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PART I

LUBRICITY PROPERTIES OF HIGH-TEMPERATURE JET FUELS

J. K. Appeldoorn
R. J. Campion
F. F. Tao, et al

ESSO RESEARCH AND ENGINEERING COMPANY

TECHNICAL REPORT AFAPL-TR-66-89, PART I
AUGUST 1966

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Air Force Aero Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force base, Ohio

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Research and Technology Division
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FOREWORD

This report was prepared by the Products Research Division, Esso Research and Engineering Company at Linden, N. J. under Contract AF33(615)2828. This program is administered by the Air Force Aero Propulsion Laboratory, Research and Technology Division, Air Force Systems Command with Arthur F. Levenstein, 1/LT, USAF as project engineer.

This report covers work conducted from 15 May, 1965 to 15 May, 1966. Significant contributions were made by W. G. Dikek, in the field survey, by C. L. Read in the literature survey and by Y-Ming Feng in the experimental data. It was submitted as a technical report by the authors 15 August, 1966.

This technical report has been reviewed and is approved.

Arthur V. Churchill

ARTHUR V. CHURCHILL, Chief
Fuels, Lubrication and Hazards Branch
Support Technology Division

ABSTRACT

A field survey of engine and pump manufacturers indicated that there is a potential problem whenever jet fuels are the only source of lubrication in pumps or controls. Problems encountered included wear, scuffing, sticking, seizure, and fatigue pitting. A literature survey confirmed that the problem existed but failed to pinpoint the causes.

The friction and wear performance of ten commercial fuels, chosen to represent a broad range of physical and chemical properties, differed markedly. These fuels were inspected for viscosity, volatility, hydrocarbon type, and trace constituents. The strongest factor affecting lubricity appeared to be the nature of trace polar components in the fuel. The exact components responsible have not yet been determined.

The occurrence of sticking in the fuel control valve of operational jet engines led to the examination of a number of commercial JP-4's from different sources. There was a good correlation between field performance of the fuels and their performance in the laboratory tests. It was found that as little as 15 ppm of corrosion inhibitors significantly improved the lubricity in laboratory tests of those fuels that lacked lubricating properties of their own. Other lubricity additives were even more effective.

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SECTION I.

INTRODUCTION

The goal of this work is to delineate the fuel variables that may affect friction, wear, and seizure of pumps and other equipment using jet fuel as the only fluid.

Field and literature surveys have shown that low viscosity, highly refined fuels have had lubrication problems, especially at higher temperatures. These surveys are reported in Section III. The cause of these problems has not been pinpointed, almost every variable having been claimed to be an initial factor: viscosity, volatility, dissolved oxygen, dissolved water, sulfur compounds, nitrogen compounds, acid compounds, aromatics, and olefins. Data are being obtained on all of these variables in this work.

Test devices used in this work are: (1) a ball-on-cylinder device, (2) four-ball wear and EP testers, (3) a Vickers vane pump, (4) a Falex tester, and (5) a Ryder gear machine. These devices are described and compared in Section IV.

Ten commercial fuels, covering a wide range of fuel types, were obtained, chemically analyzed, and tested in the devices listed above, in order to relate composition to wear, scuff, and friction performance. These results are given in Section V-A.

The effects at low concentration of a number of fuel corrosion inhibitors, EP additives, extracted polar fuel components, and various species of nitrogen and sulfur-containing compounds on the behavior of selected base stocks in the wear and scuff tests were investigated in order to determine what types of compound decrease wear and scuffing. These results, given in Section V-B and V-C will be used as the basis for further experiments aimed at elucidating the mechanism by which some compounds enhance boundary lubrication.

Included in Section V-B is a description of an investigation of the effects of temperature change on wear in the four-ball machine, aimed at separating the effect of viscosity change from other effects of temperature change.

After the start of the program, a lubricity-related sticking problem arose in the field with JP-4 in a particular jet-engine fuel-control valve, so a number of JP-4 samples were obtained and tested. The effect of JP-4 corrosion inhibitors on the lubricity of these fuels was investigated, since the discontinued use of these additives appeared to have triggered the control valve problem. This work is described in Section V-D.

A summary of the work to date, with conclusions and an outline of future work, are given in Sections VI and VII, respectively.

SECTION II

DEFINITIONS

The terminology used in friction and wear phenomena is often confusing. For this contract, the following definitions will be used:

Hydrodynamic Lubrication - lubrication when the surfaces never touch but are always separated by a fluid film. The ability of a fluid to maintain a full film is a function only of its viscosity. (This may not be true for viscoelastic liquids, but will certainly hold for the fuels being studied here.)

Boundary Lubrication - lubrication when the surfaces sometimes or always touch each other. This includes both the "mixed-film" regime, where some hydrodynamic lubrication still exists, and the "complete boundary lubrication" regime, where viscosity effects are negligible.

Viscosity - will always be in terms of absolute viscosity (centipoises) and not kinematic viscosity (centistokes). This distinction is important only when dealing with liquids of widely different densities. It should not be particularly important in this work because most of the hydrocarbons of interest are of the same density range.

Lubricity - the non-viscosity part of lubrication. Lubricity is a much abused term. In its narrow dictionary sense it means "a property that lessens friction." For this contract, however, the definition will be broadened to include friction, wear or scuffing. If two liquids have the same viscosity but one gives lower wear, or lower friction, or a lower tendency to scuff, it will be considered to have better lubricity. In general, the word will be used sparingly, and usually only to denote better performance that cannot be ascribed to viscosity. For example: "Fuel A gave lower wear, but it was not clear whether this was a result of its higher viscosity or its better lubricity." The lubricity of a liquid will depend also on the metallurgy and topography of the surface. Two liquids may have different lubricity on steel, but the same lubricity on gold.

Rubbing Wear - wear that occurs under non-scuffing conditions. This is the kind of wear that requires pencils and knives to be resharpened, that wears out shoes and courthouse steps, and is the kind usually observed in a four-ball wear test under light-load conditions. This is sometimes called "abrasive wear" but this assumes a mechanism that is not universally accepted. Other names have been "simple" wear, "normal" wear, and non-scuffing wear.

Scuffing - a severe regime of lubrication marked by higher wear and friction. This regime is entirely different from the "rubbing-wear" or "low-load" regime. Transition from one regime to the other is sudden and sometimes catastrophic. In the four-ball apparatus, a slight increase in load or speed can cause the wear scar to increase several-fold suddenly with a corresponding increase in friction. In the Falex, Almen, Timken, and SAE machines, scuffing results in seizure and failure of the parts. These tests measure the scuffing-load; that is, the load at which lubrication changes from "rubbing-wear" to scuffing. In gears, scuffing may occur without catastrophic failure because the gear teeth leave the zone of contact before extensive damage can be done.

It is important to differentiate between scuffing wear and rubbing wear. In many applications the important property is to prevent scuffing at all costs. A lubricant that gives very low wear under rubbing-wear conditions may not be at all effective in preventing the onset of scuffing. In other applications, a good E.P. lubricant (prevents scuffing) may not be at all satisfactory because it gives high wear in the low-load regime.

Abrasive Wear - wear caused by hard particles suspended in the fluid, or embedded in one of the wearing surfaces.

SECTION III

FIELD AND LITERATURE SURVEYS

1. FIELD SURVEY OF PUMP MANUFACTURERS

In order to take advantage of the existing knowledge, a number of pump manufacturers and engine builders were visited. A summary of the information gained is given in the following paragraphs. As a general conclusion, it can be stated that relatively little is known about the effect of fuel variables on pump failures except in the most general terms.

a. General

In today's jet engines the main fuel pumps are generally gear pumps operating at 800-1100 psi. These are satisfactory for the most part but are having some problems at higher fuel temperatures. These high temperatures are a result of supersonic operation and a high recycle ratio at high altitude cruise.

In advanced jet engines, the fuel is also being used as the hydraulic fluid to the nozzle control surfaces. Ordinary hydraulic oils do not have the thermal stability to survive in a closed loop system at the high temperatures involved. However, it is possible to use fuel in an open loop system that feeds to the main fuel supply to the burners.

The pump operating the fuel hydraulic system is a piston pump which must operate at 5100 rpm and 3000 psi with a fuel inlet temperature of 300 F. Fuel temperatures of over 500 F result.

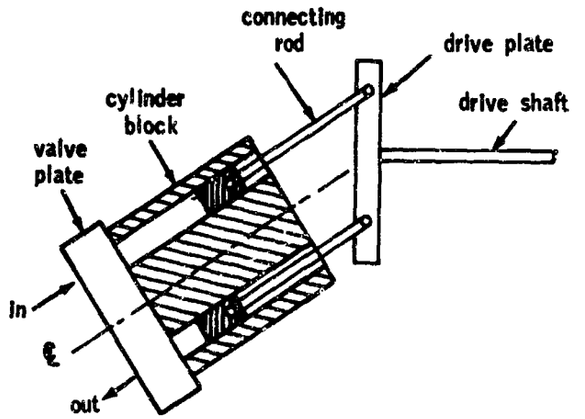
b. Pump Description and Problems

(1) Piston Pumps -

The advantages of the piston pump are higher pressures and better efficiencies than either a vane pump or gear pump. It also can be designed to give variable delivery rates. Disadvantages are complexity and high cost. The sketch on page 5 shows the configuration of a piston pump. It consists of a number of pistons (nine is a typical number) arranged axially around a center of rotation. The pistons move in cylinders cast integrally in a single block that rotates with the pistons. The pistons are attached by connecting rods to a drive plate and the main drive shaft, with swivel joints (generally ball-and-socket) at both piston end and drive plate end. The drive plate is set at an angle to the cylinder block and this angle causes the movement of the piston in the cylinder bore. The greater this angle the higher the pumping delivery rate.

As the piston-cylinder rotates upward, the piston is pulled out, drawing in fuel; as it rotates downward it pumps out fuel. Ports in the valve plates direct the flow from inlet to outlet.

PISTON PUMP



The piston pump can be made as a variable displacement pump by aligning the drive shaft and the piston axis, and using a drive plate that can be tilted at any desired angle. In this configuration the connecting rod is attached through a swivel joint to a shoe which rides against the drive plate.

There are several potential wear areas in the piston pump:

- Piston and cylinder bore.

Scoring and seizure of the piston in the cylinder has been observed. This results in a complete destruction of the pump, with ball and sockets torn loose and connecting rods bent and broken. The clearance between the piston and cylinder are necessarily small, so any lubrication failure can cause sticking, cocking of the piston, and seizure. In pumps where failure has not yet occurred, there are sometimes a number of transverse score marks indicating partial sticking and cocking. Wear of the cylinder bore is generally greatest at the center of the stroke where velocities are highest.

- Connecting rod--drive end.

The swivel joint here undergoes an angular movement equal to the angle of displacement--as much as 30°. Consequently, there is wear in this joint which shows up as end play, a looseness of the entire assembly. Although the ball is of a harder metal than the socket, one manufacturer reported the wear to be mostly on the ball. They attributed this to abrasive particles embedded in the socket that acted as a cutting tool. In the ultimate case, the ball can pull loose from the socket, resulting in pump destruction.

- Connecting rod--piston end.

This swivel joint undergoes very little motion and as a result can seize. The piston then tends to rock in the cylinder and can cause further trouble there.

- Connecting-rod shoe.

In the variable displacement version the shoe rubbing against the drive plate can wear excessively. This appears to be rubbing wear, with no evidence of scoring or seizure.

- Universal link.

Again in the variable displacement version, there is a universal link between the drive shaft and the drive plate. This is subject to wear and, if operated at zero angle for some time, to sticking.

- Ball bearing.

The ball bearing supporting the drive shaft is subject to fatigue pitting.

Wear and seizure are aggravated by higher temperatures. However, minimum clearances in the piston pump are obtained at low temperature.

(2) Vane Pump

The advantages of the vane pump over the piston pump is its ability to handle fuel containing abrasive solid particles such as rust. Its main advantage over the gear pump is its relative insensitivity to outlet pressure.

The vane pump consists of a rotor located eccentrically in a ring. The rotor has a number of radial slots fitted with vanes that are free to move radially in the slots. The vanes press outward against the ring trapping oil between them. Ports located in the side bushing control the inlet and outlet flow.

The most common type of vane pump is the double lobe type (See Figure 4). In this type the loads are balanced so there is no net load on the bearing.

The vanes are forced against the ring by a combination of centrifugal force and hydraulic pressure. In some designs, the outlet pressure is bled to the back of the vanes. This creates a sizable unbalanced pressure at the inlet side and can cause wear. For high pressure pumps, this pressure unbalance must be controlled. One design provides a passage between the outer space near the vane and the back of the vane. This balances the pressure between the two ends of the vane. In another design, the face of the vane is made concave and a hole through the length of the vane connects the face and the back to balance the pressure.

Problems with the vane pump seem to be mostly concerned with wear of the ring and the vanes against the ring, although there is occasional scoring of the port plate.

(3) Gear Pumps

Gear pumps have the advantage of simplicity and low cost. They are usually chosen for the main fuel pump on jet engines, delivering relatively large quantities of fuel at pressures of 800-1100 psi.

A gear pump consists of two intermeshing gears enclosed in a housing. Fuel enters at one side, is trapped between the teeth and the housing, and exits at the other side. An increase in outlet pressure causes an increased load on the gear teeth and also on the shaft bearings.

Failure in gear pumps can occur at either of these places. Lack of suitable lubrication can result in bearing seizure (sudden failure) or bearing wear, which allows the gears to move relative to the housing and thus cut into the softer metal of the housing. Scuffing of the gear teeth is also relatively common. The gears are case-hardened, so that as little as 0.003" wear will break through the case and then cause rapid wear. Tooth scuffing usually shows up first as a loss of volumetric efficiency at cranking speeds.

There is very little evidence of fatigue failure on gear teeth but some erosion has been noted on the non-drive side of the gears.

Wear of the side plate can also occur. If the plate is bronze, a so-called "gold-dust" failure takes place.

c. Pump Modifications for Fuel Use

It was generally agreed that wear problems increase when pumping lighter liquids. Thus, jet fuels are more troublesome than hydraulic oils, and gasoline is more troublesome than jet fuel. In pumping fuels the pump manufacturer has a more stringent requirement to meet than with oils. Several methods have been used to alleviate the problems.

- Harder metals.

In all pump designs wear and seizure are reduced by using hard metals. Tool steel against tungsten carbide is used in both piston pumps and vane pumps for high pressure output. These metals are costly and hard to fabricate, but are generally considered essential for satisfactory operation.

- Dissimilar metals.

One pump manufacturer, particularly, felt that wear and seizure were reduced by ensuring that the two rubbing surfaces were of dissimilar composition. This was considered secondary to hardness, however.

- Surface finish.

There was general agreement that very careful attention was necessary in the fabrication of parts. One manufacturer had carried out a computer solution for the hydrodynamic film thickness on the gear teeth when using jet fuel. This turned out to be 5 microinches indicating the necessity of a superfinish of 1 microinch roughness if a hydrodynamic film is to be maintained.

- Break-in.

Satisfactory performance was often highly dependent on a suitable break-in. The break-in procedure also depended on the eventual liquid to be pumped; for example, a break-in on JP-4 was satisfactory for continued use on JP-4, but was not satisfactory for further use on Avgas. For Avgas use, a slow break-in on Avgas was required.

One manufacturer said that with their gear pumps it was customary to lap in the housing with the gears, letting the pump do its own surface finishing.

- Surface plating.

For high speed operation, a thin layer of silver or gold can be plated on the rubbing parts. These are soft and prevent seizure. Lead or lead-indium flashing is also used. There was very little experience with solid lubricants such as molybdenum disulfide and those who had tried it were not enthusiastic.

d. Experience with Different Fuels

There is very little information available on the effect of fuel variables on pump wear and seizure. A summary of some of the problems that have been encountered in the field is given below.

A fuel pump wear problem was encountered many years ago with the Lucas piston pump on the Nene engine. It was found that the problem could be solved by making some mechanical changes and also by using 3% of Grade 1100 aviation oil in the fuel.

In a current engine test development program, fuel operating temperatures of 500F are encountered. This is above the thermal stability of regular jet fuels so a special high-stability fuel is used. This fuel has a lower vapor pressure, is more highly refined, and has a lower sulfur content than regular fuel. At low temperatures (120F) this fuel gave satisfactory operation in the pump (a Vickers piston pump), but when operated at 500F, a failure resulted within 50 hours. Using 3% aviation oil was not a satisfactory solution because the fuel would then no longer pass the thermal stability requirements.

Using the Ryder gear test as a screening tool, it was found that many EP and antiwear additives would give satisfactory wear performance but only three or four of these could pass the thermal stability requirements. Of these additives only one has been used in the large pump in the engine. This is used at a concentration of 320 ppm as a 50% solution in toluene. Understandably, the engine manufacturer concerned does not want to do additive testing in the full-scale engine stand, so that the data on the full-scale pump is limited. High-stability fuel is satisfactory at low temperatures, is unsatisfactory at high temperatures when run without additive, but is satisfactory at high temperatures with a suitable additive. There is no information whether ordinary jet fuel would be satisfactory at high temperatures because it has not been run under these conditions due to thermal stability limitations.

In order to screen fuels and additives, a small piston pump test has been developed by one engine manufacturer. This test utilizes a Vickers PF-24-3906-25 pump, which is not only much smaller but also differs in metallurgy from the full-scale pump: steel pistons in a bronze barrel instead of tool steel pistons in a tungsten carbide barrel. Fuel is pumped from an 8-gallon reservoir at 300F at 19.5#/min through a recycle system for 24 hours. Wear is usually observed as end play of the piston assembly. If the test is completed without failure, the pump parts are scrubbed with MEK and are used for the next test. This test has given good correlation with the larger piston pump: high-stability fuel passes at 120F inlet but fails at 300F. Failures were obtained at nine hours and eleven hours in two tests. Additives give satisfactory performance at 300F. An aviation kerosene was satisfactory at 225F.

