermal stability data are in Table 10. Data for di-2-ethylhexyl sebacate are included for comparison.

The data shown on Table 10 indicate that the components of a Spec. MIL-O-5606 fluid as well as di-2-ethylhexyl sebacate are relatively stable for the 20 hour test at 500°F. under a nitrogen atmosphere. The Acryloid polymeric additive shows a tendency to decrease somewhat in viscosity. The viscosity decrease is not accompanied by indications of

Table 8

PUMP PERFORMANCE STUDIES WITH LOW VISCOSITY HYDRAULIC FLUIDS

Tests conducted with Vickers Model PF-17-3911-10ZEL piston pump on PRL #3 pump test stand

| Pump Test No. | 240 | 245 | 246 | 247 | 248 | 249 |
|---|---|---|---|---|---|---|
| Test Fluid | PRL 3115 | PRL 3414 | PRL 3415 | | | |
| Base Stock, Wt.% | Typical Spec. MIL-O-5606 Fluid | XCT White Oil(1) 94.6 | Kendall C-13(2) 94.6 | | | |
| Antioxidant, Wt.% | | Paranox 441 0.4 | Paranox 441 0.4 | | | |
| Anti-Wear Additive, Wt.% | | Tricresyl Phosphate 5.0 | Tricresyl Phosphate 5.0 | | | |
| Viscosity at 100°F., cs. | 14.4 | 3.27 | 2.18 | | | |
| Viscosity at Test Temp., cs. | 14.4 | 3.27 | 2.18 | 1.40 | 1.06 | 2.18 |
| Pump Speed, r.p.m. | 3600 | 3600 | 3600 | 3600 | 3600 | 3600 |
| Pump Inlet Temp., °F. | 100 | 100 | 100 | 150 | 200 | 100 |
| System Pressure, p.s.i. | 2900 | 3000 | 3000 | 2950 | 2750 | 3000 |
| Test Time, hrs. | 52 | 24 | 24 | 11 | 1 | 0.5 |
| Average Flow Rate, g.p.m.(3) | 3.10 | 3.04 | 3.00 | 2.89 | 2.76 | 3.00(4) |

(1) Narrow boiling fraction of highly refined naphthenic gas oil obtained from the Standard Oil Company of New Jersey.
(2) Narrow boiling gas oil from Pennsylvania crude obtained from Kendall Refining Company.
(3) Flow rates are an average for the entire test time.
(4) Tests 246 and 249 were conducted on the same test fluid under the same conditions. The resultant flow rates indicate that the volumetric efficiency has not been altered by tests 247 and 248.

Table 9

EFFECT OF BULK OIL TEMPERATURE ON THE WEAR CHARACTERISTICS OF SEVERAL LUBRICANTS IN THE SHELL FOUR-BALL WEAR TESTER

Test Conditions Include: Test Time = 1 Hour; Test Temperature as Indicated; Test Speed = 850 r.p.m.; Steel Balls = SKF Industries Grade #1 (0.5-Inch Diameter) Steel Ball Bearings, PRL Batch #8.

Test Fluid PRL 3090 = Necton 42, a low pour point mineral oil fraction having 32.3 centistokes viscosity at 100°F. + 0.4 Wt.% Paranox 441.
PRL 3091 = 1.0 Wt.% Tricresyl Phosphate in PRL 3090.
PRL 2574 = Spec. 51-F-21 type fluid prepared without an anti-wear additive.
PRL 3078 = Spec. 51-F-21 fluid containing 1.0 Wt.% Tricresyl Phosphate.
PRL 2429 = Di-2-Ethylhexyl Sebacate.
PRL 2860 = 1.0 Wt.% Tricresyl Phosphate + 0.4 Wt.% Paranox 441 in Di-2-Ethylhexyl Sebacate.
PRL 3069 = Experimental Gear Box Lubricant prepared by Rohm and Haas. Contains 1.0 Wt.% Tricresyl Phosphate and 7.5 Wt.% Santopoid S.
PRL 3077 = Experimental ester-base hydraulic fluid prepared without an anti-wear additive.
PRL 3039 = Experimental ester-base hydraulic fluid containing 1.0 Wt.% Tricresyl Phosphate.

| PRL No. | Average Wear Scar Diameter, mm., for Steel-on-Steel Bearing Surfaces: 1 Kilogram Load, Test Temperature, °F. | | | | | 10 Kilogram Load, Test Temperature, °F. | | | | | 40 Kilogram Load, Test Temperature, °F. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 167 | 266 | 300 | 351 | 399 | 167 | 266 | 300 | 351 | 399 | 167 | 266 | 300 | 351 | 399 |
| 3090 | 0.22 | 0.28 | 0.32 | 0.38 | 0.30 | 0.58 | 0.58 | 0.56 | 0.39 | 0.35 | 0.56 | 0.64 | 0.84 | 0.84 | - |
| 3091 | 0.14 | 0.15 | 0.17 | 0.18 | 0.25 | 0.33 | 0.26 | 0.28 | 0.28 | 0.33 | 0.67 | 0.84 | 0.71 | 0.91 | - |
| 2574 | 0.35 | 0.44 | 0.38 | 0.41 | 0.33 | 0.56 | 0.65 | 0.56 | 0.57 | 0.51 | 0.66 | 0.76 | 0.84 | 0.93 | 0.91 |
| 3078 | 0.15 | 0.16 | 0.15 | 0.15 | 0.14 | 0.22 | 0.22 | 0.25 | 0.23 | 0.23 | 0.44 | 0.54 | 0.70 | 0.97 | 0.84 |
| 2429 | 0.26 | 0.49 | 0.46 | 0.44 | 0.52 | 0.55 | 0.54 | 0.58 | 0.78 | 0.84 | 0.60 | 0.91 | 0.97 | 1.04 | 1.19 |
| 2860 | 0.14 | 0.17 | 0.15 | 0.16 | 0.18 | 0.25 | 0.25 | 0.26 | 0.26 | 0.30 | 0.38 | 0.80 | 0.91 | 0.97 | 0.97 |
| 3069 | 0.27 | 0.32 | 0.32 | 0.58 | 0.57 | 0.36 | 0.43 | 0.47 | 0.78 | 0.76 | 0.50 | 0.55 | 0.70 | 0.91 | 0.91 |
| 3077 | 0.32 | 0.46 | 0.44 | 0.50 | 0.58 | 0.63 | 0.70 | 0.81 | 0.97 | 1.04 | 0.84 | 0.97 | 0.97 | 1.10 | 1.10 |
| 3039 | 0.18 | 0.16 | 0.16 | 0.18 | 0.20 | 0.28 | 0.44 | 0.59 | 0.50 | 0.58 | 0.91 | 0.91 | 0.97 | 0.84 | 0.74 |

decomposition of the ester group or the formation of volatile products. The viscosity decrease is believed to be attributable to thermal depolymerization. Thermal tests at 500°F. with the mineral oil base stock, anti-tack component, tricresyl phosphate, and di-2-ethylhexyl sebacate show no appreciable evidence of molecular decomposition. The test conducted at 500°F. in the closed pressure cylinder on a commercial Spec. MIL-O-5606 hydraulic fluid indicates that there is no significant formation of volatile products. This is indicated by the low pressure at the end of the test at 500°F. and the lack of residual pressure upon cooling to room temperature.

These data indicate that a Spec. MIL-O-5606 fluid shows adequate thermal stability up to its normal boiling point (500°F.). In general, it has been found that oxidation dominates over thermal decomposition at high temperatures for mineral oil- and ester-base hydraulic fluids and lubricants. Spec. MIL-O-5606 hydraulic fluid is no exception to this trend.

Oxidation and Corrosion Stability. The oxidation stability and corrosion behavior are two of the most important properties of hydraulic fluids and lubricants. Their oxidation and corrosion behavior play a large part in governing fluid life, or the length of time between oil changes in service. These two properties become more important with increasing operating temperatures. The rate of oxidation and corrosion increases rapidly, and the induction period, or stable life, decreases rapidly, with increasing temperature. An oxidation and corrosion stability of 168 hours at 250°F. is afforded by the specification requirements for MIL-O-5606 hydraulic fluids. To fulfill this requirement, only a so-called low temperature oxidation and corrosion inhibitor is required. This inhibitor is believed to be of the hindered phenol type in most commercial preparation.

The effect of temperature on the stable life, or induction period, for a typical Spec. MIL-O-5606 fluid is shown on Figure 7. A similar curve is obtained for a Spec. MIL-O-5606 hydraulic fluid prepared by this laboratory using 0.4 weight per cent Paranox 441 as the oxidation inhibitor.

These data indicate that the stable life of the hydraulic fluid decreases by a factor of 10 for every 60°F. increase in temperature. At 347°F. the stable life has been reduced to about 10 to 15 hours. This compares with a stable life of about 4,000 hours at 200°F. and 200 hours at 270°F. These data indicate that a typical Spec. MIL-O-5606 fluid has essentially no stable life under the oxidation conditions used at 400°F. and above. Stable life refers to the period during which little or no oxygen is absorbed by the test fluid even though there is plenty of oxygen available. During this interval most of the changes in the fluid's properties are small in magnitude. At temperatures above which there is essentially no stable life, the role of the conventional oxidation inhibitor is that of reducing the rate of oxidation, rather than of suppressing the oxidation entirely. In this latter region the oxidative

Table 10

THERMAL STABILITY OF VARIOUS COMPONENTS OF SPEC. MIL-O-5606 HYDRAULIC FLUID AT 500°F.

Tests conducted at 500 ± 5°F. for a period of 20 hours. Except where otherwise noted the fluid charge is 25 ml., and the test tubes used are sealed with a U-tube containing approximately 3 ml. of test fluid. 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 Composition | Centistoke Viscosity at 100°F. | | | % Loss in Weight(2) | Neut. No. (Mg. KOH/Gm. Oil) | |
|---|---|---|---|---|---|---|
| | Original | Final | % Change | | Orig. | Final |
| PRL 3115 (Commercial Spec. MIL-O-5606)(1) | 14.1 | 9.85 | -30 | 0.0 | 0.0 | 0.6 |
| PRL 3115 | 14.1 | 9.51 | -33 | 4.0 | 0.0 | 0.4 |
| XCT White Oil | 2.98 | 3.04 | +2 | 2.0 | 0.0 | 0.2 |
| Voltesso 36 | 9.50 | 9.59 | +1 | 0.0 | 0.1 | 0.2 |
| Di-2-Ethylhexyl Sebacate (not a -5606 Component) | 12.8 | 12.8 | 0 | 2.0 | 0.1 | 2.8 |
| Tricresyl Phosphate | 38.3 | 41.4 | +8 | 2.0 | 0.2 | 3.5 |
| 10.0 Wt.% Acryloid HF-855 in Voltesso 36 | 46.2 | 27.7 | -40 | 0.0 | 0.1 | 0.6 |
| 55.9 Wt.% Acryloid HF-855 in XCT White Oil | 1179 | 886 | -25 | 2.0 | 1.3 | 3.5 |

(1) This test conducted in a stainless steel cylinder which has a total volume of 46 ml. The fluid charged was 20 ml. (17 grams). Prior to starting the test the system is purged with nitrogen. The system is then sealed and the test started. Maximum system pressure during test was 35 p.s.i. The residual final pressure at room temperature was 0 p.s.i. The pressure of the nitrogen at 500°F. is about 15 p.s.i.

(2) Per cent loss in weight is valid to ± 2 per cent.

deterioration is generally a direct function of the amount of oxygen in contact with the test fluid.

Oxidation and corrosion tests with a typical commercial Spec. MIL-O-5606 hydraulic fluid are shown on Table 12. These tests cover temperatures from 250° to 500°F. Two different kinds of tests have been made. The majority of the tests shown have been conducted using the procedures and techniques set forth in Spec. MIL-O-5606. Two tests using the PRL thin film oxidation and corrosion test are also included. The thin film oxidation and corrosion test emphasizes the effect of large metal catalyst areas on thin films of oil in intimate contact with air. A detailed description of the thin film oxidation and corrosion procedure can be found in the Appendix of report PRL 6.1-Jan52.

Briefly the thin film procedure consists of allowing the test fluid to flow by gravity in a thin film over 2,000 sq. cm. of intimately mixed steel and copper jack chain (1,000 sq. cm. of each metal). At the same time, air is forced upwards (countercurrent) through the chain and over the falling oil film. The fluid is lifted from a reservoir below the jack chain packing to the top of the jack chain by means of a small bucket type lift pump. The oil cycling rate is about 75 ml. per minute. This test procedure is somewhat more severe than the Spec. MIL-O-5606 type oxidation and corrosion test. This test places particular emphasis on the dirtiness tendencies of the oil.

The 168 hour tests at 250°F. are shown on Table 12 to illustrate the minor property changes that occur within the induction period of a typical Spec. MIL-O-5606 fluid, in the specification oxidation and corrosion test as well as in the thin film oxidation and corrosion test. The data from the thin film test at 250°F. indicate slightly larger property changes in all cases than for the comparable test under Spec. MIL-O-5606 test conditions.

The oxidation and corrosion tests at 347°F. and higher are all beyond the stable life of the fluid. That is, all of these fluids after the test are in a state of incipient or severe oxidation. In the case of the 347°F. Spec. MIL-O-5606 type oxidation and corrosion test, the stable life of the fluid is about 12 to 14 hours under these conditions, compared with the test time of 24 and 36 hours. The thin film test at 347°F. indicates that the stable life of the fluid was exceeded in 12 hours under these conditions. The thin film test, for a lesser degree of oxidation than the Spec. MIL-O-5606 type test, shows more dirtiness.

Another point should be emphasized concerning the 347°F. tests. The 130°F. viscosity after all of the 347°F. tests show a decrease, while the 0°F. viscosity shows little decrease or an increase. These data are typical for the region of incipient oxidation of low viscosity mineral oil-Acryloid blends. This viscosity decrease is not a thermal phenomenon of the type illustrated in the previous section. Viscosity decrease of Spec. MIL-O-5606 type fluids from thermal effects begins at about 450°F. Thermal effects are believed to be a factor in the viscosity changes

noted in the 450° and 500°F. oxidation and corrosion tests.

Previous oxidation studies at 250° and 347°F. have indicated that mineral oils of the type used as base stocks and anti-tack components in Spec. MIL-O-5606 fluids show a steady increase in viscosity with incipient oxidation. An Acryloid HF 858 solution of the same mineral oils shows an initial decrease in high temperature viscosity (130°F.) with incipient oxidation. Upon further oxidation there is a subsequent increase in high temperature viscosity. In all cases at 347°F. and lower, the -40°F. viscosity shows a steady increase with incipient oxidation The overall effect of a decreasing high temperature viscosity coupled with an increasing low temperature viscosity results in an increase in A.S.T.M. slope. The cause of this behavior is not known to this Laboratory. As pointed out previously, this phenomenon is not attributable to simple thermal depolymerization. This can be seen by comparing the viscosity behavior on oxidation at higher temperatures where thermal degradation is known to occur. Under these conditions, as shown on Table 12 (data at 450° and 500°F.), the viscosity values at 130° and 0°F. show a fairly uniform decrease.

The results at 450° and 500°F., given on Table 12, differ from those at 347°F. discussed above in that the tests at the higher temperatures show no induction period. That is, oxygen absorption begins immediately in these tests. In the 450° to 500°F. temperature range, the rate of oxidation is proportional to the amount of oxygen available. These tests have, therefore, been conducted at low air rates.

The air rate of 0.6 liters per hour is still quite large in terms of air leakage into a sealed or pressurized hydraulic system. The data on Table 11 give the equivalent minimum volume of air that would be required to produce the indicated amount of oxidation in a hydraulic system of 5 gallons capacity. These data assume that all of the oxygen present in the air reacts with the hydraulic fluid. This requires very intimate contact between the air and fluid for extended periods. The data on Table 11 are calculated for the three oxidation tests conducted at 450° and 500°F. These are the only tests for which quantitative oxygen absorption data have been obtained.

Table 11

OXIDATION SEVERITY IN TERMS OF AIR VOLUME

| Oxidation Conditions for Spec. MIL-O-5606 Fluids on Table 13 | | | Approx. Min. Cu. Ft. of Air at 32°F. and 760 mm. Hg Required to Produce an Equivalent Degree of Oxidation in 5 Gal. of Fluid |
|---|---|---|---|
| Test Temp., °F. | Test Time, Hrs. | Air Rate, Liters/Hr. | |
| 450 | 24 | 0.6 | 90 |
| 500 | 24 | 0.6 | 90 |
| 500 | 20 | 5.0 | 625 |

These data illustrate that sizeable quantities of air have to enter a system to produce the oxidative deterioration shown on Table 12 under the severe high temperature conditions used. The oxidation and corrosion data at 450° and 500°F., compared with the thermal stability data at 500°F., indicate clearly the advantages of using a closed hydraulic system, or at least a system with a limited air contact in this high temperature range.

The corrosion values for all of the oxidation and corrosion tests shown on Table 12 are low. It should be noted that magnesium has been omitted from the tests at 450° and 500°F. It has been found in previous studies that the oxidation of mineral oils and many synthetics at temperatures in the region of 400° to 500°F. always results in high magnesium corrosion. Magnesium corrosion would be anticipated in high temperature hydraulic systems where hydraulic fluid oxidation is encountered, even though the magnesium exists in a portion of the systems where temperatures are well below 400°F.

Some oxidation and corrosion studies have been conducted with Spec. MIL-O-5606 and similar fluids to study the interaction of individual metals and metals other than the five listed in the MIL-O-5606 specification. The results of conventional Spec. MIL-O-5606 oxidation and corrosion tests but modified by the inclusion of lead-indium coated silver-plated steel or copper-beryllium are shown on Table 13. The Spec. 51-F-21 (Ord) fluid is prepared from essentially the same constituents as Spec. MIL-O-5606. The essential difference between these two specification fluids is in viscosity level.

It can be seen from the data on Table 13 that the corrosion of lead-indium coated silver-plated steel and copper-beryllium alloy are within the specification limit in all tests. In the case of the lead-indium coated silver-plated steel, however, there are signs of incipient corrosion and the values would be considered borderline. It can be noted that the Spec. 51-F-21 fluid also gives borderline copper corrosion. There is no indication in any of these tests that the inclusion of lead-indium coated silver-plated steel or copper-beryllium alloy has caused any deleterious effects on the fluid under these test conditions.

Several metals have been studied individually in an oxidation test for their effect on the stable life of Voltesso 36. Voltesso 36 is a naphthenic mineral oil fraction of the type used as a base stock, or anti-tack constituent, in Spec. MIL-O-5606 hydraulic fluid. The data obtained for the stable life of Voltesso 36 inhibited with Paranox 441, in the presence of various metals, is shown on Table 14. These data may also be considered typical of a complete Spec. MIL-O-5606 fluid of high quality. A temperature of 500°F. was chosen for the stable life tests to reduce the stable life values to a reasonable time for testing. These data indicate that copper, bronze, and silver-plated steel cause an appreciable drop in the stable life of the fluid. Magnesium and steel show some trend toward reducing the stable life.

The stable life in the presence of lead, cadmium, and aluminum is essentially the same as the stable life in the absence of metals.

In addition to the stable life, the total test time and the amount of metal corrosion during the test is shown on Table 14. The difference between the test time and the stable life is the amount of time during which the fluid was undergoing significant oxidation. It is interesting to note, therefore, that severe corrosion of the metals did not take place even in the presence of oxidized oil of the Spec. MIL-O-5606 type. It can also be noted that measurable corrosion of the metal specimens is not necessary to cause an appreciable reduction in the stable life of the fluid. This reduction of stable life by metals without undergoing appreciable corrosion has been noted previously for both mineral oil and synthetic fluids. These oxidation and corrosion data indicate that some of the metals tested are less desirable than others because of their ease of corrosion or their tendency to promote oxidation. However, none of the metals evaluated in Tables 13 and 14 indicate sufficient prooxidant activity (reduction in stable life) to be categorically eliminated from hydraulic systems containing high quality Spec. MIL-O-5606 fluids. Corrosion of all of the metals discussed in this report can be controlled under most normal operating conditions by high quality Spec. MIL-O-5606 hydraulic fluids.

It has been indicated previously that it is desirable to exclude magnesium from systems where high temperatures and liquid water or oxidized oil exist together. Cadmium-plated steel has also given erratic corrosion behavior with mineral oil and synthetic hydraulic fluids. The data indicate that it is possible to produce fluids of satisfactory stability with respect to all of the Spec. MIL-O-5606 requirements and, in addition, give low metal corrosion with the metals discussed on Tables 13 and 14, but still give unsatisfactory behavior with respect to cadmium corrosion. It would be desirable to eliminate cadmium completely from the portion of the hydraulic system coming in contact with the fluid.

<u>Miscellaneous Physical Properties.</u> This Laboratory receives frequent requests for various physical properties of Spec. MIL-O-5606 fluids for use primarily in engineering and design calculations. Many of these properties have been measured or extrapolated from typical Spec. MIL-O-5606 and similar fluids. While there is some variation in these properties from batch to batch and from manufacturer to manufacturer, it is believed that the values given in the following tables and figures are sufficiently accurate to be used in engineering calculations for equipment designed around Spec. MIL-O-5606 hydraulic fluid.

The effect of pressure on density for a Spec. MIL-O-5606 fluid is shown on Figure 8. The data are plotted in Figure 8 so that the density ratio at any given pressure and temperature can be determined. The density at atmospheric pressure at the same temperature is then multiplied by this ratio to give the density at the desired pressure.

Figure 7

OXIDATION BEHAVIOR OF SPECIFICATION MIL-O-5606 TYPE FLUIDS AS A FUNCTION OF TEMPERATURE

TECHNIQUE AND PROCEDURE IN ACCORDANCE WITH SPEC. MIL-O-5606.

TEST CONDITIONS INCLUDE: TEST TIME AND TEST TEMPERATURE AS INDICATED; AIR RATE = 10 ± 1 LITERS PER HOUR; TEST FLUID CHARGED = 100 ML.; AND METAL CATALYSTS PRESENT AS SPECIFIED.

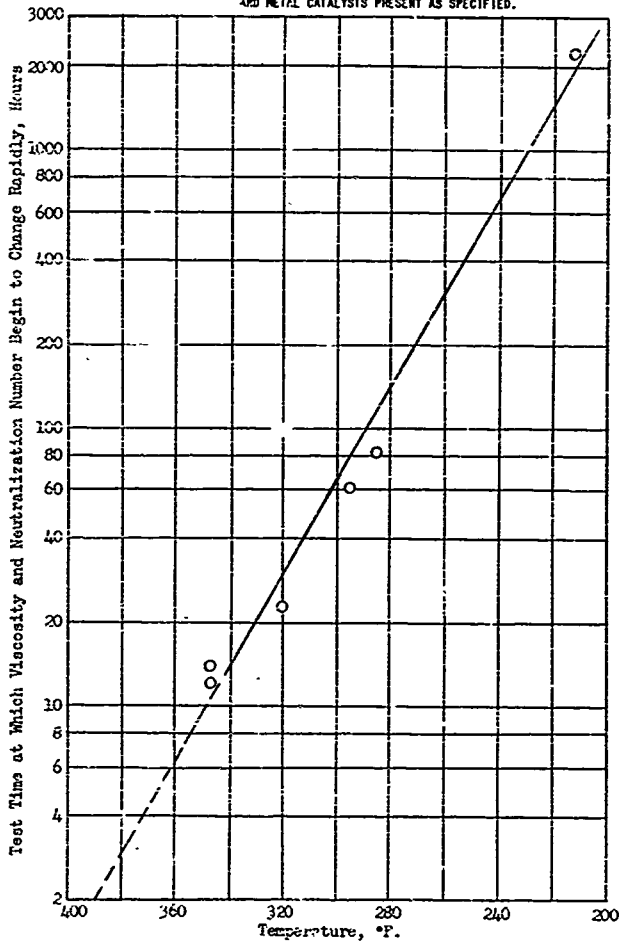


Table 12

OXIDATION AND CORROSION CHARACTERISTICS OF SPEC. MIL-O-5606 TYPE FLUIDS AT SEVERAL TEMPERATURES

TEST CONDITIONS: BULK OIL TYPE TEST: TEST TEMPERATURE, TEST TIME, AND AIR RATE AS INDICATED; TEST FLUID CHARGED = 100 ML.; AND CATALYST = A 1-INCH SQUARE OF EACH OF THE METALS INDICATED. PROCEDURE AND TECHNIQUE IN ACCORDANCE WITH SPEC. MIL-O-5606.
THIN FILM TYPE TEST: TEST TEMPERATURE, TEST TIME, AND AIR RATE AS INDICATED; TEST FLUID CHARGED = 50 ML. AND CATALYST = 1000 SQ. CM. EACH OF COPPER AND STEEL JACK CHAIN. PROCEDURE AND TECHNIQUE ARE DESCRIBED IN APPENDIX A, REPORT PRL 6.1-JAN52.

| TEST TEMPERATURE, °F. | 250 | 250 | 347 | 347 | 347 | 45[illegible] | 500 | 500 |
|---|---|---|---|---|---|---|---|---|
| TEST TIME, HOURS | 168 | 168 | 12 | 24 | 36 | 2[illegible] | 24 | 20 |
| AIR RATE, LITERS/HR. | 10 | 10 | 10 | 10 | 10 | 0.6 | 0.5 | 5 |
| TYPE TEST | BULK OIL | <--------THIN FILM----> | | <----------BULK OIL----------> | | | | |
| OVERALL LIQUID LOSS, WT.% | 2 | - | 10 | 0 | 3 | [illegible] | 8 | [illegible] |
| % CHANGE IN CENTISTOKE VISCOSITY | | | | | | | | |
| AT 130°F. | +3 | +9 | -3 | -53 | -34 | -59 | -59 | -49 |
| AT 0°F. | +8 | -21 | +106 | -3 | - | -43 | -20 | - |
| NEUT. NO. (MG. KOH/GM. OIL): | | | | | | | | |
| ORIGINAL | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| FINAL | 0.1 | 0.3 | 8.6 | 2.2 | 6.3 | 1.1 | 1.7 | 4.0 |
| A.S.T.M. UNION COLOR: | | | | | | | | |
| ORIGINAL | -(1) | -(1) | -(1) | -(1) | -(1) | - | - | - |
| FINAL | 4-1/2 | 7 | >8 | 7 | >8 | - | - | - |
| WT.% INSOLUBLE MATERIAL | NONE | TRACE | 0.6 | TRACE | 0.1 | TRACE | TRACE | 1.8 |
| FINAL CATALYST CONDITION | | | | | | | | |
| APPEARANCE | | | | | | | | |
| COPPER | DULL | DULL(2) | DULL(2) | DULL | DULL | DULL | DULL | DULL |
| STEEL | BRIGHT | DULL(3) | DULL(3) | DULL | DULL | DULL | DULL | DULL |
| ALUMINUM | BRIGHT | - | - | DULL | DULL | BRIGHT | BRIGHT | BRIGHT |
| MAGNESIUM | BRIGHT | - | - | DULL | CORRODED | - | - | - |
| CADMIUM | BRIGHT | - | - | - | - | - | - | - |
| WT. LOSS (MG./SQ. CM.) | | | | | | | | |
| COPPER | 0.13 | 0.00(2) | 0.18(2) | 0.13 | 0.17 | 0.02 | 0.06 | 0.16 |
| STEEL | 0.04 | +0.02(3) | 0.07(3) | 0.07 | +0.02 | +0.02 | 0.00 | 0.03 |
| ALUMINUM | 0.01 | - | - | 0.02 | 0.12 | 0.01 | 0.00 | 0.02 |
| MAGNESIUM | 0.02 | - | - | 0.02 | 0.29 | - | - | - |
| CADMIUM | 0.06 | - | - | - | - | - | - | - |

(1) FLUID IS DYED RED AND NO COLOR DETERMINATION IS MADE.
(2) CATALYST IS 1000 SQ. CM. OF COPPER JACK CHAIN.
(3) CATALYST IS 1000 SQ. CM. OF STEEL JACK CHAIN.