This same engine manufacturer has had a similar high temperature pump failure problem with a gear pump test. Pumping a naphtha of 306F FBP (0.03% S,

12.4% aromatic, 2.7% olefin), an immediate failure was obtained. With a small amount of lubricity additive sufficient to give a Ryder load of 700#/inch, the pump failed at 300 hours. With enough additive to give a 1100-1200# Ryder, no failure was observed in 580 hours. The fuel in this test was changed every 100 hours.

During this reporting period information was received from one of the jet engine manufacturers that malfunctioning of a fuel-control valve was occurring in the field. This trouble seemed to have started at about the time that certain changes had been made in the jet fuel at the critical location, one of the changes being that the corrosion inhibitor had been omitted. A study of this problem was made under this contract and the results are given later in this report.

2. LITERATURE SURVEY

As a part of this contract, a search has been made of the literature pertaining to the lubricity of jet fuels. This search has covered three categories as follows:

- Wear of jet-fuel pumps
- Lubricity of pure hydrocarbons and non-additive fuels.
- Effect of trace constituents and additives in jet fuels.

In making this search, the following sources were checked:

- Library abstract card file on Jet Fuels, Lubricants, Lubrication and Pumps to 1963 and API Abstracts 1963 to date.
- Engineering Index.
- U.S. Research and Development reports.
- Technical Abstracts Bulletin.
- Search by Defense Documentation Center.
- Chemical Abstracts.

a. Wear of Jet-Fuel Pumps

Very little information on the wear performance of jet fuels in service was covered in the literature.

Five series of simulated flights of 3500 miles at Mach 2-1/2 and 3 to investigate the performance of three current quality jet fuels (ASTM Jet A) are reported by CRC(1). Each series represented 35 to 100 cycles (flights). Bearing failure of the fuselage booster pump was experienced in each series except the fourth and, in this series, the pump was replaced at the start because of imminent bearing failure, and again after 106 hours for loss of volumetric efficiency.

Erratic wear of fuel pumps was found in four Canadan airline operators of jet aircraft (2). It was the author's conclusion that kerosene gives better wear protection than JP-4 and will tolerate more contamination.

b. Lubricity of Hydrocarbons & Non-Additive Fuels

The effect of chemical structure has been studied by several investigators. Sakurai (3) studied benzene, decalin, heptane, cetane and squalene; Tamai(4) studied benzene, cetane, decalin and dicyclohexylmethane. Both concluded there was little friction-reducing effect of any of the hydrocarbons, particularly when compared to more polar compounds such as esters. Nagata, et al. (5), studying alkyl benzenes, reported a minimum friction and minimum wear when the side chain had 12-14 carbon atoms. Usually, however, higher molecular weight gave lower friction & wear.

Fein & Kreuz (6), using highly purified compounds, showed that chemical structure was more important than viscosity. Aromatic compounds gave lower friction and wear than alipnatics, with unsaturates intermediate. However, all investigators agree that small amounts of impurities can mask general structure effects.

The effect of viscosity on lubrication is well-known. However, there is some debate about the importance of viscosity in low-viscosity systems or

under heavy loads. Furey and Appeldoorn (7) reported that metallic contact and friction in a sliding system decreased smoothly as the viscosity was raised from 2 to 1000 cs. A small effect for pressure viscosity was also shown. The effect for viscosity was less in the low-viscosity range of jet fuels. Klaus et al. in a series of reports (8, 9), concluded that viscosity is important in gears and hydraulic pumps, where there is a considerable hydrodynamic component in the operation. They also showed a beneficial effect for viscosity in the four-ball machine, but concluded that it was a difference in volatility rather than viscosity that accounted for the effect. This conclusion has been challenged by Fein (10) and by Rounds (11).

Temperature generally increases the severity of operation, but does not always increase wear and friction. Typical behavior is that reported by Hopkins and St. John (12): raising the temperature in a four-ball test causes a sudden increase in torque -- obviously the transition from rubbing wear to scuffing. The effect has been amply confirmed by others (e.g., 9, 13, 14).

The cause of the temperature effect is more controversial. In early reports, Klaus et al. (9) attributed this to a decrease in viscosity, and concluded that tests on a low-viscosity fluid at room temperature would be equivalent to tests on a high viscosity fluid at higher temperatures, provided the viscosities were matched. Later, they believed that volatility differences at elevated temperatures were more important. Softening of the metal surfaces has also been suggested as a possibility, but this has not yet been established as a major factor.

On the other hand, temperature can also cause an increase in oxidation, with the formation of polar compounds of good lubricity (9).

c. Effect of Additives and Trace Components

The importance of trace amounts of polar compounds is well-known. Excessive refining can remove these compounds (as, for example, in medicinal white oils) to give a liquid that is no longer a lubricant. Little has been done in identifying these polar impurities, however.

Several investigators have examined the effect of dissolved oxygen. Feng and Chalk (15) reported that removing dissolved oxygen decreased the wear rate with SAE 1015 steel, but greatly increased the wear rate with cast iron. Klaus and Bieber (8) concluded that oxygen in concentrations up to 0.2 ppm was a good antiwear agent for steel-on-steel, but their data make this appear to be more of a temperature effect. At higher concentrations of dissolved oxygen, there was a decided pro-wear effect. No effect for dissolved oxygen was found if the lubricant was an ester, polyphenyl ether, or chlorinated biphenyl. Rounds (11) has questioned the validity of Klaus' conclusion.

Fein and Kreuz (6) reported that for squalane, dissolved oxygen increased wear but prevented seizure. For cyclohexane, no effect was noted; for benzene, oxygen reduced wear but did not prevent seizure. Some change in the wear product from FeO to Fe_2O_3 and Fe_3O_4 was found as oxygen increased. The significance of oxygen has been questioned by Owens et al. (16).

Kichkin et al. (13) evaluated several additives in a wide-cut jet fuel of Russian origin. Metal deactivator had little effect, but a combination of antioxidants (substituted phenol and phenylenediamine) at 0.1% concentration improved the load-carrying ability. However, these latter may seriously affect

thermal stability, based on the adverse effect found for sulfur compounds in general (17).

In a series of reports (18), Conboy examined the feasibility of lubricating jet-engine roller-bearings with jet fuel containing various additives at 1% concentration. In a test rig at 650-700F, the best additives were found to be phosphates and phosphites, of which tri-p-tolyl phosphorothionate $(Me\bigcirc O)_3 P = S$ was preferred. This additive was evaluated in a 100-hour test at 500F in a J-65 engine, lubricating the center and rear main bearings. Wear and corrosion were low but carbon deposit was heavy in the cage pockets.

Ku and Lawler (19) evaluated the use of various EP additives in a 525F end-point kerosene as lubricants in the Ryder gear test and WADC high-temperature bearing test. The Ryder tests were at 165F so that the fuel was in the liquid phase, but in the WADC test, the bearings were at 600F and were lubricated by a jet of fuel which partially vaporized. In both tests, additive combinations were found that gave better load-carrying capacity than a MIL-L-6068A lubricant. Zinc dialkyldithiophosphate and some proprietary ashless additives were the most effective.

d. Summary

Very little information is available in the literature about the wear characteristics of fuels in actual operation of jet engines. The low viscosity, high volatility and relative purity of these fuels have been singled out as major causes for poor lubrication, with temperature aggravating the condition. Additives look promising as a way to attain better load-carrying ability, but some may lead to heavier deposits and so be unsatisfactory.

SECTION IV

TEST METHODS

1. DESCRIPTION OF TEST INSTRUMENTS

From the field survey it appears that the wear and seizure problems encountered are identical with all pump types. The maintenance of the desired hydrodynamic film is not possible because of the high loads and low viscosit'es involved. Higher speeds generate more heat, causing the viscosity to drop further, which in turn brings on increased rubbing and more heat generation. The use of harder metals helps by reducing the area of elastic contact, thereby reducing the frictional heat. Similarly, antifriction compounds in the fuel, either naturally occurring or intentionally added, reduce friction and prevent wear and scuffing. The ability of any particular pump to resist wear and scuffing depends on many factors, among which are unit load, rubbing speed, configuration of rubbing surfaces (ease of forming a hydrodynamic wedge), heat removal, viscosity and inherent coefficient of friction. It does not appear possible nor even desirable to try to duplicate all of these conditions in the laboratory. Rather it will be the objective of this program to discover the fundamental differences among fuels that govern their lubricating behavior, to apply this knowledge to the performance of laboratory pumps and gear tests, and to extend this information to predict behavior in full-scale field equipment.

In this program five test devices were used for lubrication testing. They were (1) The ball-on-cylinder device to determine friction and wear in the "mixed-film" regime between hydrodynamic and complete boundary lubrication, (2) a standard four-ball apparatus to measure wear in the more heavily loaded region and also to determine the "scuffing-load", (3) a Vickers vane pump to measure wear and loss of volumetric efficiency in an actual pump, (4) a Falex tester to measure EP performance, and (5) the Ryder gear test to measure tooth scuffing. These test devices are described below.

a. Ball-on-Cylinder Device

(1.) General Description

This apparatus measures metallic contact and friction and has been previously described.(20) The apparatus is shown in Figure 1. The system, consisting basically of a fixed metal ball loaded against a rotating cylinder, i one of pure sliding

The extent of metallic contact is determined by measuring both the instantaneous and average electrical resistance between the two surfaces. In general, the electrical resistance fluctuates very rapidly from a very high value to a very low value, suggesting that metallic contact is discontinuous. The average recorded resistance, therefore, is a time average and is consequently related to the percent of the time that metallic contact occurs--hereafter referred to as "percent metallic contact."

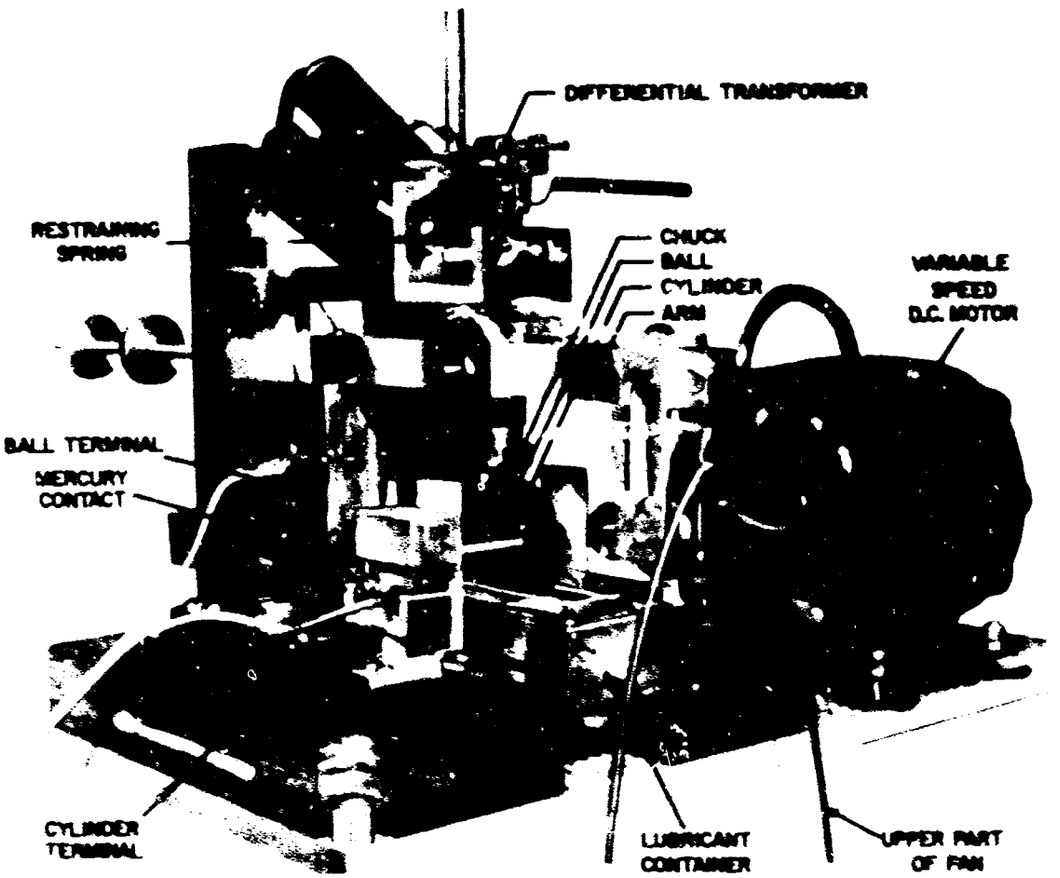


FIGURE 1 PHOTOGRAPH OF BALL-ON-CYLINDER MACHINE

The friction between the ball and cylinder is measured by means of a small differential transformer and is recorded continuously. The differences in frictional behavior between fuels is often not so much in the average level as in the relative smoothness of the trace. A poor fuel gives a jagged trace, indicating stick-slip, which is easy to see, but hard to express as a number.

Wear of the ball or cylinder can be determined by making direct measurements under a microscope. The wear scar on the ball is not circular but elliptical, with the major axis perpendicular to the direction of travel. This comes about because of the wear of the cylinder, which is somewhat softer than the ball. The wear scar reported is the average of the major and minor axis.

With this apparatus, the entire region from hydrodynamic (no metallic contact) to pure "boundary" lubrication (continuous metallic contact) can be readily investigated. There is generally a close correlation between friction, wear, and percent metallic contact. However, percent metallic contact loses its significance at higher loads where the contact is 100% for all fuels. Also, where stick-slip is observed (very erratic friction) the ball literally chatters on the track, giving a misleadingly low value of metallic contact. For this study, the metallic contact measurements are of importance mostly in detecting the formation of a non-conducting layer on the rubbing surfaces. This layer comes from the reaction between the metal surface and a fuel additive, and generally results in lower friction.

For non-additive fuels, the wear scar is a good measure of the degree of friction. Wear scar diameter (WSD) is therefore quoted extensively. For fuels containing additives or large amounts of sulfur or nitrogen compounds, the wear scar may not reflect the degree of friction. These cases are always notated in this report.

(2) Test Specimens

The test balls used in this study are standard half-inch Grade 1 balls made of AISI 52100 steel and having a surface roughness of about 2 micro-inches CLA (Center Line Average). The cylinders (1.75 in. diameter) are also made of AISI 52100 steel and have a surface roughness of about 10-12 micro-inches CLA. The hardness of the balls is 65 Rockwell C; of the cylinder 58 Rockwell C.

(3) Test Procedure and Conditions

In these tests, the metallic contact and frictional behavior of a given lubricant at a given load and speed are recorded with time. The tests were generally run for 32 minutes at room temperature (77F), and at 240 rpm (56 cm/sec sliding speed). Loads were varied from 15 to 1000 g, corresponding to mean Hertz pressures of 21,800 to 82,000 psi. In each test, a new ball and fresh track were used. There is some variation in the test results from cylinder to cylinder, probably because of minor differences in out-of-roundness. This source of error was minimized by making comparative runs on the same cylinder (10 or 12 separate tracks) thus allowing a direct relative rating.

b. Four-Ball Wear and EP Testers

One of the most common instruments used in lubricity studies is the four-ball wear tester. Basically, the machine consists of a spherical metal ball held in a rotating chuck, in contact with the faces of three stationary metal balls. This simple pyramidal geometry allows an accurate evaluation of wear caused by the sliding bodies in contact. The frictional pull can also be computed via a simple spring

gauge. At the conclusion of the test, the three cell balls are studied microscopically to determine the size of the wear scar produced. Such scars are generally circular or slightly elliptical in form, with relatively uniform vertical striations present in the worn area. The parameters that appear to be significant in determining wear scar diameter (WSD) are load, speed and time.

The instruments used in this investigation are the Normal Four-Ball Wear Tester (Scientific Precision Company, Chicago, Illinois, Catalog #73603) and the Shell Extreme Pressure Four-Ball Tester (Catalog #2008). The normal wear tester can be operated under a number of test conditions. The applied loads can be varied for 0.1 to 50 kg, the temperature can be controlled from ambient to 250C and three machine speeds are available; 600, 1200 and 1800 rpm. A modification is being made to allow the use of loads up to 100 kg.

The Shell Extreme-Pressure Four-Ball Tester is limited to one speed, 1800 rpm, has no temperature control and can be operated at loads up to 800 kg. The operation of the EP tester is similar to that described for the normal wear tester. However, it is customary to use the EP tester for a series of 10-second or 1-minute tests at increasing loads. At some load--called the "scuffing-load" or "seizure-load"--the size of the wear scar suddenly jumps from around 0.3-0.4 mm to 1.5-2.5 mm. This is accompanied by a corresponding increase in friction and noise. Further increases in load will eventually cause the four balls to weld together. The "weld-point" has not been determined in the investigation.

c. Vickers Vane Pump Test

(1) General Description

A schematic diagram and a photograph of the Vickers Vane Pump system are shown in Figures 2 and 3. The pump is a positive displacement vane pump, Vickers V-104-Y-10 type, with a rated capacity of 1.8 gpm at 0 psi and 1.1 gpm at 1,000 psi. It is driven by a 2 hp motor at 1155 rpm. The fluid circulates through a pressure relief valve, sequence valve, rotameter, cooler and sump of ten-gallon capacity. The temperature of the fluid in the sump is thermostatically controlled by an electronic relay. The flow system is connected with 3/8 inch stainless steel tubing. A calibration burette is installed in parallel with the rotameter. The fluid can be bypassed into the burette for precise measurements of the flow rate.