Table 13

CORROSION STUDIES WITH MINERAL OIL HYDRAULIC FLUIDS

TEST PROCEDURE AND TECHNIQUES IN ACCORDANCE WITH SPEC. MIL-O-5606. LEAD-INDIUM COATED SILVER-PLATED SPECIMENS HAVE BEEN INCLUDED IN THESE TESTS. THE LEAD-INDIUM SURFACE IS SUBSTITUTED FOR CADMIUM-PLATED STEEL IN THIS TEST. ALL OF THE METAL CATALYSTS EXCEPT THE LEAD-INDIUM SPECIMEN ARE 1" X 1" X 20 GAGE. THE LEAD-INDIUM CATALYST IS A SECTION OF AIRCRAFT PISTON ENGINE BEARING HAVING APPROXIMATELY 1 SQ. IN. OF LEAD-INDIUM SURFACE ON A 1 SQ. IN. STEEL BACKING. ALL TESTS ARE CONDUCTED AT AN AIR RATE OF 10 ± 1 LITERS PER HOUR.

| TEST FLUID | PRL 3115(1) | PRL 2820(2) | PRL 3115(1) |
|---|---|---|---|
| TEST TEMPERATURE, °F. | 250 | 250 | 250 |
| TEST TIME, HOURS | 168 | 168 | 168 |
| LIQUID LOSS, WT.% | 3 | 6 | 4 |
| % CHANGE IN VISCOSITY | | | |
| AT 130°F. | +7 | +10 | +6 |
| AT 0°F. | +10 | +24 | - |
| NEUT. NO. (MG. KOH/GM. OIL) | | | |
| ORIGINAL | 0.0 | 0.3 | 0.0 |
| FINAL | 0.1 | 0.5 | 0.0 |
| A.S.T.M. UNION COLOR | | | |
| ORIGINAL | 6 | 2 | 5 |
| FINAL | 6 | 5 | 6 |
| WT.% INSOLUBLE MATERIAL | NONE | TRACE | NONE |
| FINAL CATALYST CONDITION | | | |
| APPEARANCE | | | |
| COPPER | DULL | CORRODED | - |
| STEEL | DULL | COATED | - |
| ALUMINUM | DULL | DULL | - |
| MAGNESIUM | DULL | DULL | - |
| LEAD-INDIUM | DULL | DULL | - |
| COPPER-BERYLLIUM | - | - | DULL |
| WT. LOSS (MG./SQ. CM.) | | | |
| COPPER | 0.06 | 0.23 | - |
| STEEL | 0.02 | +0.16 | - |
| ALUMINUM | +0.02 | 0.02 | - |
| MAGNESIUM | 0.02 | 0.02 | - |
| LEAD-INDIUM | +0.20 | 0.13 | - |
| COPPER-BERYLLIUM | - | - | +0.03 |

(1) COMMERCIAL SPEC. MIL-O-5606 FLUID PREPARED BY THE STANDARD OIL COMPANY OF NEW JERSEY.
(2) COMMERCIAL SPEC. 51-F-21 (GRD) FLUID PREPARED BY THE STANDARD OIL COMPANY OF NEW JERSEY.

Table 14

EFFECT OF CATALYST METALS ON OXIDATION STABILITY

Test Procedures and Techniques in Accordance with Spec. MIL-O-5606.
Test Conditions Include: Test Temperature = 300 ± 3°F.; Test Time as Indicated; Test Fluid = 100 ml.; Air Rate = 10 ± 1 liters per hour; Metal Catalyst = One Inch Squares of Indicated Metals;
Test Fluid = Voltesso 36(2) + 0.4 Wt.% Paranox 441.

| Catalyst Metal | Approx. Stable Life, Hours(1) | Test Time, Hrs. | Catalyst Wt. Loss, mg./sq. cm. |
|---|---|---|---|
| No Catalyst | 300 | 365 | - |
| Copper, Steel, Aluminum, Magnesium, and Cadmium-Plated Steel | 230 | 360 | 0.03, +0.06, +0.05, +0.10, 0.37 |
| Copper | 190 | 212 | 0.02 |
| Bronze | 190 | 240 | 0.19 |
| Steel | 250 | 365 | +0.08 |
| Sheet Lead | 300 | 330 | 0.10 |
| Silver-Plated Steel | 140 | 220 | 0.29 |
| Cadmium-Plated Steel | 280 | 310 | 0.02 |
| Aluminum | 280 | 311 | 0.00 |
| Magnesium | 245 | 264 | 0.03 |

(1) Stable life determined by the sharp break in the curve of neutralization number versus time.
(2) Voltesso 36 is a highly refined naphthenic gas oil typical of good quality base stocks for Spec. MIL-O-5606, Spec. 51-F-21(Ord), Spec. 51-F-23(Ord), Spec. MIL-L-7870 and Spec. AN-O-9 fluids.

For example, at 3,000 p.s.i. and 100°F., it can be seen from Figure 8 that the ratio of the density at this pressure and temperature to the density at atmospheric pressure and 100°F. temperature is approximately 1.0127. When this value is multiplied by 0.827 which is the fluid's density at atmospheric pressure and 100°F., a value of 0.838 is obtained for the density of the fluid at 3,000 p.s.i. and 100°F.

The effect of pressure on the viscosity of a typical Spec. MIL-O-5606 hydraulic fluid has been calculated from data obtained from fluids of this class. These data are shown on Figure 9. The kinematic viscosity is plotted against absolute pressure in pounds per square inch. At a temperature of 100°F. and a pressure of 3,000 p.s.i., it can be seen that Spec. MIL-O-5606 hydraulic fluid increases in viscosity from approximately 14.2 (at 1 atmosphere pressure) to 21 centistokes. This represents an increase of 48 per cent. The rate of change in viscosity with pressure increases with decreasing temperature. At -40°F., the viscosity increase is 83 per cent for a pressure increase from one atmosphere to 3,000 p.s.i. The corresponding value for 200°F. is 36 per cent increase in viscosity.

The bulk modulus of elasticity has been calculated for Spec. MIL-O-5606 type hydraulic fluids. The bulk modulus of elasticity of a fluid is the reciprocal of the compressibility and can be defined by the equation:

$$B = \frac{\text{Stress}}{\text{Strain}} = \frac{(P - P_o)\, V_o}{(V_o - V)}$$

$B$ = Bulk modulus of elasticity
$P_o$ = Atmospheric pressure
$P$ = Absolute pressure
$V_o$ = Specific volume at $P_o$
$V$ = Specific volume at $P$

Bulk modulus data for Spec. MIL-O-5606 fluid are calculated from the compressibility data presented in Figure 10. These data are tabulated in Table 15.

Table 15

BULK MODULUS VALUES FOR SPEC. MIL-O-5606 FLUID

All values calculated for 100°F.

| Test Fluid | Pressure, p.s.i. | Sp. Vol. cm.3/gm. | Average Bulk Modulus p.s.i. x 10-5 |
|---|---|---|---|
| Spec. MIL-O-5606 (14.2 cs. at 100°F.) | 0 | 1.209 | - |
| | 1,000 | 1.203 | 2.2 |
| | 3,000 | 1.193 | 2.4 |

If the limits of error in reporting density to three decimal places are considered to be ± 0.001, the resultant error in bulk modulus is ± 0.2 x $10^5$ p.s.i. The compressibility of many mineral oils have been studied by Dow and Fink in this Laboratory*. Their conclusion is that the compressibility (and the bulk modulus) of essentially all petroleum derived mineral oils is the same within the limits of experimental error. The value for bulk modulus is not altered significantly by the Acryloid thickener used in formulating Spec. MIL-O-5606 type fluids.

The temperature function of bulk modulus has been determined for a typical Spec. MIL-O-5606 fluid. These data are shown on Figure 10, along with the effect of temperature on density. The solid line on the bulk modulus curve is for the average value over the range of 0 to 10,000 p.s.i. pressure. The dotted line is an extrapolated curve for the average value of 0 to 5,000 p.s.i. pressure.

The values for change in density with temperature shown on Figure 10 have been used to calculate the average cubical coefficient of expansion for the range of +130° to -40°F. The average values obtained are 7.9 x $10^{-4}$ cc./cc./°C. or 4.4 x $10^{-4}$ cc./cc./°F.

Data for specific heat and thermal conductivity of Spec. MIL-O-5606 type fluids are shown on Table 16. No appreciable differences in these values would be expected due to batch to batch variations.

Table 16

PHYSICAL PROPERTIES FOR SPEC. MIL-O-5606 FLUID

| Temperature, °F. | Density, g./ml. | Specific Heat B.T.U./lb./°F. | Thermal Conductivity, B.T.U./Sq. Ft./Hr./(°F. per Ft.) |
|---|---|---|---|
| | Data for Typical Spec. MIL-O-5606 Mineral Oil Hydraulic Fluid | | |
| -65 | 0.89 | - | - |
| 0 | 0.86 | 0.45 | 0.081 |
| 100 | 0.83 | 0.50 | 0.079 |
| 200 | 0.79 | 0.55 | 0.076 |
| 300 | 0.75 | 0.60 | 0.074 |

Conclusions. The high temperature studies with Spec. MIL-O-5606 hydraulic fluid indicate that one of the limitations to high temperature operation is fluid volatility. The bulk base stock component of the fluid exhibits an initial boiling point of about 500°F. at 760 mm. Hg. Extensive evaporation of the base stock results in the formation of tacky or sticky

* Dow, R. B. and Fink, C. E., Journal of Applied Physics, 11, 353 (1940).

Figure 8

THE EFFECT OF PRESSURE ON THE DENSITY OF SPECIFICATION MIL-O-5606 TYPE HYDRAULIC FLUID

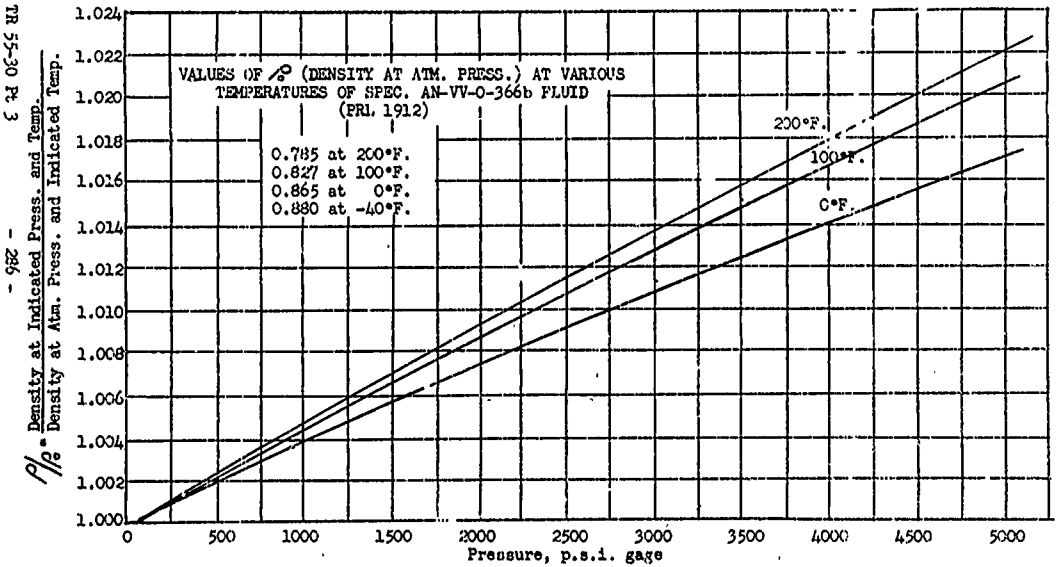


Figure 9
EFFECT OF PRESSURE ON THE VISCOSITY OF A TYPICAL SPECIFICATION MIL-O-5606 TYPE FLUID

Data based on Spec. AN-VV-O-366b Fluid Prepared by the Standard Oil Company of New Jersey, WS-491 (PRL 1912)

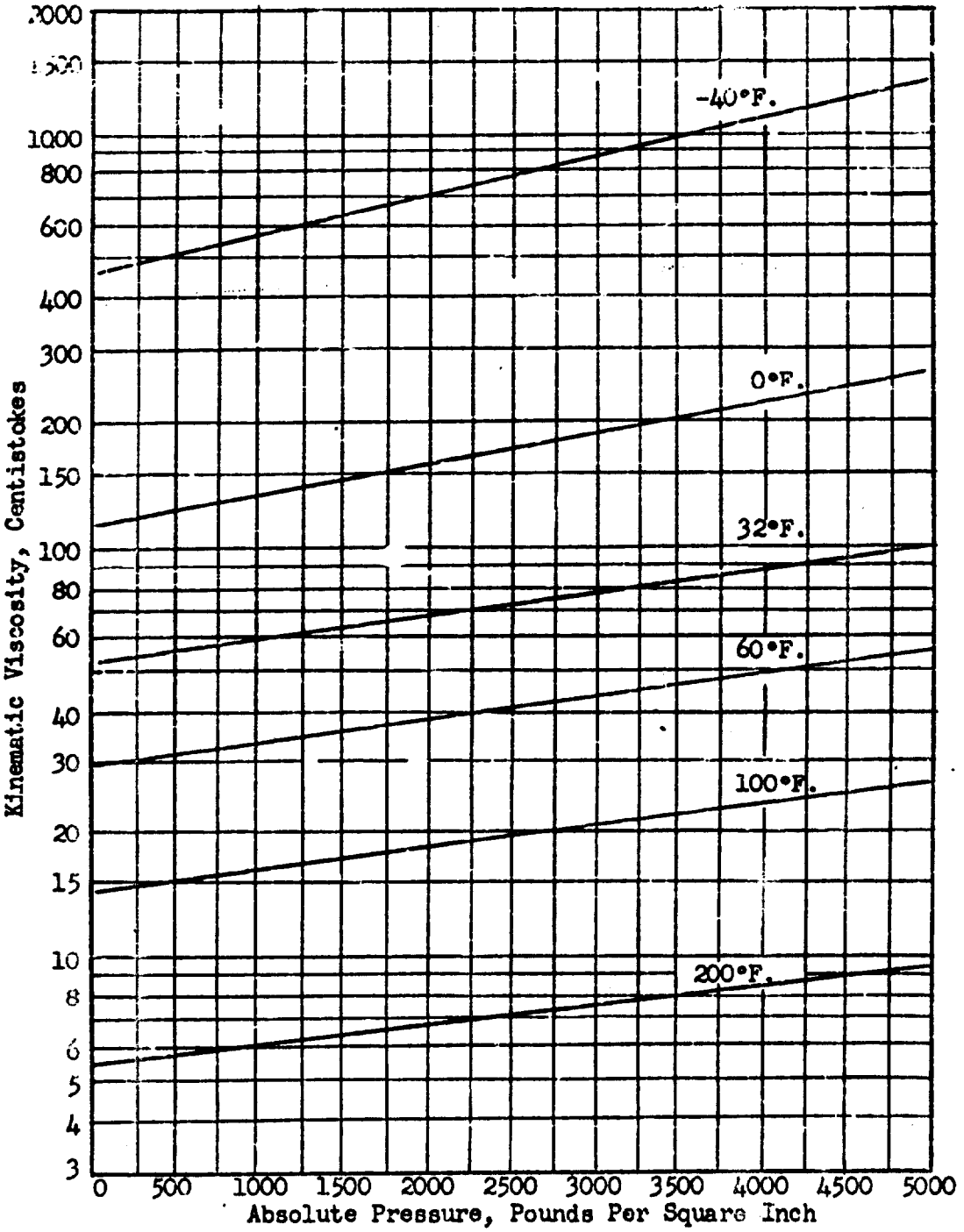
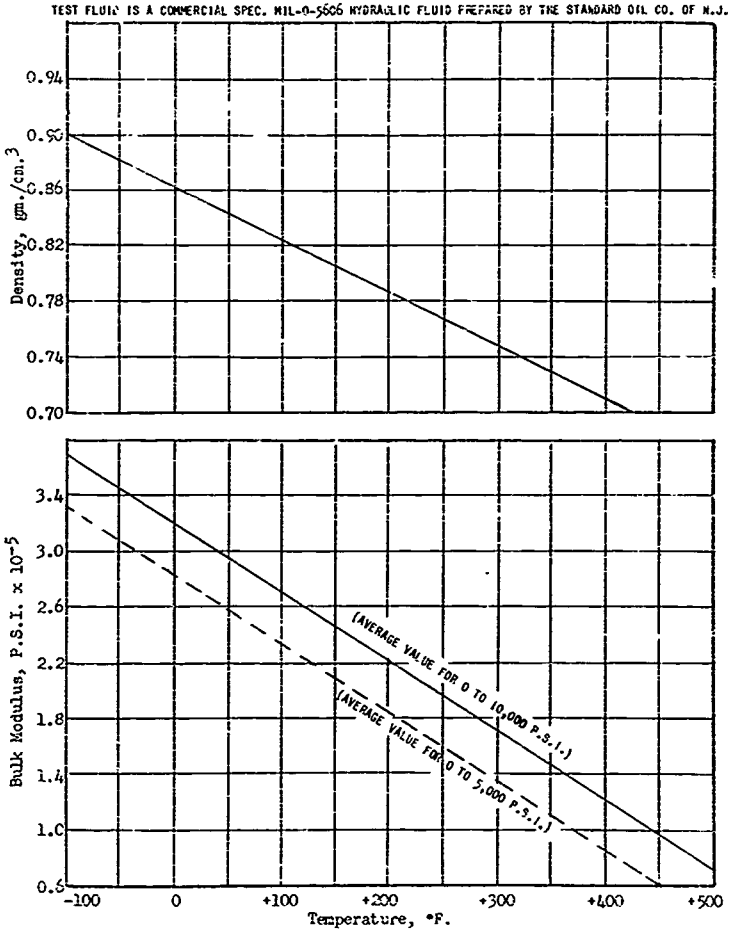


Figure 10
VARIATION OF BULK MODULUS OF ELASTICITY AND DENSITY WITH TEMPERATURE FOR A SPEC. MIL-O-5606 HYDRAULIC FLUID

TEST FLUID IS A COMMERCIAL SPEC. MIL-O-5606 HYDRAULIC FLUID PREPARED BY THE STANDARD OIL CO. OF N.J.



films when Spec. MIL-O-5606 fluid is exposed to reasonably high temperatures (200°F. and upwards) in a thin film for extended periods of time when exposed to circulating air.

This problem of tacky film formation can be solved by: (1) changes in the mechanical design of hydraulic systems to reduce the amount of air in contact with oil films, and (2) the inclusion of a more effective anti-tack component such as di-2-ethylhexyl sebacate.

Tests indicate that Spec. MIL-O-5606 fluid has sufficient viscosity and lubricity at 400° to 500°F. to operate satisfactorily in properly designed high temperature hydraulic pumps. Such data are based on the operation of a standard Vickers piston pump at 200°F. on fluids with viscosity and lubricity properties at 200°F. that match those of Spec. MIL-O-5606 fluid at 400° to 500°F. These data further indicate that fluid volatility will be the limiting factor in high temperature pump operation.

All of the components as well as the finished Spec. MIL-O-5606 fluid show adequate thermal stability at 500°F. for extended periods. The conventional oxidation stability, or the length of time the fluid is inhibited against oxidation, for a Spec. MIL-O-5606 fluid decreases rapidly with increasing temperature. Stable life values for a typical fluid decrease from about 3,000 hours at 200°F., to 200 hours at 275°F., and to 10 to 15 hours at 347°F. There is essentially no induction period above 400°F. Test data indicate that the Spec. MIL-O-5606 fluid can be used for considerable lengths of time in the region of 347° to 500°F. if care is taken to control or to limit the amount of air or oxygen filtering into the hydraulic system (see Tables 12 and 13). A reasonable amount of oxygen can be assimilated by the hydraulic fluid without causing sufficient property changes to render the fluid inoperative. The extent of service life might effectively be increased for operations above 200°F. by the use of a closed hydraulic system pressurized by nitrogen or separated from the pressurizing medium by a diaphragm.

No appreciable metal corrosion has been noted in oxidation and corrosion tests with Spec. MIL-O-5606 fluids over the temperature range of 250° to 500°F. under conditions of incipient oxidation of the fluid.

The reduction in the stable life of Spec. MIL-O-5606 type hydraulic fluid by the presence of silver, copper, and some copper alloys is readily demonstrated. The extent of the reduction in stable life is not believed to be sufficient, however, to exclude these metals from hydraulic systems for this reason alone. The corrosion of cadmium plated surfaces by otherwise satisfactory hydraulic fluids makes it desirable to eliminate wherever possible the use of cadmium plated surfaces in hydraulic systems. The use of magnesium in hydraulic systems containing hot spots or bulk temperatures in excess of 250°F. is not recommended where liquid water and/or oxidized hydraulic fluid may exist or be formed at an appreciable rate.

Several physical properties of Spec. MIL-O-5606 including: viscosity as a function of pressure, density as a function of pressure, density as a function of temperature, the bulk modulus as a function of temperature, specific heat, thermal conductivity, and the cubical coefficient of expansion have been measured and/or calculated. These properties are given primarily as an aid in engineering and design calculations.

In general these studies show that temperatures up to 500°F. can be tolerated by Spec. MIL-O-5606 fluid under a variety of conditions. The formulation of specific limitations will require testing in actual hydraulic systems with the individual hydraulic system components.

APPENDIX B
WADC TR 55-30 PT 3

PETROLEUM REFINING

LABORATORY

PROGRESS REPORT

FOR THE PERIOD

1 OCTOBER 1953 THROUGH 31 JANUARY 1954

ON THE

# DEVELOPMENT OF A THIN FILM PRESERVATIVE COMPOSITION FOR HYDRAULIC SYSTEMS

TO THE

NAVY BUREAU OF ORDNANCE


CONTRACT NO. AF33(038)18193

REPORT NO. PRL 7.1-JAN54

DATE 6 FEBRUARY 1954



THE PENNSYLVANIA STATE UNIVERSITY

*College of Chemistry and Physics*

STATE COLLEGE, PENNSYLVANIA

APPENDIX B
WADC TR 55-30 PT 3

PETROLEUM REFINING LABORATORY
MERRELL R. FENSKE, DIRECTOR

COLLEGE OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE UNIVERSITY
STATE COLLEGE, PENNSYLVANIA

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Introduction. The Navy Bureau of Ordnance requested this Laboratory to investigate preservative compounds of the Specification MIL-C-972 type. Currently approved products that are used as protective coatings constitute, in many cases, undesirable contaminants for Navy hydraulic fluids. The development of a preservative compound which is soluble in Navy hydraulic fluid, and by its presence does not cause a significant decrease in hydraulic fluid quality, is desired.

The study of the preservative characteristics of a thin film of oil on steel is carried out in a humidity cabinet to simulate accelerated rusting conditions. This testing phase of this study has been delayed by the delivery schedule of the humidity cabinet and control equipment. This equipment arrived and was installed in this Laboratory in October 1953.

Test Equipment. The humidity cabinet used for conducting the accelerated rusting tests consists of an Aminco Aire 160 control unit to supply conditioned air. This control unit allows accurate control of the temperature and humidity of the air supplied by the unit. The unit for conditioning the air comprises three chambers: an air inlet chamber, the spray chamber, and an air outlet chamber. The temperature and humidity are controlled by a refrigerator unit, electrical heaters in the air space, electrical heaters in the water reservoir, and a water pump which sprays water as a mist into the air stream. Using the controls available, conditioned air can be supplied for any value of temperature and humidity above the minimum operating line shown on Figure 1. It can be seen that the humidity range increases with increasing temperature, and ranges from 80 to 100 per cent relative humidity at 40°F. to 10 to 100 per cent relative humidity at 160°F.

The test chamber used in this case is an Aminco, 8 cubic foot cabinet, designed to mount directly on top of the Aminco Aire 160 unit. The humidity is measured in the test cabinet by means of a recording wet and dry bulb thermometer. The conditioned air is circulated through the test chamber by means of a blower fan and the rate of circulation is controlled by a manually operated damper.

The Aminco Aire 160 conditioner and test cabinet have been in operation for over two months. Operation has been satisfactory. Except for a few brief exploratory tests, the cabinet has been run continuously at 120°F. and 100 per cent relative humidity with condensation on the steel test specimens and cabinet walls.