The pumping cartridge, as shown in Figure 4, is replaceable. It consists of 12 vanes (15 mm x 12 mm x 2 mm) placed freely in the slots of a rotor and confined by a ring. The vanes are forced outward by both centrifuged force and the outlet pressure of the fluid which is fed behind the vane. Both sides are covered with a bronze bushing. Major wear takes place due to the sliding action between vanes and the ring. Minor wear occurs on the surface of the bushings.

A secondary device is attached to the pump system. It consists of a pair of hydraulic cylinders, one of which is deiven by pump pressure through an arrangement of a solenoid valve and limit switches. Its reciprocating motion drives the piston of the second cylinder in which the test fluid is charged under N_2-pressure at one end and discharged at the other end. Wear, leakage rate past the piston rings and surface finish of piston assembly are measured. To date, this secondary device has not yet been used for this project.

Each test was made at a specified pump discharge pressure and specified sump temperature. Because of the low viscosity of jet fuels relative to the usual hydraulic oils, the highest pressure possible was only 350 psig. Test duration was

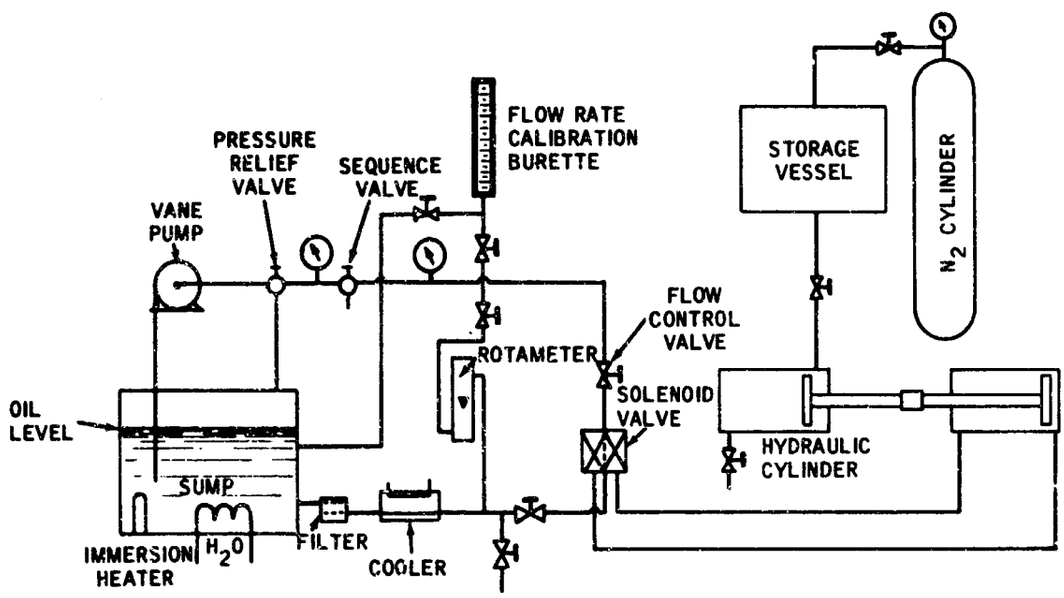


FIGURE 2 SCHEMATIC DIAGRAM OF VICKERS VANE PUMP SYSTEM

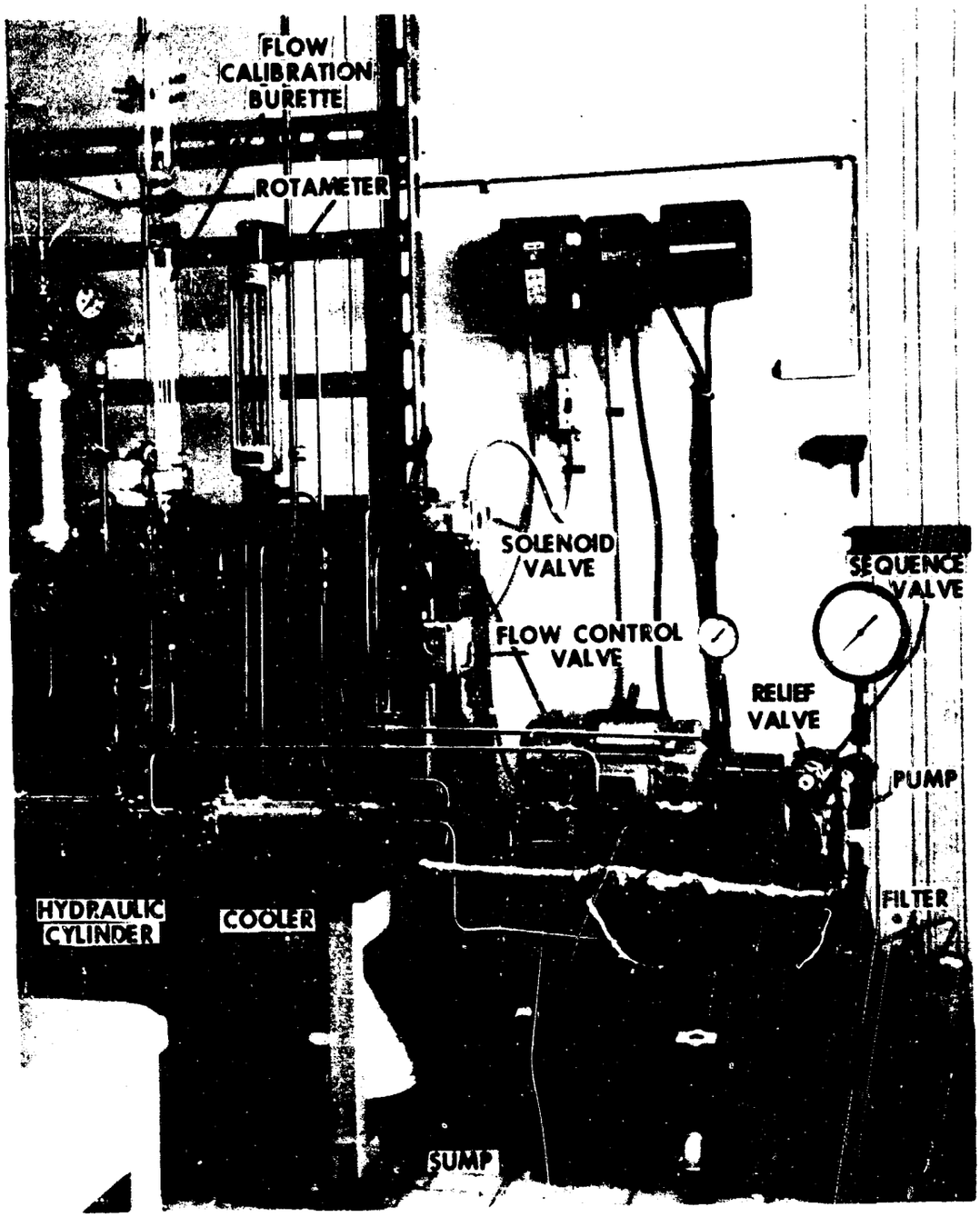


FIGURE 3 PHOTOGRAPH OF VICKERS VANE PUMP SYSTEM

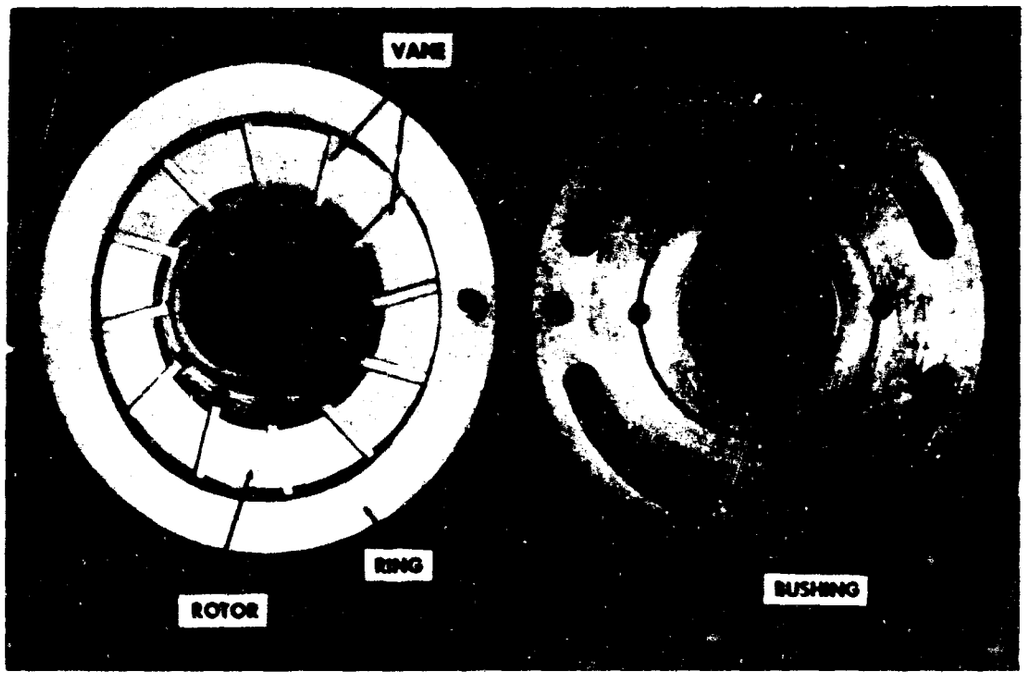


FIGURE 4 COMPONENTS OF PUMPING CARTRIDGE OF VICKERS VANE PUMP

24 hours, and a new pumping cartridge was used for each run. All the components were weighed and their surface roughness measured by a Talysurf Profilimeter.

d. Falex Wear Tester

This apparatus, commonly used as an EP wear tester, consists of a 1/4-inch diameter pin (SAE 3135 steel) rotating at a constant speed between two V-shape blocks (AISI 1137 steel). This assembly is immersed in the test fuel during a test. The load is applied by pressing the V-blocks against the pin and is measured on a gauge calibrated to read total pounds on the faces of V-blocks. The friction between the contact surfaces is measured by a strain gauge.

In these tests, a starting load of 100 lbs is held for two minutes. The load is then increased in 50 lb increments and held for one minute after increment until failure occurs. The criteria for failures is that the load cannot be maintained at a constant level without an abrupt increase of friction torque being observed. This is recorded as scuffing load.

e. Ryder Gear Test

(1) General Description

The Ryder Gear Test is a standard method (Federal Test Method 791a) to measure the load-carrying ability of lubricating oils. The test gears are special AMS-6260 steel spur gears which are combined with two "slave gears" in a "four square" arrangement. Loading via oil pressure causes an axial movement of one gear shaft relative to the other, imposing a load on the test gears. The lubricant (a fuel, in this case) is sprayed on the teeth of the test gears. The operating conditions, which were set up to evaluate lubricants rather than fuels, call for an inlet fuel temperature of 165F and incremental five-pound loading steps of 10-minute duration. After each 10-minute period the gears are inspected through a microscope and the area of scuff on each tooth is noted. The average area of scuff is then computed.

This sequence is followed until the average gear tooth scuff is 40%. The average percent of tooth area scuffed is plotted on a semi-logarithmic scale against the load pressure, in psig. By convention, the result at 22.5% scuff is used in the evaluation. Two determinations can be made for each set of gears by a simple reversal of the two gears on their shafts. (These are referred to as tests on side "A" and side "B".)

(2) Smaller Load Increments to be Adopted

Since the Ryder Gear-Erdco Universal Tester is accepted as a useful measure of the load-carrying ability of fuels and lubricants, several antiwear additives were evaluated by this technique. Because the test was originally developed to evaluate lubricants rather than fuels, the specified loading conditions may be too severe for fuels if the load-carrying capacity of the fuel is low. In this case, few steps will be necessary to produce high scuff with resulting error in the evaluation of the 22.5% scuff point. For instance, less severe increments which can be used are three-pound steps of ten-minute duration or three-pound steps of five-minute duration. For the base case, pure Bayol 35, this was especially important since at five-pound per ten-minute steps, Side A had no points below 22.5% and Side B had only one. Under the more gradual loading conditions of three pounds per ten-minutes and three-pounds per five minutes, two points were obtained below 22.5% for each side.

As can be seen in the table below, the choice of load and time increments (whether five-pound or three-pound steps, five-minute or ten-minute duration) had little effect.

Effect of Load and Time Increments in Ryder Test

Fuel: Bayol 35

Operating Increments		Scuff Load, Pound/Inch	
Load, lb	Time, min	Single Test	Average
3	10	339, 678	508
3	10	493, 493	493
3	5	628, 452	540

Therefore, the more precise 3 lb/10-minute step will be used for most of the Ryder Gear tests in this program.

2. COMPARISON AND EVALUATION OF TEST INSTRUMENTS

A necessary part of this program was to establish the ability of the various test devices to detect small differences in lubricating properties between fuels, since in most cases the devices had been developed to test more viscous lubricating oils. Both wear and scuff testers were used. Their usefulness for this program is discussed below.

a. Comparison

(1) Wear Testers

There was general agreement in the ranking of fuels between the three devices used to measure wear--the ball-on-cylinder, four-ball, and Vickers vane pump. This is shown in Table I which compares wear results for the three devices for nine of the commercial fuels. The ranking correlation analyses in Table I show that the correlation between the ball-on-cylinder and four-ball testers is significant at the 99% level. The ranking correlation between the four-ball machine and the Vickers vane pump was significant at the 95% level. These good correlations, together with the fact that the rankings by these machines agree with field experience with pump-wear problems, indicate that these tests give useful measurements of the wear prevention properties of jet fuels under loaded boundary lubrication conditions.

(2) Scuff Testers

Three devices were used to measure scuffing effects--the four-ball tester, Falex tester, and Ryder gear test. The Ryder gear machine was too severe to detect the differences in EP performance of fuels, although the effect of high (0.1%) concentrations of lubricity additives in fuels could be seen. The Falex test was capable of dividing the 10 commercial fuels into two broad classifications--the five most highly refined fuels (Bayol 35, RAF-173-61, PW-523, 75LN-LV and AFFB-3-65) and the low viscosity naphtha were grouped together as the poorest antiscuff performers. The JP-4, JP-5, RAF-176-64 and the diesel fuel were shown to have better load-carrying ability than the above six fuels. This classification is in agreement with the more selective ranking given by the ball-on-cylinder, Vickers vane pump and four-ball wear results in a rubbing wear regime.

The four-ball machine has not been evaluated as a scuff-tester at this time.

Table I

Correlation Between Wear Testers

A

Comparative Wear Test Data (*)

Fuel	Four-Ball Test (10 Kg, 1200 RPM, 97F) Wear Scar Diameter (mm) (Adjusted to 60 min.)	Ball-On-Cylinder Test (240g, 240 RPM, 77F) Wear Scar Diameter (mm) (at 32 minutes)	Vickers Vane Pump (350 psig, 90F) Wear mg
AFFB-3-65	1.04	0.58	4317
PW-523	0.86	0.64	4944
RAF-173-61	0.81	0.56	266
BAYOL 35	0.80	0.42	5354
75-LN-LV	0.70	0.53	250
JP-5	0.70	0.42	646
JP-4	0.62	0.37	160
RAF-176-64	0.61	0.30	71
Diesel Fuel	0.52	0.29	4

B

Degree of Correlation

(Spearmans Rank Correlation Method, see page 59)

Acceptance Limits $\gamma_{s,\ 0.01} = 0.83$ $\gamma_{s,\ 0.05} = 0.64$

Tests Being Compared	γ_s	Evidence of Significance
Four-Ball and Ball-On-Cylinder	0.96	Significant at 99% A.L.
Four Ball and Vickers Vane Pump	0.82	Significant at 95% A.L.
Ball-On-Cylinder and Vickers Vane Pump	0.78	Significant at 95% A.L.

- - - - -

(*) Naphtha data are not included because its low volatility meant that (a) it could not be pumped in the Vickers vane pump and (b) evaporation induced cooling and concentration of heavy ends occurred in the ball-on-cylinder test, which probably caused a reduction in wear rate during runs.

b. Evaluation of Individual Test Devices

(1) Ball-on-Cylinder Machine

The ball-on-cylinder device was developed to fill the need for a rugged, yet sensitive, device for evaluating surface-action lubricity additives. It is uniquely capable of detecting differences in the lubricating properties of distillate fuels under boundary and mixed hydrodynamic and boundary conditions. This sensitivity was clearly shown during this program and is demonstrated here by the results given in Table II for 15 ppm solutions of commercial additives in isooctane.

It can be seen from the results in Table II that the highly-purified, poor-lubricity isooctane was clearly distinguished from the same isooctane with trace (15 ppm) quantities of surface-active additives. The wear scar diameter was reduced by as much as 67% by the additives. The time-averaged friction reading showed a significant decrease, both in absolute value of the coefficient of friction and the smoothness of the friction trace. During all these runs with pure isooctane, the oscillation of the friction reading suddenly became so violent that the range of the recorder was exceeded, and in one of these cases the run had to be discontinued because of excessive vibration of the test instrument.

(2) Wear Behavior in Four-Ball Tester

In comparing the wear characteristics of different lubricants in the four-ball wear tester, it may be misleading to use only one length of test, say 5 minutes or 1 hour. Feng[21] has shown that three separate numbers are required to characterize each fluid: a "zero-time" wear, which is obtained almost instantaneously; a normal wear rate where the wear volume is directly proportional to time; and an equilibrium wear at which any further increases in time do not increase the scar diameter.