Preliminary Studies. Preliminary tests of three general types have been conducted in the exploratory stages of this program. (1) The thickness and physical characteristics of the plasticized

polymer films proposed for use in this study were surveyed. (2) The severity of the humidity cabinet test apparatus was evaluated with a series of fluids comprising mineral oil fractions, hydraulic fluids without rust preventives, hydraulic fluids of the Spec. 51-F-21 type with mild turbine oil type rust preventives, and the Spec. MIL-O-6085A humidity cabinet type preservative instrument oil. (3) An investigation was made of quantitative methods for evaluating the extent of rusting of the test specimens in the humidity cabinet as a supplement to the visual observation.

Evaluation of Plasticized Acryloid Polymer. The study of film thickness and tackiness has been conducted so far with plasticized Acryloid polymers. That is, the final film on a solvent-free basis consists of Acryloid containing as a thinner, or plasticizing agent, from 20 to 50 weight per cent of a relatively non-volatile ester.

Acryloid-ester films have been chosen for study on the basis of compatibility with the hydrocarbon type of hydraulic fluids as well as the good low temperature properties of the Acryloid and ester components. Acryloid films plasticized with mineral oil fractions in the heavy neutral and bright stock range will also be included. If these studies show sufficient promise for a viscous thin film preservative as compared to the present solid or waxy thin film preservative, development work on a polybutene film plasticized with hydrocarbon oils will be conducted to parallel the work with the Acryloid-ester composition.

While the present Navy hydraulic oils, namely Spec. 51-F-21 and Spec. 51-F-23, are hydrocarbon compositions, there are some ester type hydraulic fluids in use. Acryloid-ester films can be redissolved by either hydrocarbons or esters, without impairing any of the properties of these fluids. Accordingly, this type of preservative film can be removed by the simple expedient of circulating the operational hydraulic fluid or lubricant through the system.

The ester-plasticized Acryloid film, for the same viscosity, can be formulated to have a lower vapor pressure than hydrocarbon-Acryloid films, thereby reducing the loss of the film by evaporation.

The final film will also contain on the order of 2 to 5 weight per cent of a humidity cabinet type rust preventive together with a small amount of an antioxidant. This latter additive would prevent the film from oxidizing to a degree that it was no longer soluble in the hydraulic oil when the equipment was activated.

There are a variety of Acryloids available and types can be selected to have good film forming and adhesive properties on metals and a high viscosity to prevent excessive drainage of the film from vertical surfaces. Acryloid is also a constituent of Spec. 51-F-21 and some Spec. 51-F-23 hydraulic fluids and is, in general, compatible with mineral oil lubricants. In addition, Acryloid shows good oxidation stability when protected with common anti-oxidants or oxidation inhibitors.

Acryloid type, as well as Acryloid molecular weight, can be varied. An Acryloid type that produces a hard "label lacquer" type of finish has been evaluated. This material is only sparingly soluble in mineral oil hydraulic fluids and lubricants. Further investigations have been confined to the Acryloid HF type, which is conventionally used in thickening mineral oil and ester-base hydraulic fluids and lubricants.

Tackiness of the film has been evaluated with a touch test. It should be emphasized that some degree of tackiness or stickiness will be encountered with Acryloid and other polymer films (V.I. improver types). It is believed that tackiness as such is secondary to the ease of re-dissolving the film in the hydraulic fluid and lubricant, and to obtaining an adequate film thickness.

Qualitative studies indicate that decreasing the relative molecular weight of the Acryloid will decrease the resultant tackiness of the film. Similarly, these studies show that for a given Acryloid molecular weight, increasing the concentration of a relatively non-volatile plasticizer component in the form of an ester reduces film tackiness.

It has been found that Acryloid HF 25 plasticized with 30 to 50 weight per cent of di-2-ethylhexyl sebacate results in a relatively non-tacky film. Compositions in this range have, therefore, been studied further in terms of film thickness and as a base for rust inhibitors.

A petroleum naphtha of 100°F. flash point has been used as a solvent for the Acryloid ester compositions. This naphtha is a straight run or virgin naphtha fraction with a boiling range of 275° to 336°F. and a viscosity at 100°F. of 0.77 centistokes.

Preparation of Test Specimens. The metal test specimens used in the film thickness and rusting work are either Armco iron or SAE 1010 steel, 16 gage sheet stock, 2 inches wide by 3 inches long. The specimens are rough polished with a disc sander using first 60 grit then 100 grit Behr Manning Speed Wet Metalite Durabonded discs. The final polishing is done by means of a motor driven vibrator (Black and Decker No. 44 sander) using first 1/2 then 3/0 Emery cloth. This polishing procedure is used for all of the test specimens for rusting and film thickness studies. The final polishing with the 3/0 Emery cloth is done immediately before use of the specimen. Rough polished strips are stored under Spec. 51-F-21 rust preventive hydraulic oil.

The strips, after the final polish, are washed successively in a good grade of thiophene-free benzene and diethyl ether, and immediately upon drying are immersed in the test fluid. The weight of the test strip is determined while immersed in a special weighing bucket filled with test fluid.

Film Thickness Studies. Some studies have been conducted on film thickness as a function of solvent concentration, Acryloid HF 25-

ester ratio in the non-volatile component, and temperature. To determine the film thickness, the test specimen is first weighed as described above. The test specimen is allowed to soak in the fluid for 15 minutes. The history of the test specimens following the soak period is given in the attached Table and Figures. In all cases where a film thickness is recorded, the test procedure includes wiping any excess fluid drainage off of the bottom edge with a clean Lucite scraper. That is, the film thickness represents essentially a uniform film, and the bead of fluid that collects on the bottom edge of the specimen during drainage is not included in determining this value.

The effect of volatile solvent concentration on film thickness is shown on Figure 2. These data were taken after 24 hours drainage at room temperature using as the non-volatile component a solution of 50 weight per cent Acryloid HF 25 in di-2-ethylhexyl sebacate. It can be seen that the film thickness increases with decreasing solvent concentration. The film thickness in this series of tests is probably related to the viscosity of the fluid containing the solvent and the rate of solvent evaporation. For a given solvent concentration, film thickness would be increased if the rate of solvent evaporation were increased by forced air circulation. For comparison, Tectyl grade 2 gives a film thickness of 0.0012 ($12 \times 10^{-4}$) inches, and Tectyl clear amber a film thickness of 0.0001 ($1 \times 10^{-4}$) inches under the same test conditions The Tectyl films, in general, are waxy or solid films while the Acryloid HF 25-di-2-ethylhexyl sebacate films are very viscous liquids.

The viscosity properties of these films are known, and compositions of this general type have been used as damping fluids. The viscosity properties of the Acryloid HF 25-di-2-ethylhexyl sebacate blends (solvent-free) are shown as a function of temperature on Figure 3, and as a function of Acryloid HF 25 concentration on Figure 4. The techniques used in measuring these high viscosity values are described in detail in report PRL 3.46-Apr49 entitled VISCOUS DAMPING FLUIDS.

The effect of Acryloid HF 25 concentration in the non-volatile component on film thickness is shown on Figure 5. These data are shown after draining at room temperature and also after drainage at 110°F. They indicate that there is little additional drainage for an increase in temperature of the test specimen from room temperature (70° to 80°F.) to 110°F. There is an increase in film thickness with increasing Acryloid HF 25 concentration. This is the trend anticipated on the basis o fluid viscosity.

The series of tests shown on Figure 6 have been carried out to determine the level at which the film thickness will be stabilized. The strips were initially allowed to drain and evaporate for 30 minutes at room temperature to permit the bulk of the naphtha to evaporate. The film thickness was determined on one strip at this point. This is the value shown for zero drainage time on Figure 6. The remaining eight specimens were placed in a convection oven at 110°F. Periodically, a strip was removed and the film thickness determined. Before each weighing

the excess fluid, which had drained to the bottom edge of the strip, was removed. These data indicated that a fairly stable film thickness is established after about 3 hours under these conditions.

These data show that films of a thickness comparable to commercial Spec. MIL-C-972 products can be achieved with an ester plasticized film.

Pumpability of Preservative Fluid. The preservative film considered here is being designed particularly for hydraulic and lubricant systems. One consideration in such applications would be the pumpability of the preservative compound through the lubricant or hydraulic system. Some thought has been given to this matter. The viscosity range of the preservative compositions considered thus far are well within the viscosity range of conventional lubricants. The viscosity properties of two compositions typical of those discussed are tabulated below.

| Preservative Fluid Composition, Wt.% | | | Centistoke |
|---|---|---|---|
| Petroleum Naphtha Solvent | Acryloid HF 25 | Di-2-Ethylhexyl Sebacate | Viscosity at 100°F. |
| 50 | 25 | 25 | 27 |
| 50 | 40 | 10 | 73 |
| Spec. 51-F-21 Hydraulic Fluid | | | 28 |
| Spec. 51-F-23 Hydraulic Fluid | | | 41 |

This Laboratory has conducted hydraulic pump tests using fluids containing bulk constituents of high volatility to determine the effect of high volatility on pump wear. These tests were conducted with a "mock up" hydraulic system using a Pesco model 349 gear pump. The test fluids consisted of a Spec. 51-F-21 type hydraulic fluid to which 30 weight per cent of hexane was added in one case, and 30 weight per cent isooctane was added in the other case. Isooctane has a normal boiling point of 211°F.; that of hexane is 137°F. Pump tests at 100°F. under severe conditions gave tolerable wear values and no operational problems in 100 hours of testing. Tests with the isooctane fluid were conducted at 180°F. and with the hexane fluid at 130°F. for 100 hours under severe pressure conditions without failure. These tests are described in detail in report PRL 3.35-May47 entitled A SUMMARY OF THE WEAR AND LUBRICATION PROPERTIES OF HYDRAULIC FLUIDS AS DETERMINED IN THE PESCO MODEL 349 GEAR PUMP AND THE SHELL FOUR-BALL WEAR TESTER. Thus, it would appear that a preservative fluid comprising a blend of Acryloid HF 25 in di-2-ethylhexyl sebacate with petroleum naphtha as a diluent can be prepared to have the desired viscosity range for hydraulic system operation. In addition, it should be operable as a fluid and lubricant for short periods of time under light loads without injury to the pump and other critical bearings in the systems.

Rust Tests Conducted in the Aminco Aire Humidity Cabinet. The Aminco Aire humidity cabinet described previously in this report has been

operated at 100 per cent relative humidity with condensation on the steel test specimens and on the cabinet walls for this series of rusting tests. As a check on the severity of the cabinet, a series of test fluids representing varying degrees of rust protection have been evaluated. Specimens of SAE 1010 steel and cold rolled Armco iron, polished in the manner described previously, have been used in these tests.

The results of these rust tests are shown on Table 1. Spec. MIL-O-5606 and PRL 3161 (a Spec. MIL-L-7808 type synthetic ester-base lubricant) do not contain rust preventives. Spec. 51-F-21 and 51-F-23 hydraulic oils contain a mild turbine oil type of rust preventive. PRL 3313 is a synthetic ester type of gear lubricant. It contains 0.5 weight per cent of Ortholeum 162, which is a commercial alkyl acid phosphate lubricity additive. The Ortholeum 162 apparently provides the rust protection in this fluid.

The remainder of the fluids listed are mineral oils or esters compounded to contain a humidity cabinet type of rust preventive. The rust preventive in all of these fluids is believed to be of the sulfonate class. The intervals during which rust was noted have some apparent lapses in observation times. These time intervals, in most cases, occurred during week-ends. The largest interval occurred over the Christmas period.

Several trends are evident from the data on Table 1. The use of mild rust inhibitors of the type employed in Spec. 51-F-21, Spec. 51-F-23, and in turbine oils are not effective in a humidity cabinet type of rust test. There is essentially no differentiation between Spec. 51-F-21 with a mild rust preventive and Spec. MIL-O-5606 with no rust preventive. The fluids containing sulfonates as the rust preventives show large improvements in rust protection in this test.

The rust protection afforded by the Spec. MIL-O-6085A requirements under the humidity cabinet rusting procedure is of the order of 4 days to a week. The rust protection obtained, as shown on Table 1, is much greater than the minimum listed in the specification. This may indicate that the test conditions in the PRL humidity cabinet may be milder than in some other humidity cabinet tests. Attempts should be made to correlate interlaboratory test severity with several reference fluids.

Current work shows rust preventives capable of tolerating the humidity cabinet conditions can be readily distinguished from mild rust preventives, or no rust preventive at all. A further distinguishing characteristic between a good rust preventive oil, and an oil with little or no rust preventive characteristics, is the amount of rusting noted for a comparable time interval after the first rusting is discerned. Rusting of the specimen with a non-additive oil is quite rapid and widespread. Rusting of the specimen with a humidity cabinet rust preventive is very slow by comparison with the non-additive oil. As indicated in the data on Table 1, a single rust spot in the significant area may be the only sign of rust for several hundred hours of test time. This points up the

value of a quantitative measure of rusting. Some work along these lines will be discussed in a subsequent paragraph of this report.

The synthetic gear lubricant, PRL 3313, evaluated in the humidity cabinet shows good rust protection. The PRL 3313 composition contains only 0.5 weight per cent of a commercial acid phosphate (Ortholuem 162) in addition to the constituents of the synthetic lubricant designated PRL 3161. PRL 3161 does not show good humidity cabinet rust protection.