In order to ensure that meaningful comparisons could be made between fuels with respect to their behavior in the four-ball tester under non-scuffing wear conditions, a series of studies were carried out in this machine, using cetane as the test fluid, in which wear was measured as a function of load, speed and time. The purpose was to find the most suitable speed and load conditions for future testing and to establish that the test was well behaved, in that wear volume was proportional to running time.

As indicated above, the time dependence of wear can be represented by three distinct regions, the "zero time" wear, the normal wear, and the equilibrium wear regions. Feng pointed out that on a log-log plot of time vs. wear scar diameter the slope of the line representing the normal wear region would be 0.25. Therefore, a comprehensive study has been made of this time dependence for four loads: 5, 10, 30, and 50 kg. The results of this study are shown in Figures 5 to 13.

TABLE II

BALL-ON-CYLINDER RESULTS

Steel on Steel; 240 RPM; 32 Minute Tests;
15 ppm Additive Solutions in Isooctane

Additive	Wear Scar Diameter (mm)	Coefficient Of Friction At End of Test	Amplitude[1] of Friction Record As % of Average Value	Notes on Friction
60 g Load				
None	0.60	(0.30)[2]	(± 20)[2]	Suddenly too erratic to record at 20 min.
None	0.62	(0.30)[2]	(± 11)[2]	Suddenly too erratic to record at 15 min.
Oleic Acid	0.21	0.13	± 2	
ER-3[3]	0.27	0.14	± 3	
ER-4	0.46	0.14	± 6	
ER-5	0.28	0.14	± 3	
ER-6	0.21	0.13	± 3	
ER-10	0.21	0.14	± 3	
240 g Load				
None	(0.73)[2]	(0.30)[2]	(± 25)[2]	Suddenly too erratic to record at 20 min. Run discontinued.
ER-3	0.32	0.18	± 4	
ER-5	0.32	0.19	± 5	

(1) The period of oscillation for the friction read-out on the strip chart recorder is about 1.5 seconds and is limited by the detection and recording mechanism. Although this represents about 5 cylinder revolutions, or 33 inches of travel for the ball across the cylinder surface per oscillation, there is a consistent relationship between the amplitude of oscillation and severity of wear.

(2) Readings taken just prior to break into highly erratic friction regime.

(3) Code numbers refer to proprietary additives. See Section V-3.

The running-in wear region and the normal wear region are present in all cases. In all tests, except the 10 kg, 1800 rpm series, there is no indication that an equilibrium wear scar region has been attained. Feng's interpretation of four-ball test results is a general one, meant to hold over a wide range of fluids. He had found that low viscosity fluids were not as likely to attain this final equilibrium regime in reasonable test periods, as were fluids of higher viscosity. This is probably due to the extremely poor load-carrying capacity of these light fluids. As the wear volume grows larger, the unit loading decreases since the area of contact is increasing. Hence, a point is reached at which the fluid is able to support this unit load in a mixed boundary-hydrodynamic fashion and no further wear occurs. In light fluids with poor lubricity properties, this point is difficult to reach.

The initial wear scar diameter represents the early part of the run, where even at a few seconds running time an appreciable wear scar is obtained. This is somewhat above the Hertz diameter calculated for each load. The initial WSD increases with load, but is independent of speed. At 5 and 10 kg this initial wear period is only about one minute long; at 30 kg it is about five minutes and at 50 kg about ten minutes long.

The normal wear region is well behaved throughout these tests; all conditions except one yielding a slope of 0.25 as predicted by Feng. The exception, 50 kg at 1200 RPM, occurs in a region of high running-in wear and is quite close to the catastrophic wear regime as shown in Figure 14.

The running-in wear and log-log slopes for the various runs are tabulated below:

Wear vs. Time Tests--Four-Ball Wear Tester

Load, kg	Speed, RPM	Initial WSD, mm	Wear Rate, $\frac{mm^3}{min.} \times 10^4$
5	600	0.19	0.306
10	600	0.22	0.486
	1200	0.24	1.06
	1800	0.22	1.04
30	600	0.50	1.85
	1200	0.56	3.20
	1800	0.58	1.55
50	600	0.70	2.48
	1200	0.70	

The normal wear rate constant, k, is obtained from the equation

$$k = 1.545 \times 10^{-2}\, d^4/t$$

where d is the wear scar diameter and t is the test duration, and 1.545 is a constant for a system of this metallurgy and ball size. This equation is valid for tests of such duration that the running-in wear, by comparison, is negligibly small. An alternative expression can be used if this running-in period must be taken into account.

The steady-state wear region shows that the wear rate is a function of both load and speed. However, at the highest load and speed the points do not give slopes equal to 0.25. For future comparisons of wear rate the conditions of 10 kg and 1200 RPM will be used.