It has been noted that acid phosphates and acid phosphites have been studied as corrosion preventives by the Armour Research Institute under an Air Force Contract. In general, the acid phosphates and phosphites were rated as relatively ineffective rust preventives. This Laboratory has, therefore, studied the rust protection of synthetic ester-base lubricants containing alkyl acid phosphates and alkyl acid phosphites. Some of the test results from this survey are shown on Table 2. It is apparent from these data that freshly prepared ester blends containing acid phosphates and acid phosphites are not effective rust preventives in the humidity cabinet tests.

The blends containing the acid phosphates and acid phosphites all show increases in neutralization number on storage at room temperature. The original PRL 3313 formulation that showed good humidity cabinet rust protection, was a sample which had been stored for about a year, and had incurred during this storage a neutralization number increase of about 5 mg. KOH per gram of fluid. Several blends containing alkyl acid phosphites were evaluated after storage and found to be good rust preventives in the humidity cabinet test. It can be noted, however, that the effectiveness as a rust preventive appears to be a function of neutralization number increase rather than storage time. Thus, samples containing secondary alkyl acid phosphites, which show good neutralization number stability on storage, are ineffective as rust preventives after storage.

It has been found in simple hydrolysis tests that alkyl acid phosphates and, to a lesser extent alkyl acid phosphites, can act as a catalyst to hydrolyze the ester linkages of the ester base stock to make an acidic component.

Perfluorobutyric acid is an additive which has the same general effect on the hydrolysis of an ester, but does not involve the presence of phosphorus in the additive molecule. It can be seen on Table 2 that the blend containing 1.0 weight per cent perfluorobutyric acid behaves the same way as the blends containing the acid phosphates and acid phosphites. That is, a fresh blend has essentially no rust preventive properties while a stored sample, which has an increased neutralization number, does exhibit good rust preventive properties in the humidity cabinet rust test.

Thus, it appears that the effective rust preventive is a soluble acidic material formed from the ester base stock itself. This is not unreasonable since compounds like lauryl acid maleate have long been known

to be rust preventives, and certain dibasic acids are excellent metal deactivators and metal coaters in oxidation and corrosion studies. The effect of the acidic component in the stored samples as well as its identity deserves more study. The preservative films being studied for application to hydraulic and lubricant systems contain the same ester and Acryloid as the synthetic gear lubricants on Table 2.

Preliminary Tests with Acryloid-Ester Films. Rusting tests have been conducted on the ester-plasticized Acryloid films without additives. These data are shown on Table 3. They indicate that in the humidity cabinet test there is no appreciable protection from rust by the Acryloid film without additives.

Several tests on Acryloid films with sulfonate type rust inhibitors are shown on Table 3 These tests are still in progress. The results of the protection achieved by conventional sulfonate type rust preventives in a plasticized Acryloid film appear promising.

Quantitative Rust Test Studies. Some work has been done to evaluate quantitatively the amount of rusting obtained on the test strip. Studies of this type have been conducted previously by this Laboratory in conjunction with a modified turbine oil rust test. These earlier studies are given in report PRL 3.28-Jan47 entitled DEVELOPMENT OF AN IMPROVED TEST FOR EVALUATING RUST PREVENTING CHARACTERISTICS OF FLUIDS, LUBRICANTS, AND ADDITIVES. Briefly, the quantitative procedure consists of weighing the polished steel strip before the rust test, subjecting the strip to rusting, pickling the rusted strip in an inhibited acid solution to dissolve only the rust, and then reweighing the strip. The amount of rusting is determined by the difference in specimen or strip weight as obtained from the two weighings.

The following is a brief description of a typical set of test conditions for pickling a specimen taken from the humidity cabinet. The specimen is immersed for 30 minutes in 180 ml. of the pickling solution maintained at a temperature of 70° to 80°F. The pickling solution contains phosphoric and hydrochloric acids with acridine as a pickling inhibitor; it is 13.5 normal with respect to phosphoric acid, 3.6 normal with respect to hydrochloric acid, and 0.009 molar with respect to acridine. The metal specimen is removed from the pickling solution, washed with distilled water, and then with acetone, air dried, and placed immediately in a tared weighing container under a mineral oil to prevent rusting of the active surface formed by the pickling. The cleaned strip is then weighed. The difference in weight between this final weighing and the weight of the polished strip before the rust test is reported in terms of milligrams of weight loss per square centimeter of surface.

Results of pickling both unrusted strips and strips that have been subjected to the humidity cabinet rust test are shown on Table 4. The weight loss from a freshly polished strip in the pickling procedure has been determined to be between 0.10 to 0.15 mg. per sq. cm. for both

the SAE 1010 steel and Armco iron test specimens. On the basis of past experience, values of 0.10 to 0.30 can be classed as light rusting, 0.30 to 0.60 as moderate rusting, and above 0.60 as heavy rusting. In general, the quantitative value agrees with the visual observation. There are some discrepancies, particularly in the case of inhibited fluids. These discrepancies between the quantitative measurement and visual evaluation are probably due to the difficulty in estimating visually the depth of the rust and corrosion. These quantitative rust determinations show promise of defining better the degree of rusting.

Modified Turbine-Oil Rust Test. Some previous work on a modified turbine oil rust test may be of considerable interest in the current PRL rust evaluations. These tests are described in Progress Reports issued by this Laboratory under Contract NOrd 7958(B). Reports PRL 2.36-Jan49 and PRL 2.40-May49 are two such reports containing pertinent information. Data are given on water leaching and water erosion in rusting tests conducted in the presence of high concentrations of liquid water and small quantities of preservative oil. These tests showed that some rust preventives could be leached from the oil phase by liquid water and yet the rusting of steel specimens placed in the water was prevented without being in direct contact with oil.

Conclusions. The ester-plasticized Acryloid HF 25 film exhibits desirable properties for a thin film type of preservative. A satisfactory film thickness can be achieved without undue film tackiness. The solubility of additives in the ester-plasticized Acryloid film is also good. Viscosities in the lubricant range can be achieved by petroleum naphtha solutions of the ester-plasticized Acryloid film. On the basis of data on compositions having similar lubricity and volatility properties, the petroleum naphtha solutions of ester-plasticized Acryloid should afford adequate lubrication for short time operation of hydraulic and lubricant systems under moderate loads and temperatures.

The Aminco Aire 160 humidity cabinet is operating satisfactorily. The severity of tests in this cabinet has not been evaluated, or calibrated, on an interlaboratory basis. The unit appears capable of distinguishing readily between no rust preventive and a good humidity cabinet type of rust preventive.

The ester-plasticized Acryloid films are not, by themselves, adequate rust preventives as judged by these humidity cabinet tests. However, the ester-plasticized Acryloid films show good susceptibility to rust preventives.

The effect of alkyl acid phosphites and phosphates on stored ester-base compositions indicate that an acidic product of the ester is an effective rust preventive. This behavior of the ester-plasticized Acryloid films will be investigated.

The use of a pickling procedure to remove rust quantitatively, without disturbing the unrusted surface, warrants further study. This

quantitative measure of rusting emphasizes differences in the degree of rusting that are not adequately brought out by visual observation alone. The quantitative rust measurement is being designed to complement the visual observation and not as a replacement for it.

Figure 1
OPERATING LIMITS OF AMINCO-AIRE 160 CONTROL UNIT

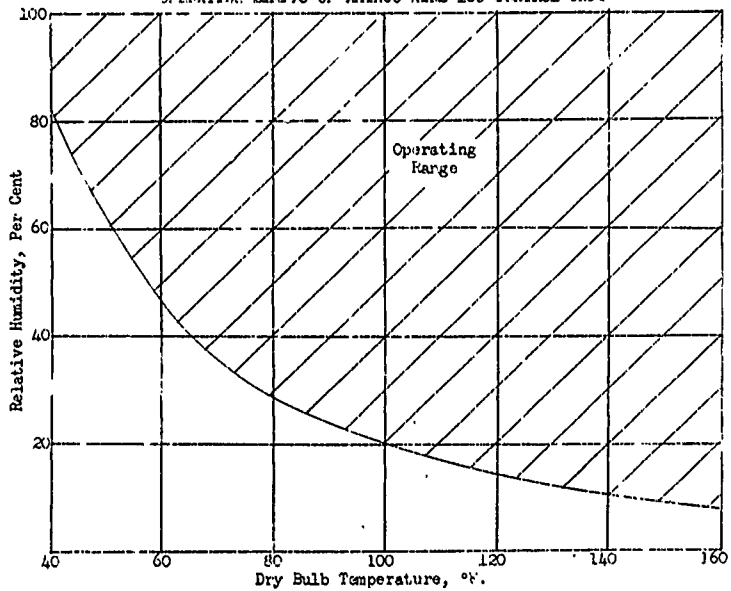


Figure 2

EFFECT OF VOLATILE SOLVENT CONCENTRATION ON FILM THICKNESS

TEST CONDITIONS: 2 X 3 INCH STEEL STRIPS SOAKED IN TEST FLUID FOR 15 MINUTES AND ALLOWED TO DRAIN AT ROOM TEMPERATURE FOR 24 HOURS.

NON-VOLATILE FILM - 50 WT.% ACRYLOID HF-25 IN DI-2-ETHYLHEXYL SEBACATE

TEST FLUID = INDICATED PER CENT OF NON VOLATILE FILM IN VOLATILE SOLVENT

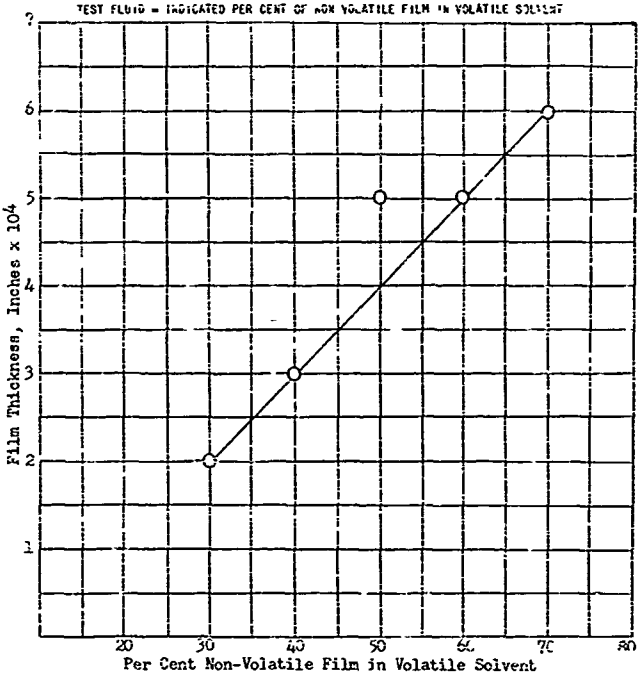


Figure 3

VISCOSITY-TEMPERATURE CHARACTERISTICS OF SEVERAL ACRYLOID-ESTER BLENDS

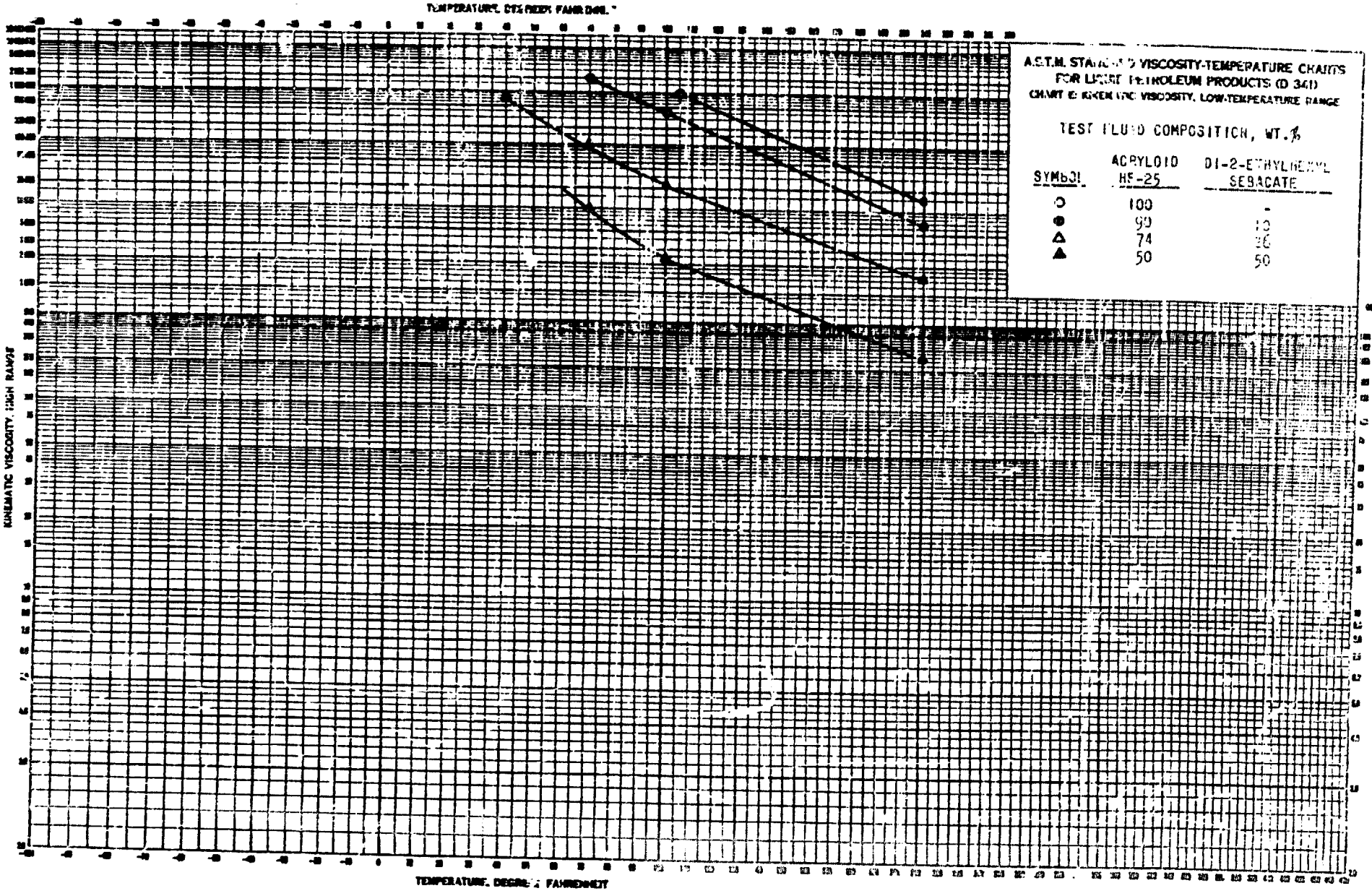


Figure 4

VISCOSITY-CONCENTRATION RELATIONSHIP FOR SEVERAL ACRYLOID-ESTER BLENDS

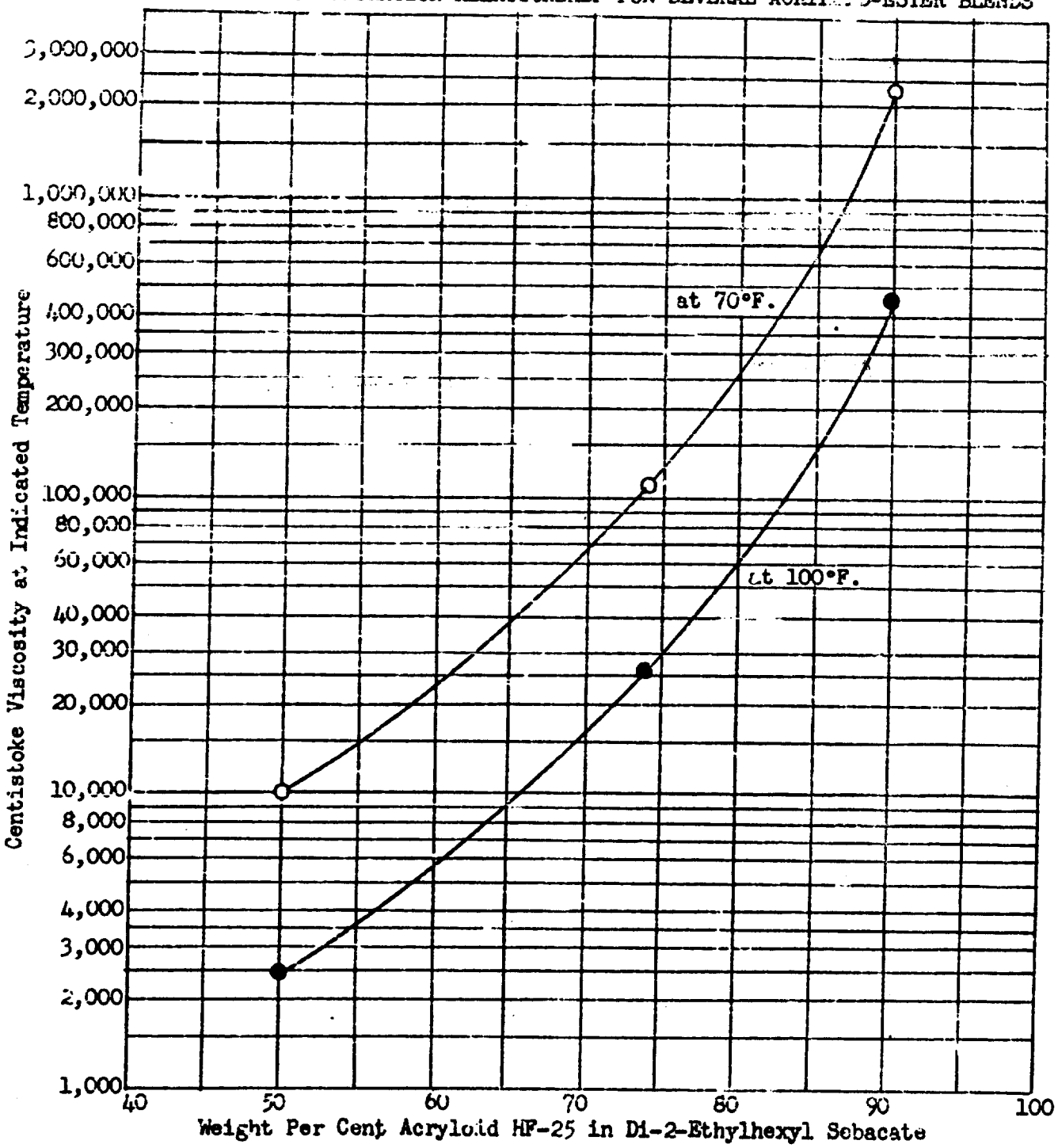


Figure 5

EFFECT OF ACRYLOID HF-25 CONCENTRATION ON FILM THICKNESS

TEST CONDITIONS: 2 X 3 INCH STEEL STRIPS SOAKED IN TEST FLUID FOR 15 MINUTES; ALLOWED TO DRAIN AT ROOM TEMPERATURE FOR 2.5 HOURS; AND PLACED IN CONVECTION OVEN AT 110°F. FOR 2 ADDITIONAL HOURS.

NON-VOLATILE FILM AS INDICATED

TEST FLUID = 50 WT.% NON-VOLATILES IN VOLATILE SOLVENT

○ = AFTER 2.5 HOURS DRAINAGE TIME AT ROOM TEMPERATURE
△ = AFTER 2 ADDITIONAL HOURS DRAINAGE TIME AT 110°F.

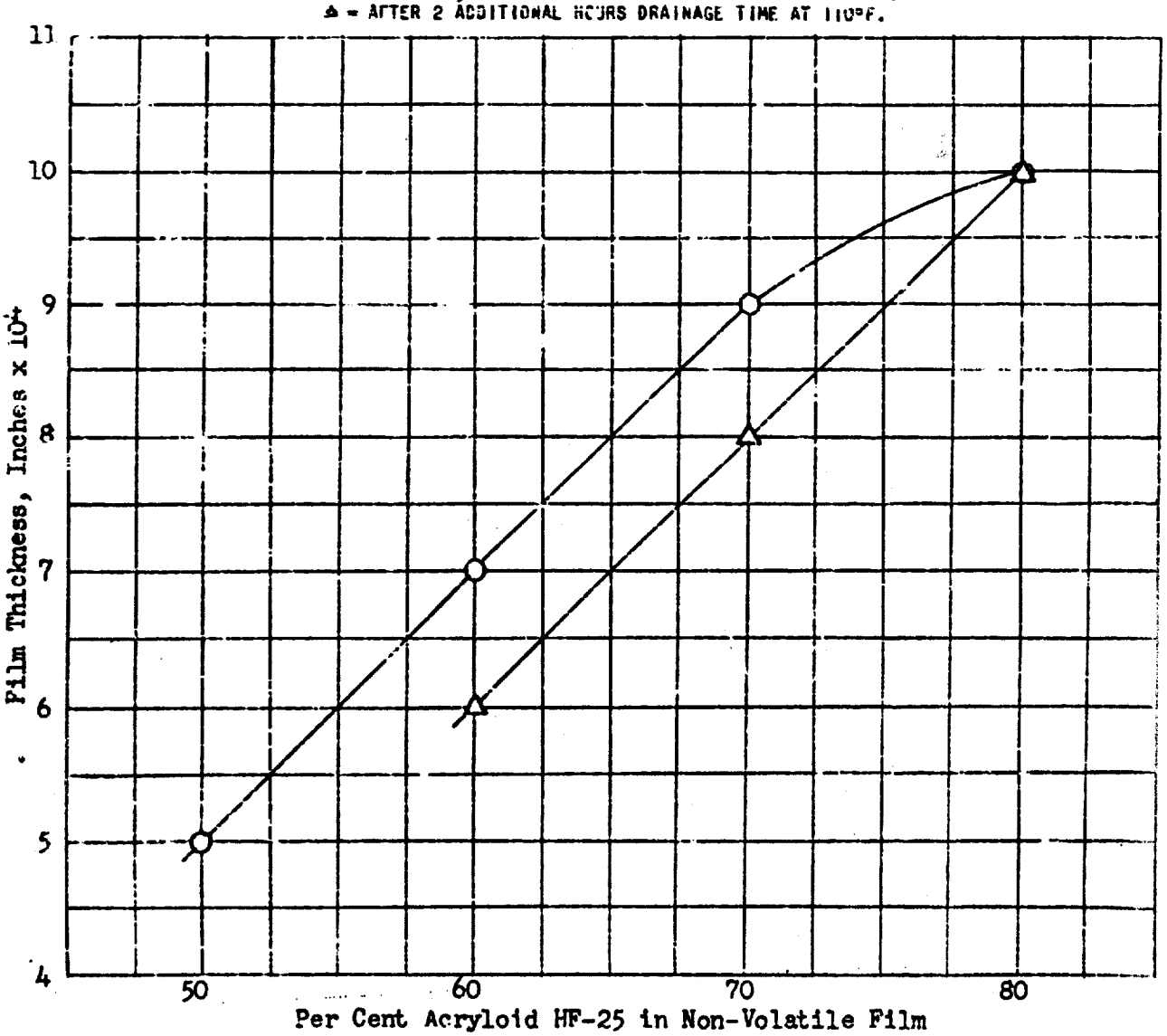


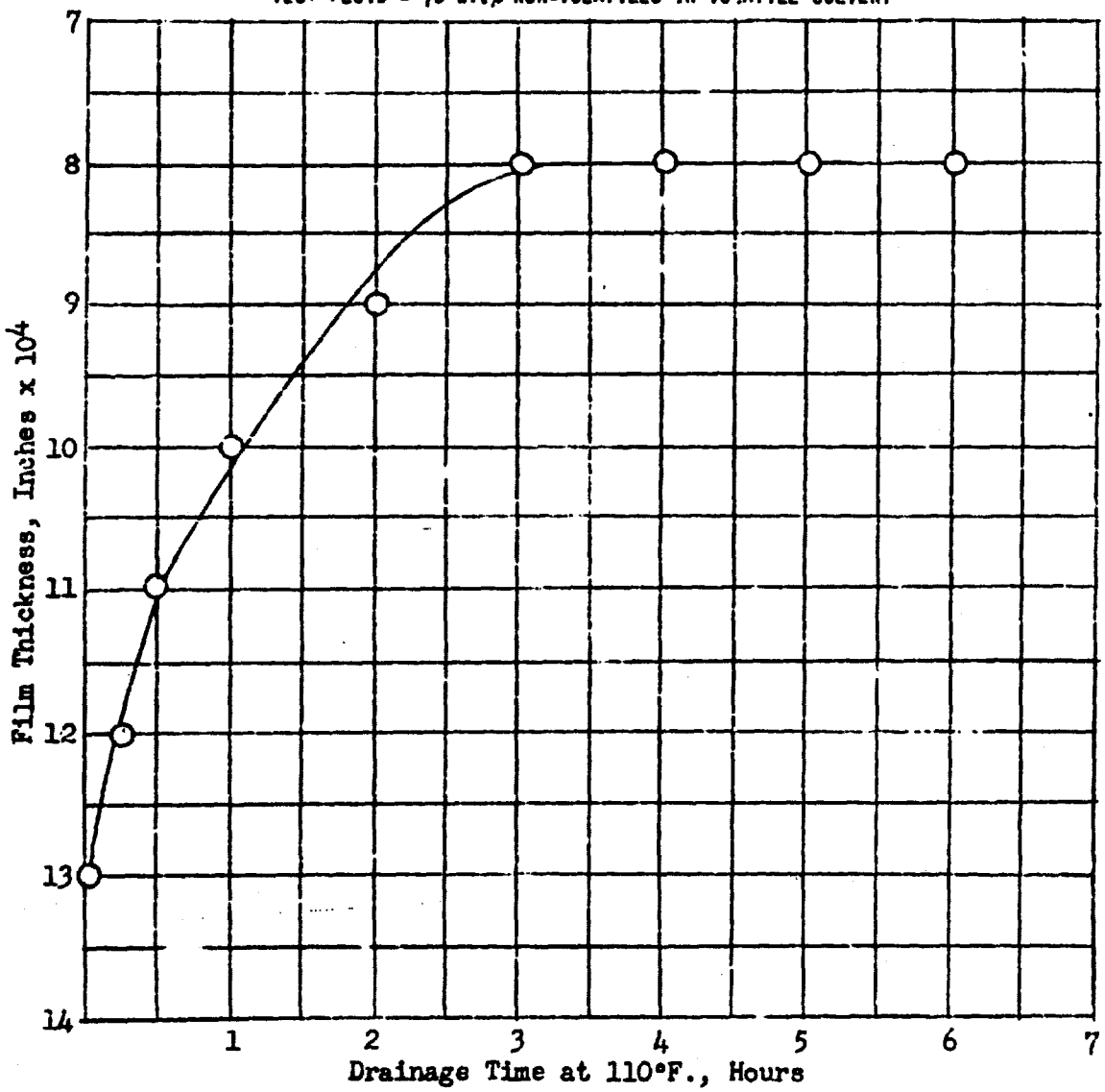
Figure 6

EFFECT OF DRAINAGE TIME ON FILM THICKNESS

TEST CONDITIONS: 2 x 3 INCH STEEL STRIPS SOAKED IN TEST FLUID FOR 15 MINUTES; ALLOWED TO DRAIN AT ROOM TEMPERATURE FOR 30 MINUTES; AND PLACED IN CONVECTION OVEN AT 110°F. FOR TIME INDICATED.