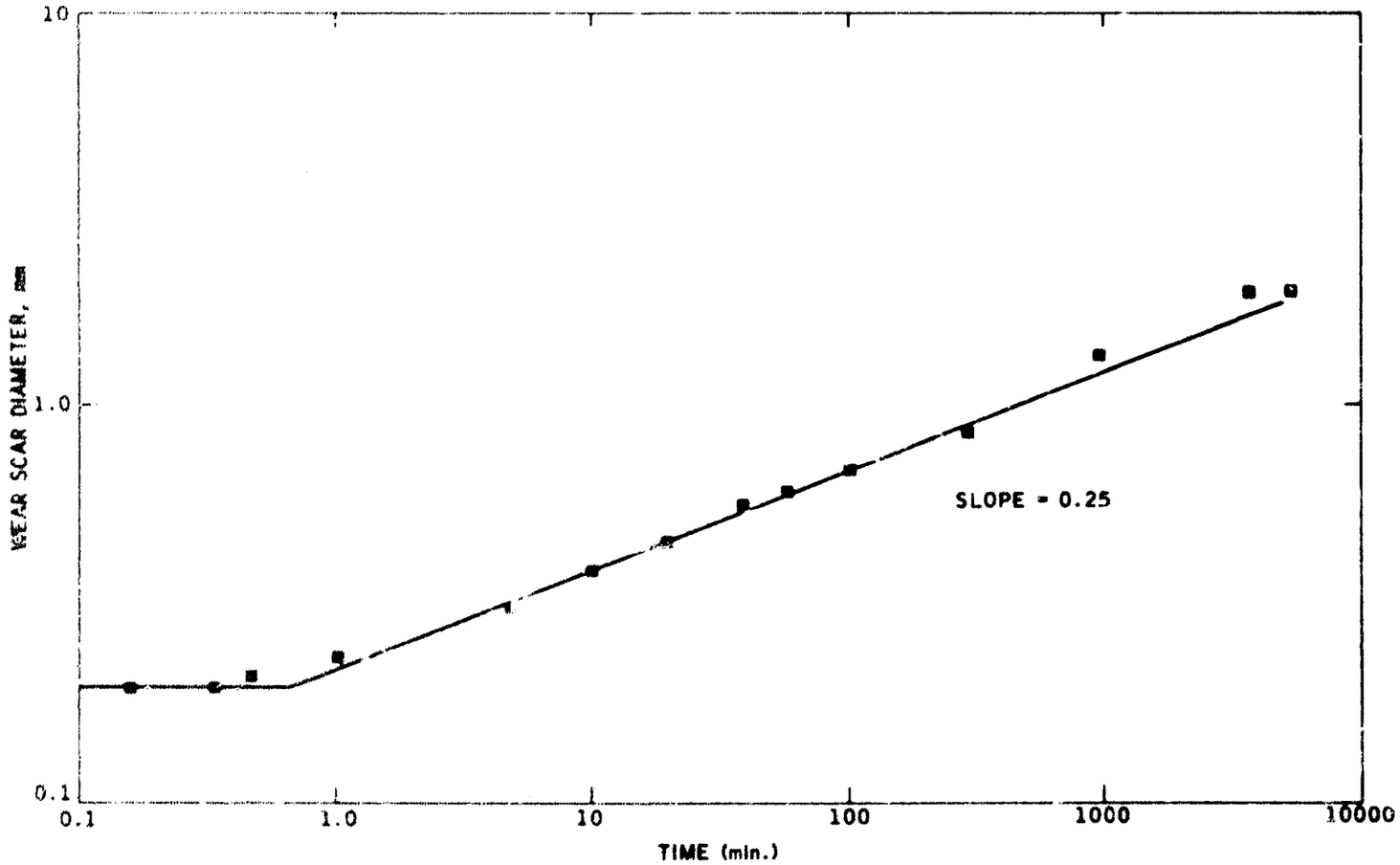


FIGURE 5 - CETANE IN FOUR-BALL TESTER: TIME DEPENDENCE OF WEAR: 5 kg, 600 rpm, 77F

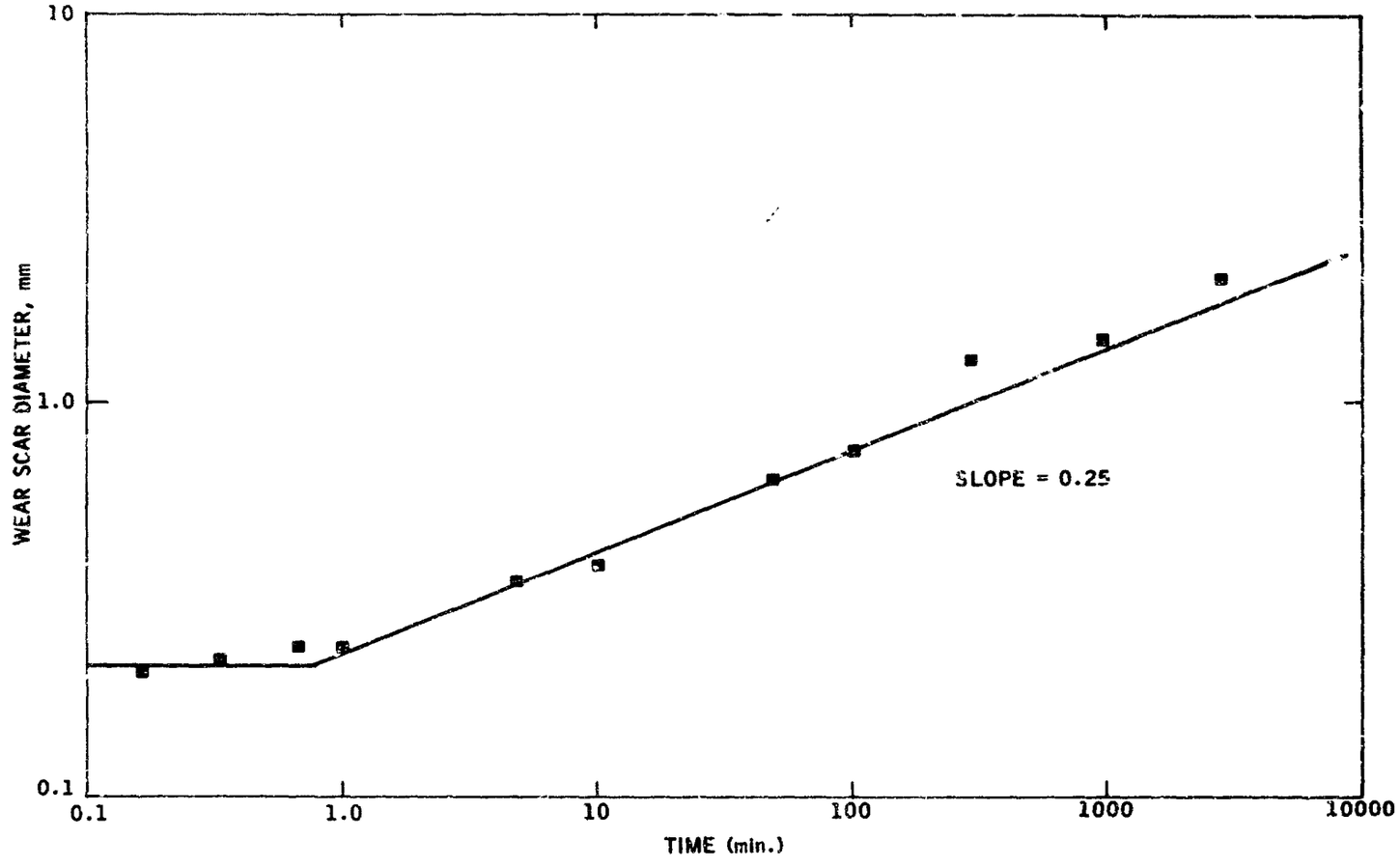


FIGURE 6 - CETANE IN FOUR-BALL TESTER: TIME DEPENDENCE OF WEAR: 10 kg, 600 rpm, 77F

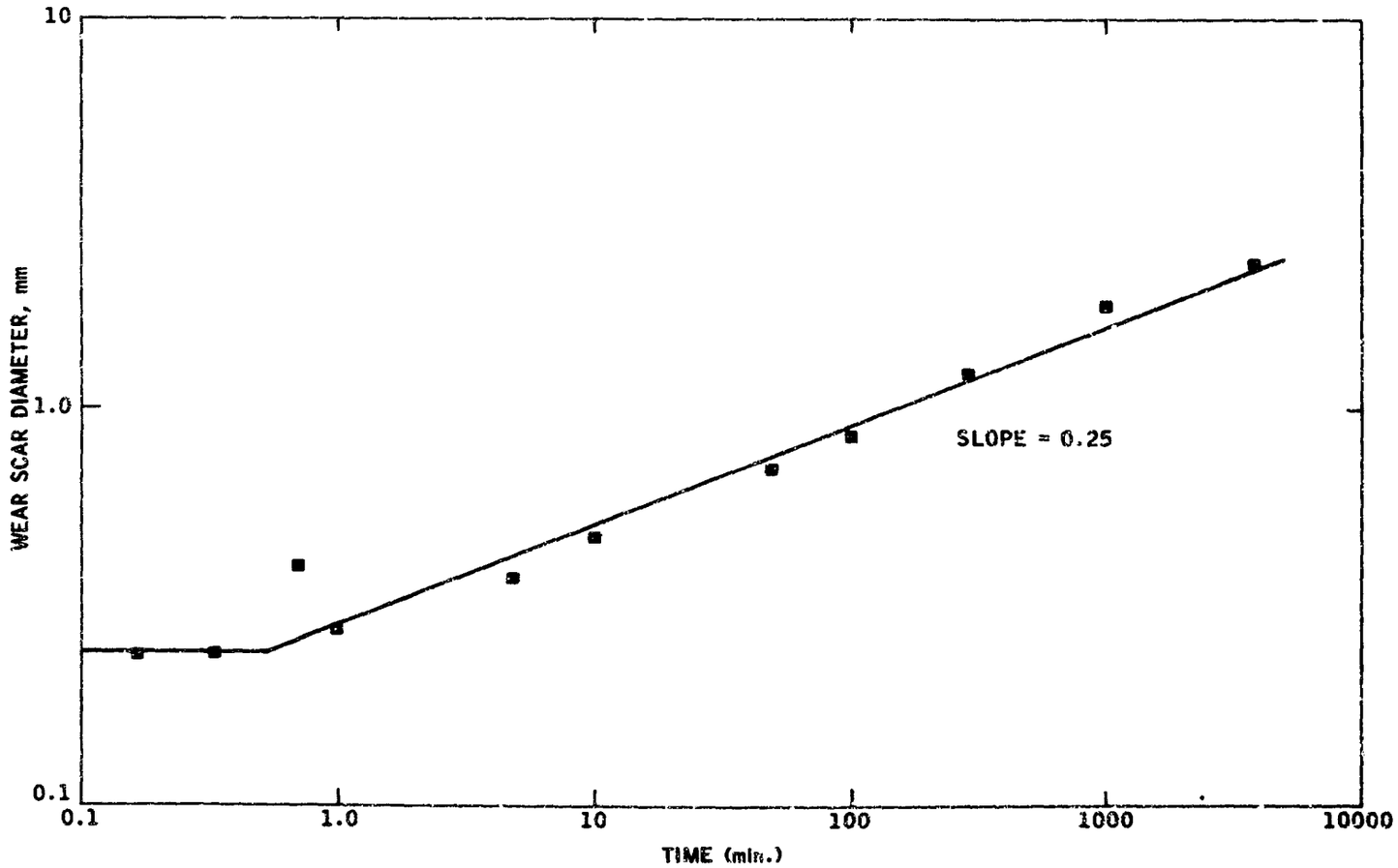


FIGURE 7 CETANE IN FOUR-BALL TESTER: TIME DEPENDENCE OF WEAR: 10 kg, 1200 rpm, 77F

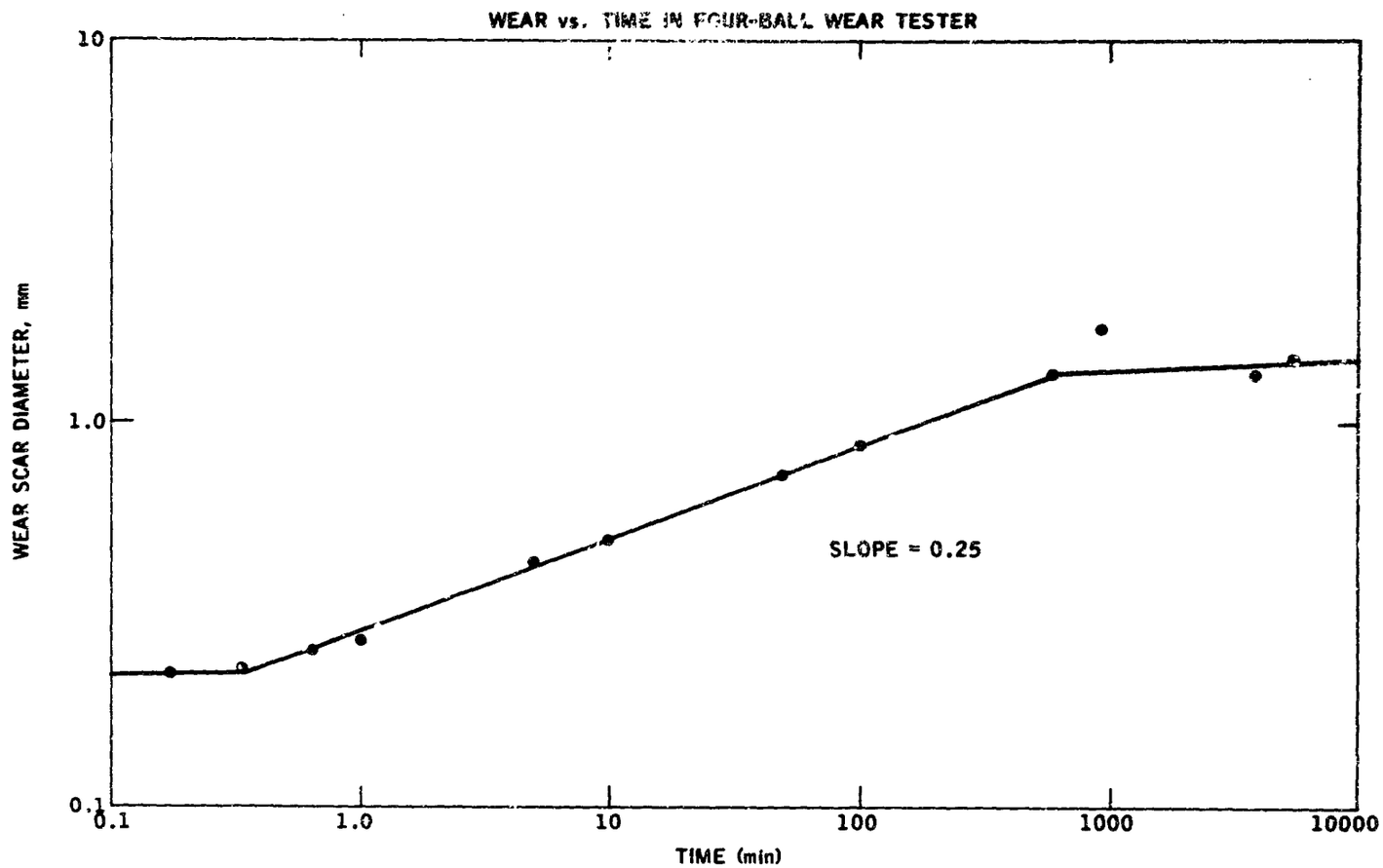


FIGURE 8 CETANE IN FOUR-BALL TESTER: TIME DEPENDENCE OF WEAR: 10 kg, 1800 rpm, 77F

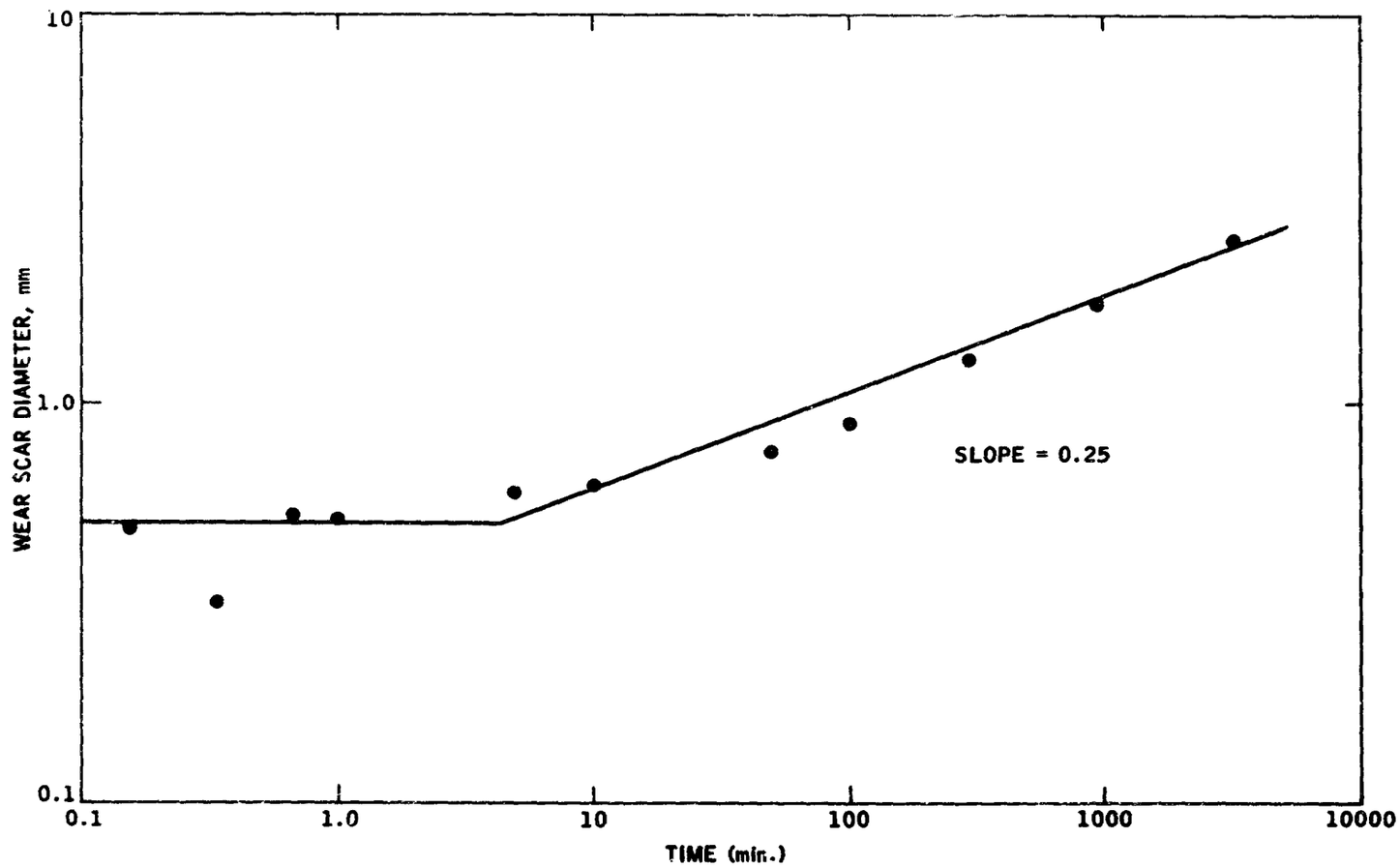


FIGURE 9 CETANE IN FOUR-BALL TESTER: TIME DEPENDENCE OF WEAR: 30 kg, 600 rpm, 77F

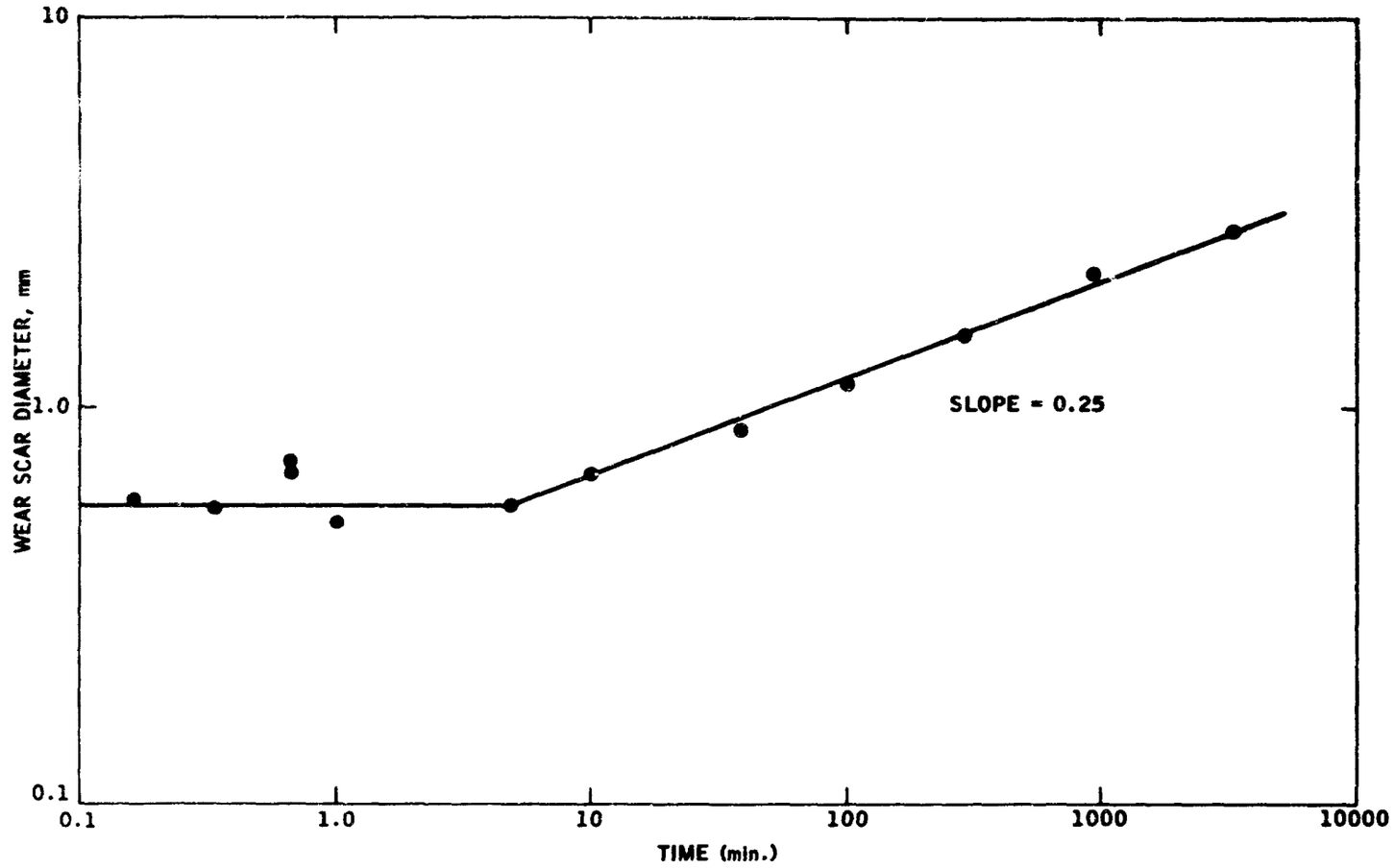


FIGURE 10 CETANE IN FOUR-BALL TESTER: TIME DEPENDENCE OF WEAR: 30 kg, 1200 rpm, 77F

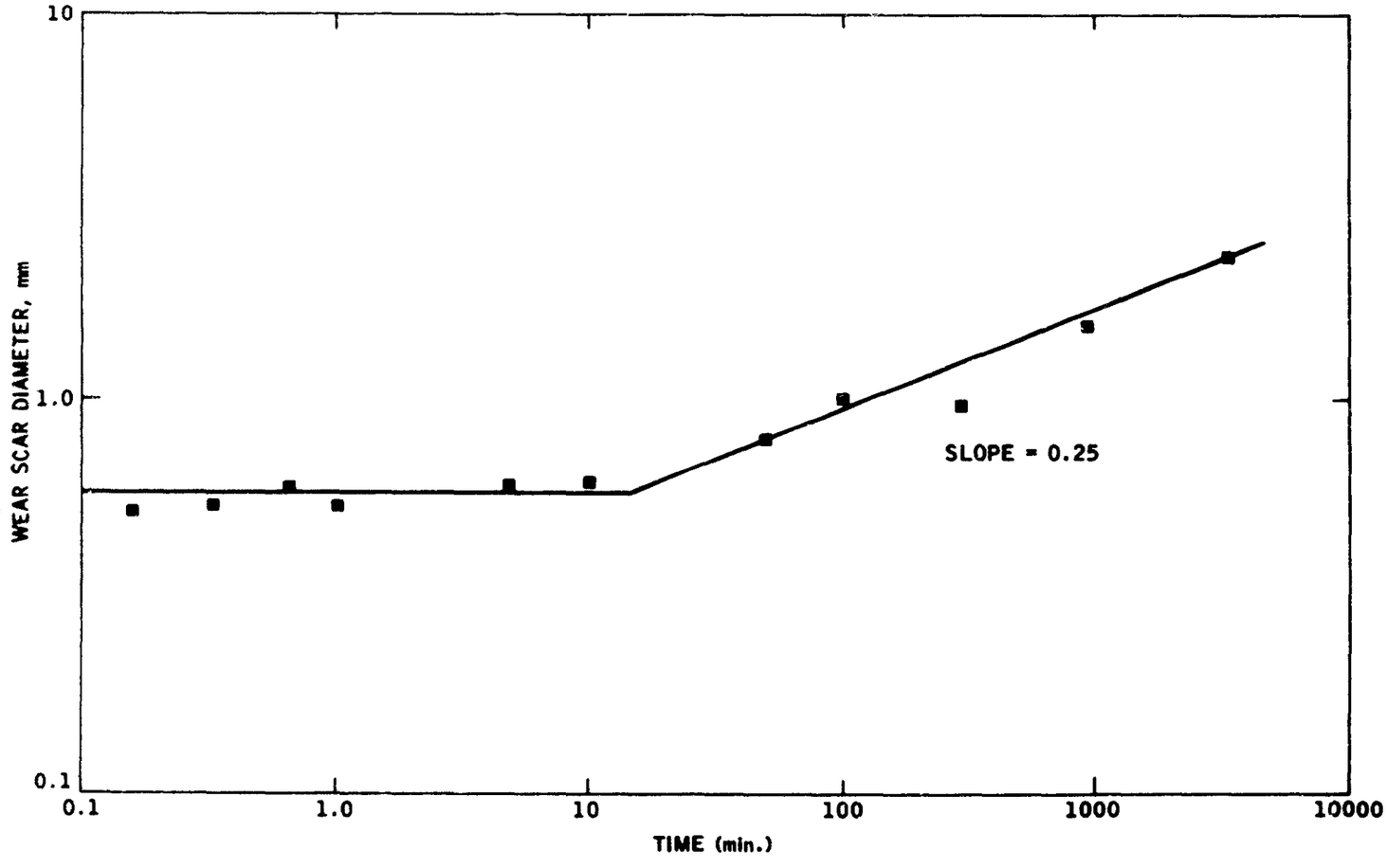


FIGURE 11 CETANE IN FOUR-BALL TESTER: TIME DEPENDENCE OF WEAR: 30 kg, 1800 rpm, 77F

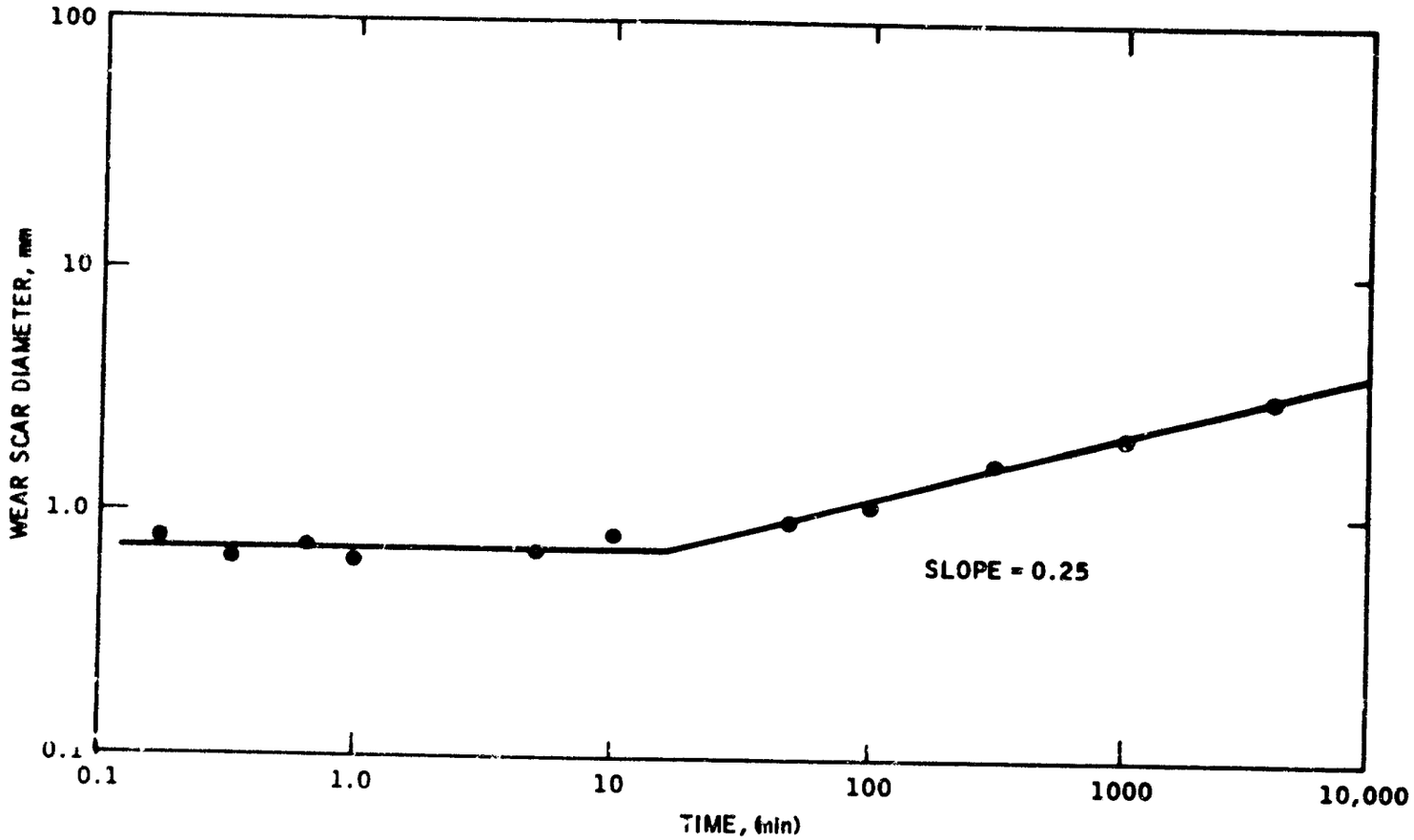


FIGURE 12 CETANE IN FOUR-BALL TESTER: TIME DEPENDENCE OF WEAR: 50 kg, 600 rpm, 77F

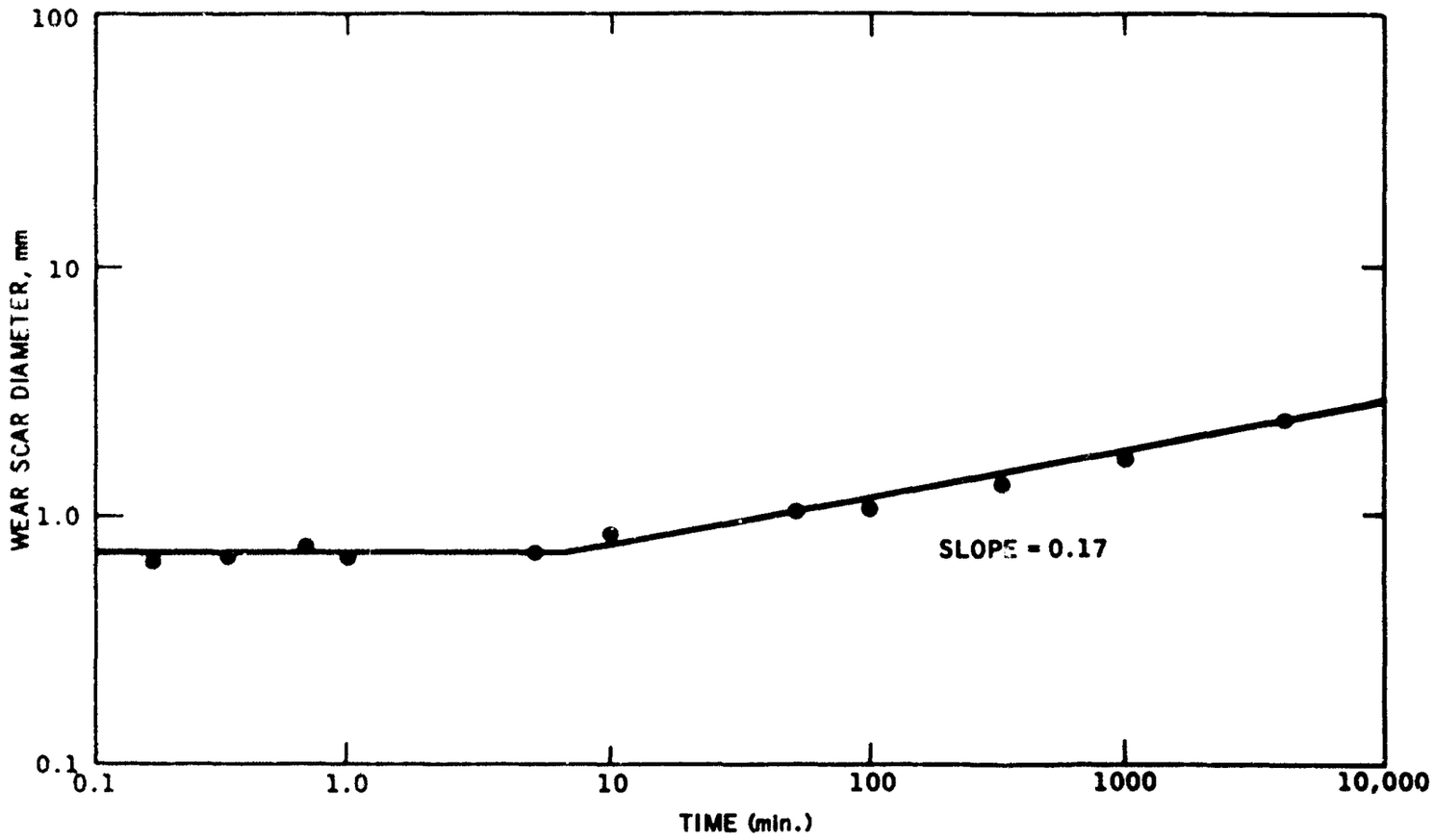


FIGURE 13 CETANE IN FOUR-BALL TESTER: TIME DEPENDENCE OF WEAR: 50 kg, 1200 rpm, 77F

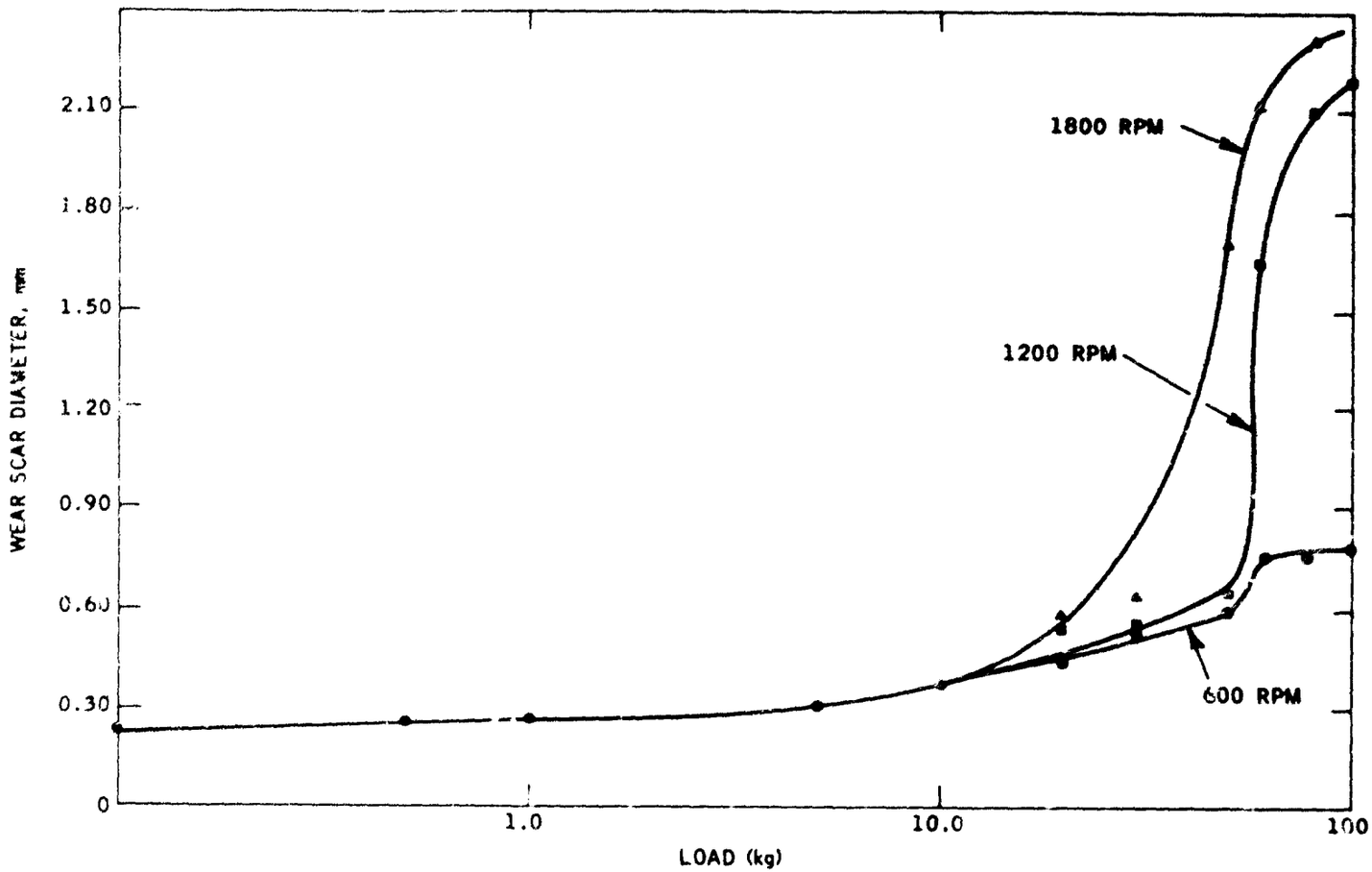


FIGURE 14 WEAR SCAR DIAMETER VS. LOAD FOR n-CETANE AT 600, 1200 and 1800 rpm ON FOUR-BALL TESTER

SECTION V

EXPERIMENTAL RESULTS

1. COMPARISON OF TEN COMMERCIAL FUELS

a. Program Outline

With the aim of establishing a relationship between composition and lubricating properties, ten commercially-available distillate fuels were obtained for laboratory investigation.

The chemical composition and appropriate physical properties of the fuels were analyzed as thoroughly as possible using established analytical methods. The lubricating properties of the fuels were measured in the ball-on-cylinder, four-ball, Falex and Vickers vane pump devices.

b. Description of Fuels

A list of the fuels are given in Table III together with a brief description of the fuel characteristics. A full description of the fuel analyses is given in the next section, followed by the experimental lubricity results.

c. Fuel Analyses

(1) Viscosity and Density

The viscosities and densities of the fuels investigated in this work are given in Table IV. The viscosities were obtained with an Ubbelohde capillary viscometer and the densities by precision hydrometers. For all fuels the density shows an almost constant decrease of 0.00040 g/ml per °F.

The absolute viscosities (cp) of the fuels are plotted in Figure 15 using a modified ASTM chart. The ASTM chart was developed for kinematic viscosities (cs) and has been modified for absolute viscosity (cp) by relocating the vertical ordinate so that the line representing 0.4 cs becomes 0.3 cp and so on. The equation for the modified chart is thus:

$$\log \log (cp + 0.1 + k) = -m \log T + C$$

where k = 0.6 at viscosities above 1.4 cp and gradually increases at viscosities below 1.4 cp. This chart gives a relatively straight line over the range of 77-300F (25-150C).

It will be seen from Figure 15 that the jet fuels, with the exception of JP-4, have viscosities within the narrow range of 1.02-1.64 cp/100F. JP-4 is considerably lighter at 0.49 cp. Bayol 35, the white oil used as reference, is 1.84 cp. The bracketing fuels are a diesel fuel of 2.15 cp and a naphtha of 0.25 cp, these represent the extremes of the mixed fuels.

The viscosity-temperature lines of the fuels are roughly parallel; i.e., crossovers are negligible. Thus, if one fuel is more viscous than another at one temperature, it will be more viscous at all temperatures, with only minor exceptions. The same can be expected to hold for viscosity-pressure relationships.

TABLE III

COMMERCIAL FUELS

Fuel	Source	Characteristics
Highly Refined		
RAF-173-61	USAF - CRC Fuel Bank, Wood River, Ill.	Highly naphthenic, C_9-C_{16} hydrocarbons 375-500°F boiling range; relatively high viscosity.
AFFB - 3-65	USAF - Fuel Bank Wood River, Ill.	Highly naphthenic and isoparaffinic, C_9-C_{12} hydrocarbons 325-425°F boiling range; relatively low viscosity.
Bayol 35	Humble Oil & Refining Co.	Isoparaffinic and naphthenic, C_{11}-C_{14} hydrocarbons, 400-500°F boiling range, relatively high viscosity.
PW-523	Humble Oil & Refining Co.	Low aromatics, C_{10}-C_{14} hydrocarbons, 400-475°F boiling range.
Standard Refining		
JP-5	USAF - University of Dayton	C_9-C_{15} blend, 375-475°F boiling range.
RAF-176-64	USAF - CRC Fuel Bank Wood River, Ill.	Standard Jet-A, C_9-C_{16} blend.
75 LN-LV	USAF - University of Dayton	Mainly C_{10}-C_{13} hydrocarbons 325-425°F boiling range.
JP-4	Humble Oil & Refining Co.	Wide-cut fuel, C_5-C_{15} hydrocarbons, 175-425°F boiling range. Low viscosity.
Diesel Fuel	Humble Oil & Refining Co.	Mainly C_{10}-C_{17} hydrocarbons, 425-575°F boiling range, highest viscosity.
Light Naphtha	Humble Oil & Refining Co.	C_4-C_7 lowest viscosity, 100-200°F boiling range.

TABLE IV

VISCOSITY AND DENSITY OF COMMERCIAL FUELS

	Kinematic Viscosity, cs					Density, g/ml					Absolute Viscosity, cp				
Temp. °F	77	100	140	210	300	77	100	140*	210	300	77	100	140	210	300
Fuels															
Bayol 35	3.121	2.400	1.634	0.993	0.625	0.774	0.765	0.749	0.722	0.687	2.416	1.836	1.224	0.717	0.429
JP-5	1.835	1.486	1.102	0.728	0.494	0.799	0.790	0.774	0.747	0.711	1.466	1.174	0.853	0.544	0.351
AFTB-3-65	1.493	1.244	0.935	0.643	0.438	0.773	0.764	0.747	0.718	0.680	1.154	0.950	0.658	0.462	0.298
R6F-173-61	2.573	1.980	1.420	0.883	0.580	0.836	0.826	0.810	0.783	0.747	2.151	1.635	1.150	0.691	0.432
RAF-176-64	1.646	1.362	1.013	0.686	0.470	0.796	0.786	0.770	0.[illegible]1	0.705	1.310	1.070	0.780	0.508	0.371
JC 1H-1V	1.607	1.336	1.003	0.673	0.458	0.776	0.766	0.749	0.720	0.683	1.247	1.023	0.751	0.485	0.313
PW-521	1.986	1.602	1.161	0.762	0.512	0.762	0.752	0.736	0.709	0.674	1.513	1.205	0.854	0.540	0.345
JP-4	0.755	0.658	0.538	--	--	0.750	0.740	0.724	--	--	0.566	0.487	0.390	--	--
Diesel Fuel	3.416	2.608	--	1.067	0.681	0.833	0.824	0.809	0.782	0.746	2.847	2.149	--	0.834	0.508
Light Naphtha	0.429	0.386	--	--	--	0.655	0.642	--	--	--	0.281	0.248	--	--	-

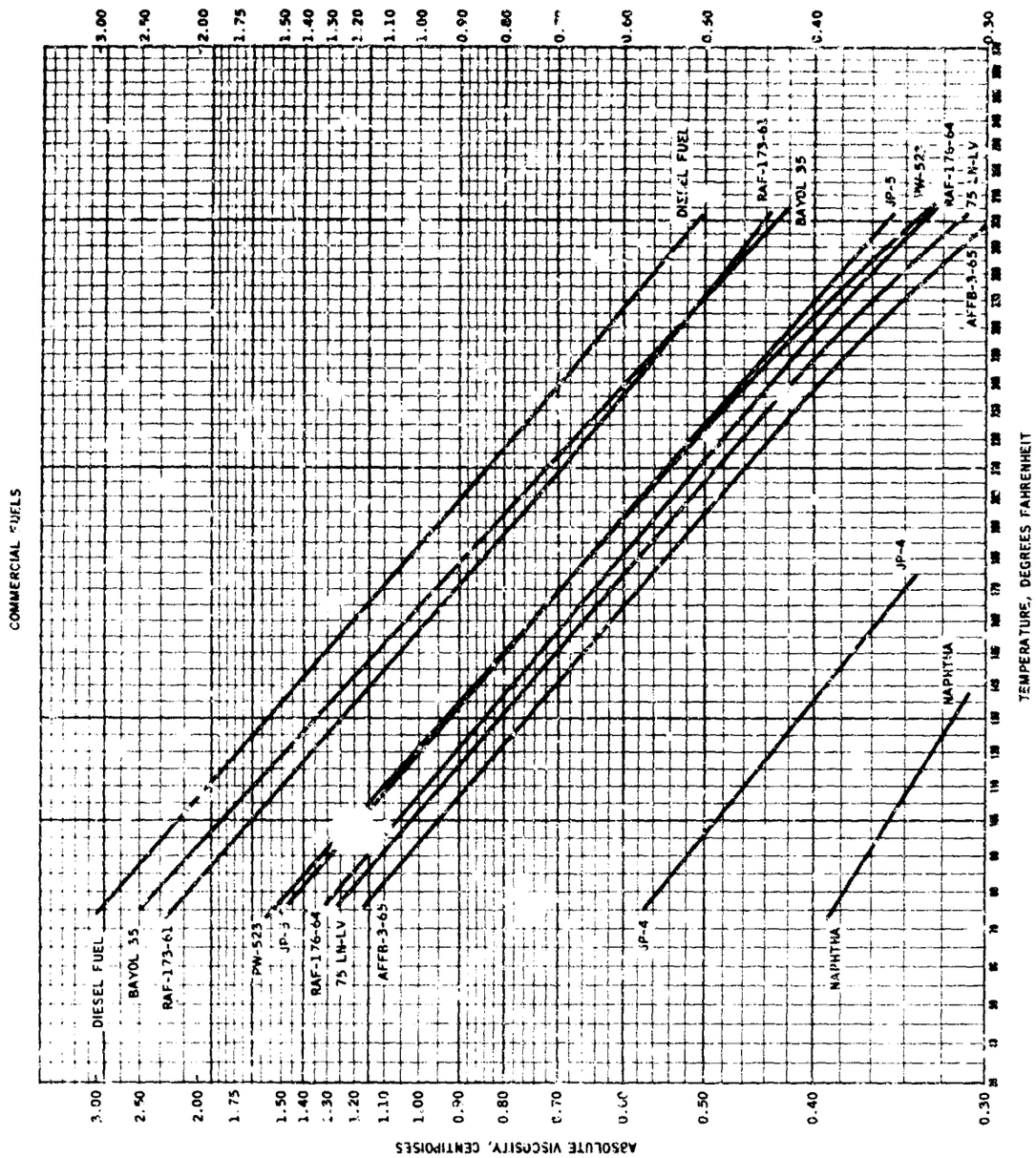


FIGURE 15 VISCOSITY TEMPERATURE PROPERTIES OF COMMERCIAL FUELS

(2) Volatility and Carbon Number Breakdown

Engler distillations of the fuels are presented in Table V and shown graphically in Figure 16. Gas chromatographic separation by carbon number are given in Table VI. Again, as in the case of viscosity, it can be seen that the bracketing fuels are naphtha and diesel fuel. This is demonstrated in Figure 17 showing the relationship between the 50% distillation temperature and viscosity. Essentially all of the naphtha boils below the lowest boiling fraction of any other fuel; and 75% of the diesel fuel boils above the highest boiling fraction of any other fuel. The widecut nature of JP-4 is easily seen. Bayol 35, PW-523, 75 LN-LV, and JP-5 all have very narrow boiling ranges. AFFB-3-65 is a slightly wider cut, and RAF-173 and RAF-176 wider still, but all are relatively narrow compared to JP-4. Of the jet fuels only RAF-176-64 has an appreciable amount as high as the C_{16} fraction - 3.7%. The 75 LN-LV is almost entirely C_{13} and below; AFFB-3-65 almost entirely C_{12} and below.