NON-VOLATILE FILM = 50 WT.% ACRYLOID HF-25 IN DI-2-ETHYLHEXYL SEBACATE

TEST FLUID = 70 WT.% NON-VOLATILES IN VOLATILE SOLVENT



## Table 1

### RUSTING CHARACTERISTICS OF SOME HYDRAULIC FLUIDS AND LUBRICANTS

TEST CONDITIONS: TEST TEMPERATURE = 120°F.; RELATIVE HUMIDITY = 100%; TEST SPECIMENS = 2 X 3 INCH BY 16 GAGE STRIPS OF METAL INDICATED. SPECIMENS SOAKED IN TEST OIL FOR 15 MINUTES, DRAINED AT ROOM TEMPERATURE FOR 2 HOURS, AND PLACED IN AMINCO AIRE 160 HUMIDITY CABINET.

| PRL NO. | SPECIFICATION | FLUID TYPE | SOURCE | TEST TIME, HOURS WHEN FIRST RUST APPEARED IN SIGNIFICANT AREA: SAE 1010 STEEL | AMINCO IRON | TOTAL TIME IN CABINET, HOURS | APPEARANCE AT END OF TEST TIME(3) |
|---|---|---|---|---|---|---|---|
| 3115 | MIL-O-5606 | AIRCRAFT HYDRAULIC FLUID | SODC(1) | 0-17 | 0-17 | 216 | HEAVY RUST |
| 3151 | MIL-L-7808 TYPE | SYNTHETIC GEAR LUBRICANT | PRL | 1-5 | 22-48 | 220 | MEDIUM RUST |
| 3313 | - | SYNTHETIC GEAR LUBRICANT | PRL | 622-695 | 622-695 | 1266 | LIGHT RUST |
| 2828 | 51-F-21 | NAVY GEAR OIL | SODC(1) | 0-5 | 0-5 | 220 | MEDIUM RUST |
| 2753 | 51-F-21 | NAVY GEAR OIL | SO CAL(2) | 0-24, 0-24 | - | 336 | MEDIUM RUST |
| 3297 | 51-F-23 | NAVY HYDRAULIC FLUID | SODC(1) | 3-20 | 3-20 | 500 | MEDIUM RUST |
| 2245 | 51-F-23 | NAVY HYDRAULIC FLUID | SO CAL(2) | 0-24, 0-24 | - | 500 | MEDIUM RUST |
| 2814 | AN-O-6A | LUBE OIL, LOW TEMP. | SO CAL(2) | 23-40 23-40 | - | 622 | MEDIUM RUST |
| 2595 | AN-O-7A | HYDRAULIC FLUID, PRESERVATIVE | SO CAL(2) | 500-550 622-695 | - | 1290 | LIGHT RUST |
| 2855 | AN-O-11 | MS-1465 INSTRUMENT OIL | SODC(1) | 550-600 | 550-600 | 1266 | LIGHT RUST |
| 2854 | AN-O-11 | UNIVIS P-38 | SODC(1) | 288-336 1000-1290 | - | 1290 | LIGHT RUST |
| 2866 | AN-O-11 | L-401 INSTRUMENT OIL | LEHIGH CHEM. CO. | 1000 | 1000 | 1900 | LIGHT RUST |
| 2864 | AN-O-11 | L-245 INSTRUMENT OIL | ANDERSON OIL CO. | 622-695 1458-1500 | - | 1500 | LIGHT RUST |
| 2920 | AN-O-11 | INSTRUMENT OIL | SHELL OIL CO. | 1000, >2000 | - | >2000 | NO RUST |
| 2907 | AN-O-11 | PC-10 INSTRUMENT OIL | ECLIPSE-PIONEER | 550-695 | 550-695 | 696 | LIGHT RUST |

(1) STANDARD OIL DEVELOPMENT COMPANY.
(2) STANDARD OIL COMPANY OF CALIFORNIA.
(3) THE SIGNIFICANT AREA OF THE PLATE IS DEFINED AS AN AREA 1-3/4 IN. BY 2-1/2 IN. CENTERED ON THE FACE OF THE PLATE. HEAVY RUST INDICATES PITTING AND RUSTING OVER 75 PER CENT OR MORE OF THE SIGNIFICANT AREA. MEDIUM RUST INDICATES PITTING AND RUSTING IN SEVERAL AREAS TOTALING 25 TO 75 PER CENT OF THE SIGNIFICANT AREA. LIGHT RUST INDICATES A FEW ISOLATED RUST SPOTS OVER THE SIGNIFICANT AREA.

Table 2

## RUSTING CHARACTERISTICS OF SOME EXPERIMENTAL GEAR LUBRICANTS

TEST CONDITIONS: TEST TEMPERATURE = 120°F.; RELATIVE HUMIDITY = 100%; TEST SPECIMENS = 2 X 3 INCH BY 16 GAGE STRIPS OF METALS INDICATED. SPECIMENS SOAKED IN TEST OIL FOR 15 MINUTES, DRAINED AT ROOM TEMPERATURE FOR 2 HOURS, AND PLACED IN AMINCO AIRE 100 HUMIDITY CABINET.

TEST FLUID PRL 3379 = 9.0 WT.% ACRYLOID HF-25 + 0.5 WT.% PHENOTHIAZINE IN DI-2-ETHYLHEXYL SEBACATE.
PRL 3405 = 9.0 WT.% ACRYLOID HF-25 + 1.0 WT.% PARANOX 441 IN DI-2-ETHYLHEXYL SEBACATE.

| PRL NO. | TEST FLUID (COMPOSITIONS IN WT.%) | NEUT. NO. (MG. KOH/GM. OIL) | FLUID STORAGE TIME, MONTHS | TEST TIME, HOURS WHEN FIRST RUST APPEARED IN SIGNIFICANT AREA: SAE 1010 STEEL | ARMCO IRON | TOTAL TIME IN CABINET, HOURS | APPEARANCE WHEN REMOVED FROM CABINET(1) |
|---|---|---|---|---|---|---|---|
| 3313 | COMMERCIAL BATCH 6931. 5.0 TRICRESYL PHOSPHATE + 0.5 ORTHOLEUM 162 + 0.001 SILICONE ANTI-FOAM IN PRL 3379 | 7.1 | 17 | 622-695 | 622-695 | 1266 | LIGHT RUST |
| 3313A | 5.0 TRICRESYL PHOSPHATE + 0.5 ORTHOLEUM 162 IN PRL 3379 | 5.1 | 17 | 336-400 | 336-400 | 984 | LIGHT RUST |
| - | 0.05 ORTHOLEUM 162 IN PRL 3379 | 0.2 | NONE | 0-24 | - | 72 | MEDIUM RUST |
| - | 0.10 ORTHOLEUM 162 IN PRL 3379 | 0.5 | NONE | 0-24 | - | 72 | MEDIUM RUST |
| - | 0.50 ORTHOLEUM 162 IN PRL 3379 | 2.0 | NONE | 0-24 | - | 96 | LIGHT RUST |
| - | 0.5 DI-2-ETHYLHEXYL ACID PYROPHOSPHATE IN PRL 3379 | [illegible] | NONE | 0-4 | 0-4 | [illegible] | MEDIUM RUST |
| | | 8.0 | 19 | 600-670 | - | 670 | LIGHT RUST |
| - | 0.5 DIMETHYL ACID PHOSPHITE IN PRL 3379 | 0.4 | NONE | 0-24 | 0-24 | 48 | HEAVY RUST |
| - | 0.5 DIETHYL ACID PHOSPHITE IN PRL 3379 | 8.2 | 18 | 622-670 | - | 670 | LIGHT RUST |
| - | 0.5 DIEUTYL ACID PHOSPHITE IN PRL 3379 | 0.1 | NONE | 0-24 | - | 48 | HEAVY RUST |
| | | 1.6 | 13 | 0-24 | - | 24 | HEAVY RUST |
| | | 12.9 | 17 | 600-670 | - | 670 | LIGHT RUST |
| - | 0.5 DIBUTYL ACID PHOSPHITE IN PRL 3405 | 0.2 | NONE | 0-24 | - | 48 | HEAVY RUST |
| - | 0.5 DIISOPROPYL ACID PHOSPHITE IN PRL 3379 | 2.0 | 13 | 0-24 | - | 24 | HEAVY RUST |
| - | 0.5 BIS (2-OCTYL) ACID PHOSPHITE IN PRL 3379 | 2.0 | 13 | 0-24 | - | 24 | HEAVY RUST |
| - | 0.5 DIMETHYL ACID PHOSPHITE IN PRL 2807 (A SPEC. AN-C-11 INSTRUMENT OIL) | 0.5 | NONE | 336-360 | - | 1248 | LIGHT RUST |
| - | 1.0 PERFLUOROBUTYRIC ACID IN PRL 3379 | 2.9 | NONE | 0-3 | - | 3 | MEDIUM RUST |
| | | 7.0 | 6 | 432-480 | - | >1000 | LIGHT RUST |

(1) THE SIGNIFICANT AREA OF THE PLATE IS DEFINED AS AN AREA 1-3/4 IN. BY 2-1/2 IN. CENTERED ON THE FACE OF THE PLATE. HEAVY RUST INDICATES PITTING AND RUSTING OVER 75 PER CENT OR MORE OF THE SIGNIFICANT AREA. MEDIUM RUST INDICATES PITTING AND RUSTING IN SEVERAL AREAS TOTALING 25 TO 75 PER CENT OF THE SIGNIFICANT AREA. LIGHT RUST INDICATES A FEW ISOLATED SPOTS OVER THE SIGNIFICANT AREA.



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Table 3

## FILM THICKNESS STUDIES WITH ACRYLOID-ESTER-VOLATILE SOLVENT BLENDS

TEST CONDITIONS: 2 X 3 INCH BY 16 GAGE STEEL STRIPS SOAKED IN TEST FLUID (INDICATED NON-VOLATILE BLEND IN VOLATILE SOLVENT) FOR 15 MINUTES STRIP ALLOWED TO DRAIN AS INDICATED. ACCUMULATED FLUID AT BOTTOM OF STRIP REMOVED BEFORE FILM THICKNESS DETERMINATION.

| BLEND | FILM THICKNESS, INCHES | | TEST TIME, HOURS WHEN FIRST RUST APPEARS IN SIGNIFICANT AREA(1) |
|---|---|---|---|
| | AFTER DRAINAGE AT ROOM TEMP. FOR 24 HOURS | | |
| 50 WT.% ACRYLOID HF-25 + 50 WT.% DI-2-ETHYLHEXYL SEBACATE RATIO OF NON-VOLATILE BLEND TO VOLATILE SOLVENT | | | |
| 30:70 | 0.0002 | | -- |
| 40:60 | 0.0003 | | 1-4 |
| 50:50 | 0.0005 | | 1-4 |
| 60:40 | 0.0005 | | 1-4 |
| 70:30 | 0.0006 | | 1 4 |
| | AFTER DRAINAGE AT ROOM TEMP. FOR 2-1/2 HOURS. | AFTER DRAINAGE FOR ADDITIONAL 2 HOURS AT 110°F. | |
| RATIO OF NON-VOLATILE BLEND TO VOLATILE SOLVENT = 50:50 RATIO OF ACRYLOID HF-25 TO DI-2-ETHYLHEXYL SEBACATE | | | |
| 50:50 | 0.0005 | - | |
| 60:40 | 0.0007 | 0.0006 | LESS THAN 1 |
| 70:30 | 0.0009 | 0.0008 | LESS THAN 1 |
| 80:20 | 0.0010 | 0.0010 | LESS THAN 18 |
| | AFTER DRAINAGE AT ROOM TEMP. FOR 2 HOURS AND AT 120°F. FOR 3 ADDITIONAL HOURS. | | |
| RATIO OF NON-VOLATILE BLEND TO VOLATILE SOLVENT = 50:50 50 WT.% ACRYLOID HF-25 IN DI-2-ETHYLHEXYL SEBACATE | | | |
| + 3.0 WT.% BARIUM SULFONATE | 0.0006 | | MORE THAN 168 |
| + 3.0 WT.% L-402 RUST INHIBITOR | 0.0006 | | MORE THAN 168 |
| 80 WT.% ACRYLOID HF-25 IN DI-2-ETHYLHEXYL SEBACATE | | | |
| + 3.0 WT.% BARIUM SULFONATE | 0.001[illegible] | | |
| + 3.0 WT.% L-402 RUST INHIBITOR | | | |

(1) THE [illegible]



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