(3) Breakdown by Hydrocarbon Type

A hydrocarbon type analysis was carried out using mass spectrometry. This analysis separates fuels into paraffins, 1-ring naphthenes, condensed 2-ring naphthenes, condensed 3-ring naphthenes, indenes, 1-ring aromatics, condensed 2-ring aromatics, and condensed 3-ring aromatics. Because of the low carbon number of these fuels, most of the naphthenes and aromatics are 1-ring compounds. Condensed 2-ring and 3-ring naphthenes have been grouped as are condensed 2-ring and 3-ring aromatics and indenes. Combining these data with the data on n-paraffins obtained from the G. C. analysis, the iso-paraffinic content can also be obtained. Sulfur compounds are not identified separately but are included in the aromatic fractions. The mass spectra combined with the gas chromatography results described above, yield the breakdown by species given in Table VII. Examples of highly paraffinic (PW-523 and light naphtha), highly naphthenic (RAF-173-61) fuels and a wide range of aromatic contents are included.

(4) Trace Impurities

The three most important impurities likely to influence lubricity are sulfur, nitrogen, and acidic compounds. Analyses for these classes of material are given in Table VIII. The most highly-refined fuels, particularly the hydro-fined PW-523 and Bayol 35, are low in all three impurities. The diesel fuel was highest in all categories.

The acidity of all 10 fuels was run in duplicate by two analysts using extreme care. This was necessary because of the profound effect (noted in Table II) of only 15 ppm of oleic acid on friction and wear. This amount of oleic acid gives a neutralization number of only 0.003 mg KOH/g, so an accuracy of 0.0002 in neutralization number is required. The procedure is as follows: add 25 ml absolute alcohol to 100 g fuel, sparge with nitrogen for 5 minutes, then, without interrupting the nitrogen supply, titrate with 0.01 KOH using neutralized bromothymol blue (end point pH 7.6) as indicator.

The agreement between analysts was quite good, differing significantly only for the naphtha sample. Only two of the fuels--diesel fuel and RAF-176-64--had acidities of more than 0.015 (7 ppm as oleic acid). Acidity of the diesel fuel was 0.12, RAF-176-64 was 0.010.

TABLE V

ENGLER DISTILLATIONS OF COMMERCIAL FUELS, °F

% Dist.	Bayol 35	JP-5	RA 173-61	RAF 176-64	AFFB-3-65	75 LN-LV	JP-4	Naphtha	Diesel	FW-523
Initial Boiling Point	402	380	372	318	312	358	156	100	402	406
5%	412	384	381	346	329	370	193	110	437	414
10%	413	388	389	348	332	371	203	114	454	416
20%	416	391	396	358	336	373	218	122	470	419
30%	421	398	405	372	343	374	230	126	483	422
40%	425	404	413	381	347	375	244	130	493	425
50%	429	407	423	392	352	376	260	135	501	428
60%	434	411	434	409	356	379	280	142	508	432
70%	439	415	444	421	363	381	306	150	522	437
80%	446	420	454	438	372	384	337	160	534	443
90%	459	429	468	456	386	390	378	173	554	454
95%	470	439	480	470	404	395	410	186	570	464
Final Boiling Point	506	469	498	482	427	422	422	205	581	482
% Recovery	98.0	98.5	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0
% Residue	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.6	1.0	1.0
% Loss	1.0	0.5	1.0	1.0	1.0	1.0	1.0	1.4	1.0	1.0

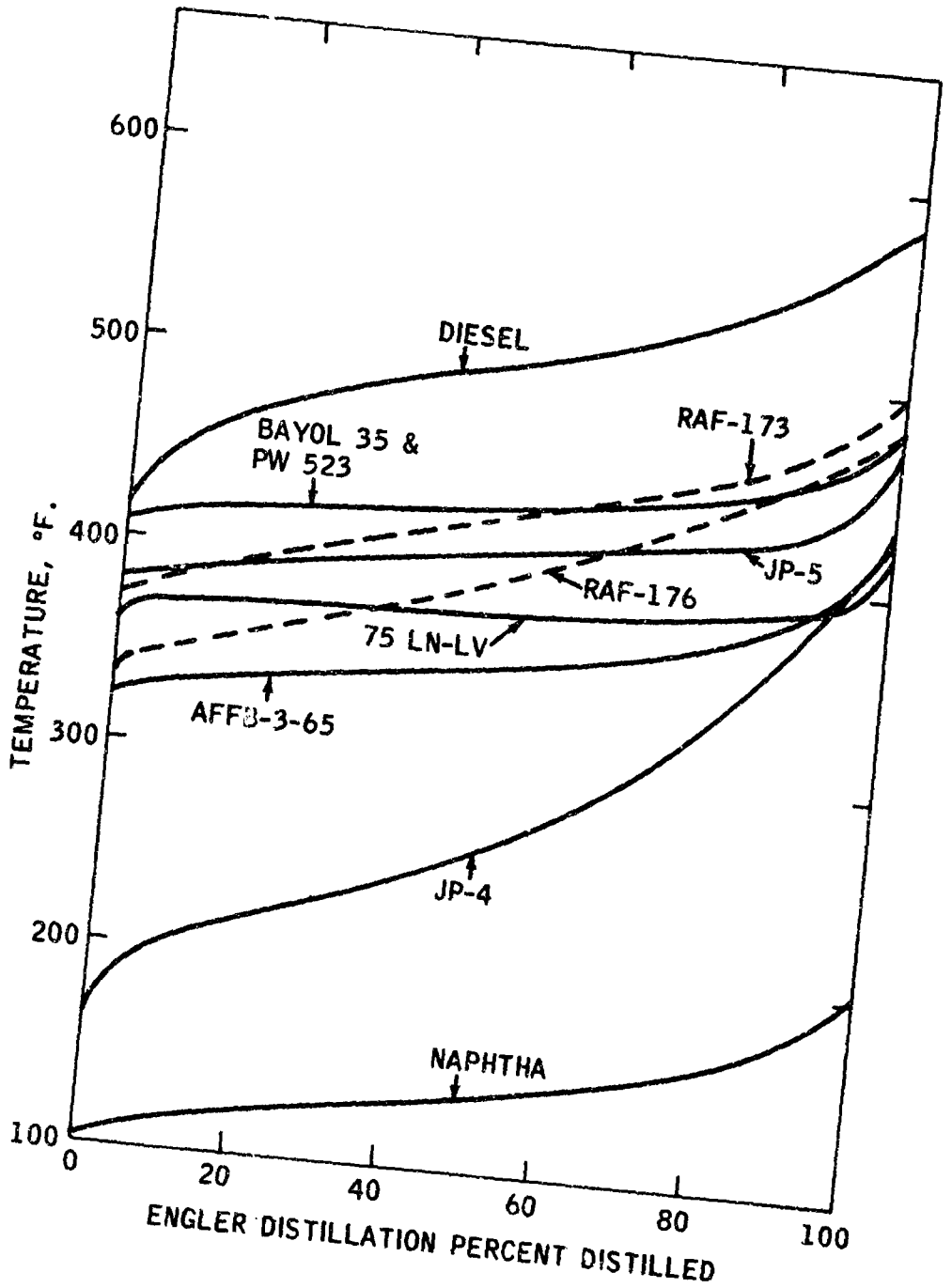


FIGURE 16 ENGLER DISTILLATIONS OF COMMERCIAL FUELS

TABLE VI

GAS CHROMATOGRAPHIC ANALYSES OF COMMERCIAL FUELS[1]

Carbon Number	JP-4	Naphtha	Diesel Fuel	P&W 523	JP-5	75 LN-LV	RAF-176-64	AFFB-3-65	RAF-173-61	Bayol 35[3]
n-C_4		1.45								
C_4		0.02								
n-C_5	1.8	19.56								
C_5	1.4	14.93								
n-C_6	3.8	19.16								
C_6	4.6	30.73								
n-C_7	6.5	2.73								
C_7	11.6	11.19								
n-C_8	5.5	0.04	Trace							
C_8	21.3	0.19	0.2							
n-C_9	2.7		0.2		0.2		1.1	1.5	0.1	
C_9	5.7		0.3		0.6		4.0	6.8	0.5	
n-C_{10}	2.7		0.5		1.2	2.9	3.7	1.5	0.3	
C_{10}	13.1		1.0		1.7	2.7	10.4	42.6	17.6	0.2
n-C_{11}	2.1		1.0	5.5	6.2	12.5	3.8	1.4	0.4	0.0
C_{11}	8.3		2.0	6.5	8.6	43.4	16.1	35.7	18.0	13.4
n-C_{12}	1.3		2.0	9.0	12.3	3.0	3.2	0.2	0.2	0.0
C_{12}	3.9		3.7	25.0	24.3	35.1	13.1	8.9	22.1	41.3
n-C_{13}	0.5		4.1	6.5	4.2	0.5	3.1	0.1	0.2	0.0
C_{13}	2.3		8.6	28.0	28.3	8.6	14.1	1.0	23.8	34.5
n-C_{14}	0.1		5.0	2.7	0.9		2.5	0.1	0.1	0.0
C_{14}	0.4		12.9	14.6	9.2	0.3	11.2	0.1	12.7	10.6
n-C_{15}			5.1		0.1		0.8			
C_{15}	0.4		17.0	2.2	2.1		9.2	0.1	4.0	
n-C_{16}			4.6							
C_{16}			15.7		0.1		3.7			
n-C_{17}			2.7							
C_{17}			13.1							
n-C_{18}			--							
C_{18}			0.2							

(1) GC Analysis via Perkin-Elmer 226; 300' Column, DC 350.

(2) Normal hydrocarbons as reported are a maximum value and may include other unresolvable compounds.

(3) Normal paraffinic content of Bayol 35 too low for estimation.

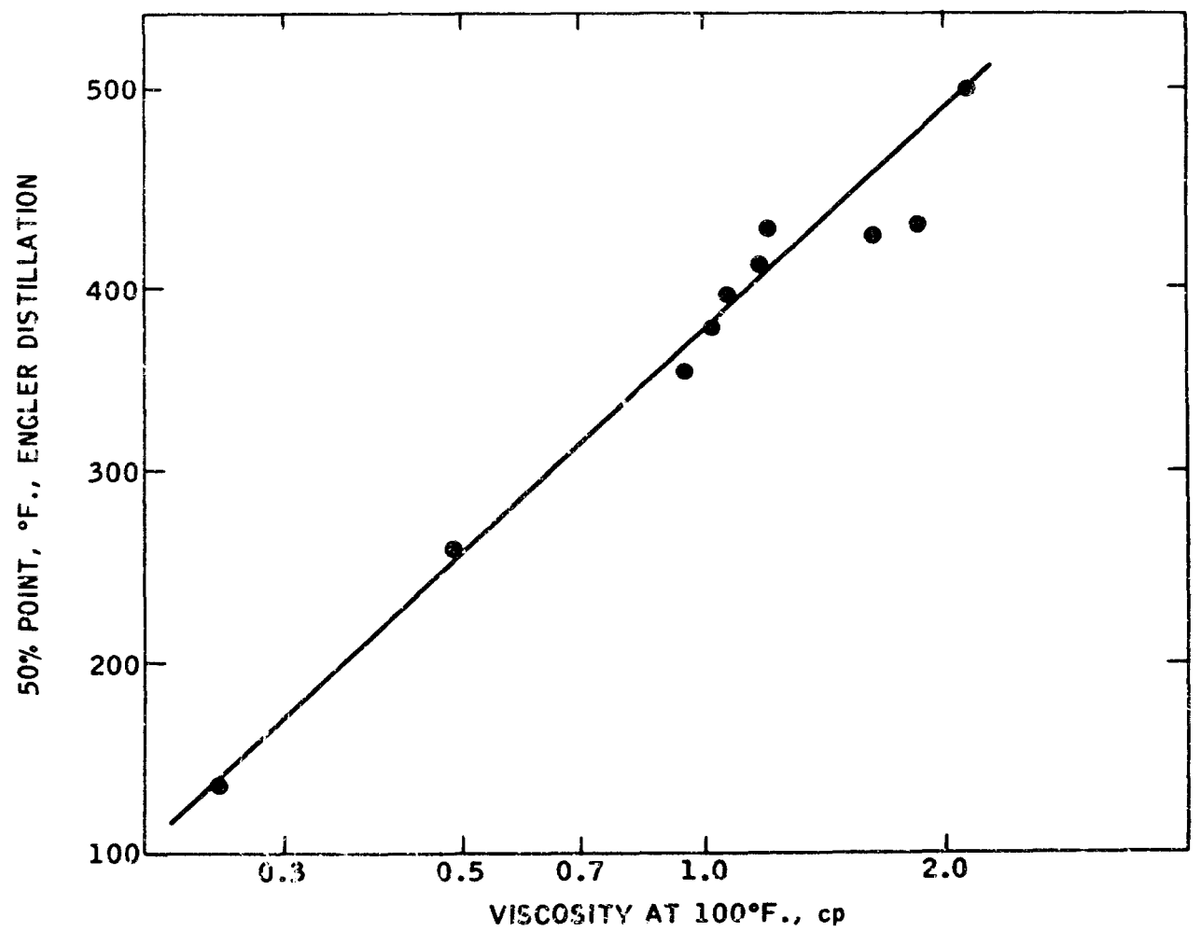


FIGURE 17 CORRELATION BETWEEN VISCOSITY AND VOLATILITY

TABLE VII

HYDROCARBON TYPE ANALYSIS

	Naphtha	JP-4	75 LN-LV	AFFB-3-65	RAF-176-64	FW-323	JP-5	RAF-173-61	Bayol 35	Diesel Fuel
Paraffins	82.8	41.2	64.3	54.0	44.9	87.6	46.1	17.9	100	42.7
Naphthenes	15.3	34.3	25.6	44.6	39.8	10.8	38.3	79.7		30.3
Aromatics(1)	1.9	24.5	10.1	1.4	15.3	1.6	15.6	2.4	0	27.0
n-paraffins	42.9	27.0	18.9	4.8	18.2	23.7	25.1	1.3	0	25.2
iso-paraffins	39.9	14.2	45.4	49.2	26.7	63.9	21.0	16.6	--	17.5
1-ring naphthenes	15.3	31.9	20.3	39.4	28.3	7.5	25.2	33.2	--	14.9
2-ring naphthenes	0	2.4	5.3	5.2	11.5	3.3	13.1	46.5	--	15.4
1-ring aromatics	1.9	24.5	8.9	1.4	10.6	1.6	10.0	2.4	0	10.2
2-ring aromatics	0	0	1.2	0	4.7	0	5.6	0	0	16.8

(1) No distinction is made between substituted and unsubstituted aromatics in this analysis.

TABLE VIII

SULFUR, NITROGEN AND ACIDITY OF THE COMMERCIAL FUELS

	Sulfur, ppm(1)	Nitrogen, ppm(2)	Acidity(3) Neut. No. X 10^3	
			(a)	(b)
PW-523	< 0.2	< 1	nil	<0.2
Bayol 35	< 0.2	< 1	1	<0.2
75 LN-LV	< 0.2	2	1	0.5
AFFB-3-65	75-80	4	1	1.4
RAF-173-61	29	< 1	3	0.3
JP-4	32-34	2	4	1.5
JP-5	162	< 1	nil	0.8
Naphtha	135	3	5	<0.2
RAF 176-64	560	< 1	8	9.5
Diesel Fuel	2300	13	158	120.0

(1) Sulfur determination via Lamp method.

(2) Nitrogen determination via Kjeldahl method.

(3) Colorimetric titration. Values are in ppm KOH/g.

(a) (b) Different analysts. Analysis (b) is probably more accurate.

d. Wear Results on Commercial Fuels

The ten commercial fuels have been evaluated in three different wear tests: ball-on-cylinder, four-ball, and Vickers vane pump. There is a general agreement among the three test methods. Diesel fuel and RAF-176-64 consistently rate best and next best; JP-4 is considerably better than would be expected from its viscosity; PW-523 and AFFB-3-65 are generally the poorest in wear and friction. The results are discussed below:

(1) Ball-on-Cylinder Tests

This test has been found to be quite sensitive to fuel behavior. Three values are measured: friction, metallic contact, and wear.

Friction generally correlated well with wear in these tests. For example, at the 60 g level, diesel fuel (lowest wear) gave a steady coefficient of friction of about 0.11 throughout the entire run. This contrasts with PW-523 (highest wear) which gave friction values oscillating between 0.13 and 0.29. At the 240 g level, wear and friction correlated quantitatively. Again, diesel fuel gave a constant, steady coefficient of friction (0.13) compared to fluctuating values from 0.16 to 0.19 for PW-523.

As already mentioned, metallic contact at the 60 g level was more an indication of stick-slip and bouncing than it was of true severity of operation. At 240 g load the film thickness was so low that metallic contact existed 100% of the time for most fuels. Only for the three best lubricants--diesel fuel, RAF-176-64, and Bayol 35--was a decrease in metallic contact noted.

Tests were run on the ten fuels at loads from 60 g to 1000 g, at a speed of 240 rpm (60 cm/sec) and for a 32-minute period. The wear data are presented in Table IX, where the fuels are arranged in order from bad to good. The last two columns are tests run all on the same cylinder and for 64 minutes. These tests eliminate any differences due to cylinder-to-cylinder variation, which may be present in the 32-minute tests.

It will be seen that the Diesel fuel is consistently the best in lubricity. This is to be expected, for this fuel has the highest viscosity, lowest volatility, and has by far the greatest amount of sulfur, nitrogen and acidic compounds. RAF-176-64 consistently rates second. This fuel is also high in sulfur and acidic components. Of the fuels poorest in lubricity, PW-523 and 75-LN-LV are also the most highly refined, with low sulfur and acidity. AFFB-3-65 and RAF-173-61, also relatively low in trace constituents, were also poor in lubricity.

A fairly good correlation appears to exist with aromatic content. JP-4 for example has 24.5% aromatics, and this may be the explanation for its unexpectedly good performance. JP-5, RAF-176-64 and diesel fuel -- all good in lubricity -- also are high in aromatics. There are two exceptions: Bayol 35, which is completely free of aromatics, was surprisingly good in this test; possibly its higher viscosity is partly responsible. 75 LN-LV, which is fairly high in aromatics, 10%, was one of the poorest.

It is obvious that the components most responsible for good lubricity have not been pin-pointed.

TABLE IX

BALL-ON-CYLINDER RESULTS FOR COMMERCIAL FUELS

	Wear Scar Diameter, mm												
	32 Min						64 Min						
Load, g:	30	60	120	240	480	1000	60	240	Vis/77F cp	S, ppm	N, ppm	Arom. %	Acidity ppm KOH/g
PW-523	0.27	0.32	0.36	0.50	0.64	Fail(1)	0.36	0.47	1.51	<0.2	<1	1.6	0.2
75-LN-LV	0.26	0.31	0.41	0.52	0.53	0.55	0.31	0.57	1.25	<0.2	2	10.1	0.5
AFFB-3-65	0.26	0.31	0.38	0.46	0.58	Fail	0.30	0.52	1.15	80	4	1.4	1.4
RAF-173-61	0.23	0.28	0.32	0.41	0.56	Fail	0.34	0.47	2.15	29	<1	2.4	0.3
Naphtha	0.26	0.30	0.37	0.38	0.47	Fail	0.30	0.47	0.28	135	3	1.9	0.2
JP-5	0.22	0.25	0.32	0.35	0.42	0.50	0.28	0.44	1.47	162	<1	15.6	0.8
JP-4	0.23	0.28	0.29	0.33	0.37	0.[illegible]	0.26	0.44	0.57	34	2	24.5	1.5
Bayol 35	0.21	0.25	0.29	0.35	0.42	Fail	0.24	0.46	2.42	<0.2	<1	0	0.2
RAF-176-64	0.17	0.20	0.25	0.28	0.30	0.34	0.22	0.34	1.31	560	<1	15.3	9.5
Diesel Fuel	0.20	0.20	0.21	0.26	0.29	0.31	0.21	0.29	2.85	2300	13	27.0	120.0

(1) Fail indicates that run was discontinued before 32 minutes because of excessive vibration of the instrument as the friction suddenly increased.

These runs establish several important points:

- Fuels differ markedly in their friction and wear behavior.
- The differences are apparently more a function of polar constituents than bulk properties, but this is not entirely clear cut.
- Frictional behavior can be determined from the wear scar for non-additive fuels.
- The ball-on-cylinder machine is a useful laboratory device for assessing frictional behavior of jet fuels.

(2) Four-Ball Tests

Based on the study of the wear behavior of cetane, discussed in Section IV-2 above, the following standardized test conditions were used.

- Test loads and speed have been chosen to be 10 Kg and 1200 rpm, respectively.
- The equilibrium wear scar requires excessively long test durations for low viscosity fluids and is therefore not pursued.
- Five test durations, 15 sec, 1 min, 4 min, 15 min, and 1 hr, have been chosen to define the normal wear region and to get some indication of the level of initial wear.
- For less extensive tests three test durations, 4 min, 15 min, and 1 hr have been chosen for determining the normal wear region.
- A test temperature of 97F (36C) was adopted as a convenient temperature--somewhat above ambient--that could be maintained in spite of frictional heating. This particular temperature was chosen because it formed the base of another part of the program: n-heptane has the same viscosity at 97F as JP-5 at 300F.

Figures 18 and 19 are log plots of WSD vs. time and show the relative performance of the ten commercial fuels. The data are summarized in Table X, which gives the wear rate (mm^3/min), and the corresponding WSD at 60 minutes.

Diesel fuel was again best, as would be expected, and RAF-176-64 again second best. PW-523, 75-LN-LV, AFFB-3-65 and RAF-173-61 all gave relatively high wear. Again, JP-4 outperformed all other jet fuels in spite of its low viscosity, possibly because its wide-cut nature permits a relatively large amount of high-lubricity compounds.

In contrast to its behavior in the ball-on-cylinder tests, naphtha in the four-ball test gave by far the highest wear, possibly because its very low viscosity is more critical in this test, or the effects of evaporation less marked. Bayol 35 was also relatively poor compared to the ball-on-cylinder results, being little better than PW-523.

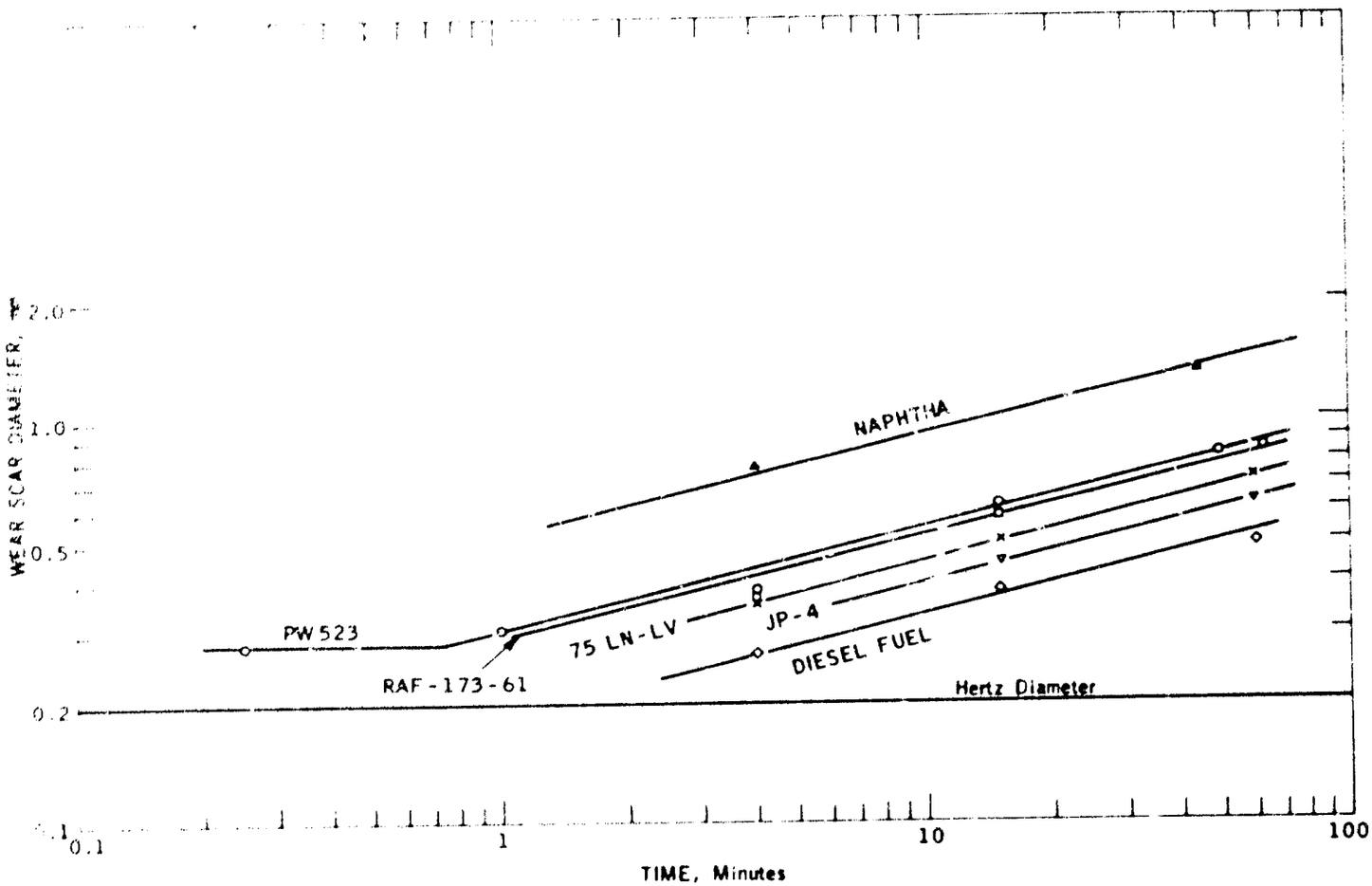


FIGURE 18 FOUR-BALL WEAR RESULTS FOR COMMERCIAL FUELS - I

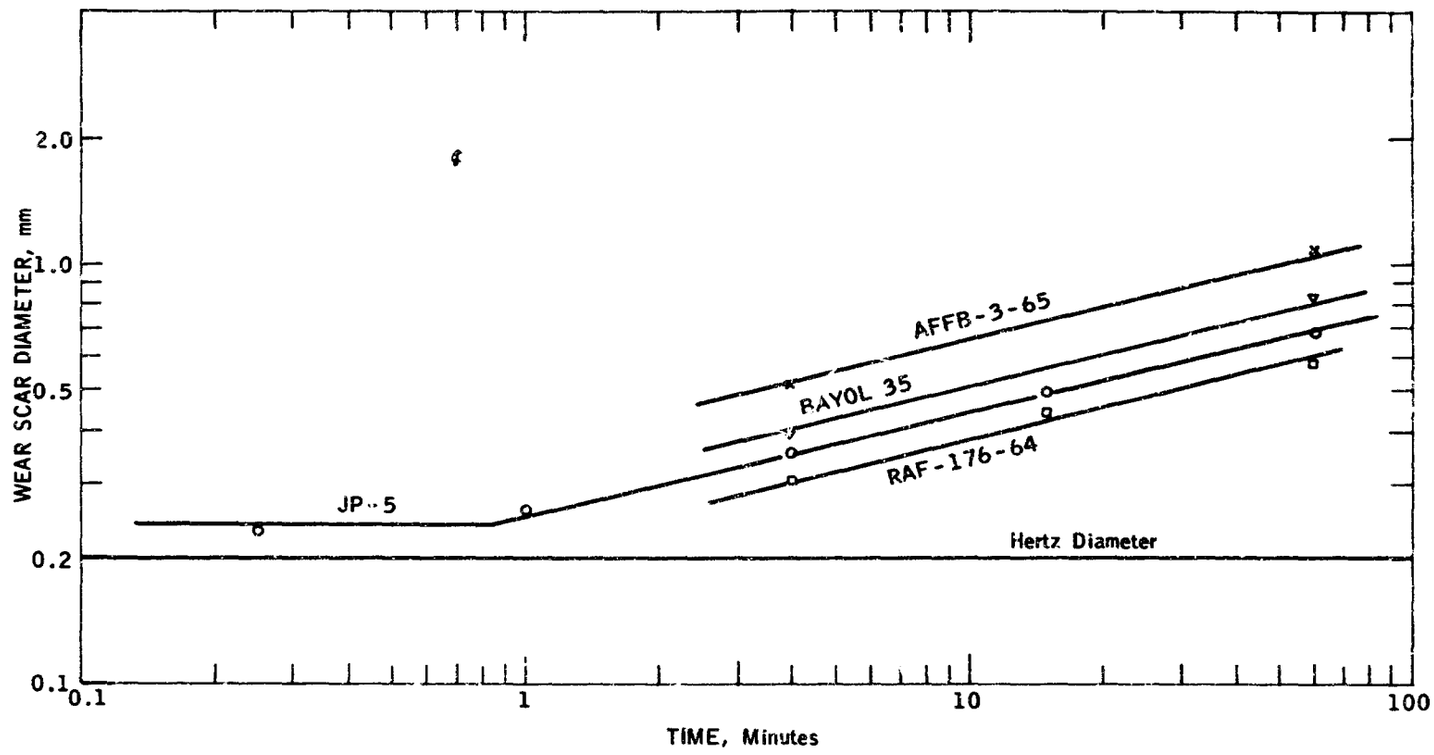


FIGURE 19 FOUR-BALL WEAR RESULTS ON COMMERCIAL FUELS - II

There appears to be a reasonably good correlation with aromatic content in that the five worst fuels have < 3% aromatics and the five best fuels have > 10% aromatics. However, it is impossible with these data alone to decide definitely which of the many variables is most important.

The differences in the behavior in these two test methods and the anomalous behaviour of certain fuels will be examined more closely in future work.

Table X

Four-Ball Wear Results for Commercial Fuels

10 Kg, 1200 rpm, 97F

Fuel	Wear Rate $mm^3/Min \times 10^4$	Calc WSD at 60 Min	Vis/97F, cp	Arom. %	Acidity ppm KOH/g	S, ppm	N, ppm
Naphtha	11.1	1.44	0.25	1.9	0.2	135	3
AFFB-3-65	3.0	1.04	0.98	1.4	1.4	80	4
PW-523	1.3	0.86	1.21	1.6	0.2	<0.2	1
RAF-173-61	1.1	0.81	1.70	2.4	0.3	29	<1
Bayol 35	1.0	0.80	1.88	0	0.2	<0.2	<1
75-LN-LV	0.61	0.70	1.04	10.1	0.5	<0.2	2
JP-5	0.61	0.70	1.21	15.6	0.8	162	<1
JP-4	0.37	0.62	0.50	24.5	1.5	34	2
RAF-176-64	0.33	0.61	1.09	15.3	9.5	560	<1
Diesel Fuel	0.18	0.52	2.18	27.0	120.0	2300	13

(3) Vickers Vane Pump Tests

(a) Commercial Fuels Show Marked Differences in Pump Wear

Of the ten commercial fuels, nine have been tested in the Vickers vane pump. The naphtha was found to be too low in viscosity, giving essentially no output. JP-4, because of its relatively low viscosity, could only be tested at a slightly lower pressure (300 psi) and lower sump temperature (83F); otherwise volumetric efficiency was nearly zero. Test data are shown in Table XI. As in the laboratory rigs, these fuels gave a very different pump wear. For highly-refined fuels, such as PW-523 and Bayol 35, severe wear occurred. The total wear amounted to approximately 5000 mg. For some other fuels like RAF-176-64 and diesel fuel, the wear was very mild, < 100 mg. It was noted during the tests that for fuels giving low wear (< 200 mg weight loss), a visible deposited film was coated on the rubbing area of contact and might account for the wear protection.

TABLE XI

VICKERS PUMP RESULTS FOR COMMERCIAL FUELS

	Revol 35	JP-5		FW-523		AFFB-3-65		RAF 176-64		RAF-173-61		75-LH-LV		Diesel Fuel		JP-4
Pressure, psig	350[a]	350	350	350	350[b]	350	330[c]	350	300	350	350[d]	350	350	350	350	300
Sump Temp., °F	90	90	124	90	125	90	125	90	125	90	125	90	125	90	125	83
Outlet Temp., °F	115	94	134	110	146	106	145	96	142	98	164	104	136	94	136	104
Pumping Rate, gpm	0.43	0.77	0.55	0.46	0.29	0.47	0.35	0.87	0.32	103	0.28	0.67	0.46	1.10	0.77	0.32
Vol. Eff., %	24	43	30	26	16	26	18	48	18	57	16	37	26	61	43	18
Wear, mg:																
Wt. Loss of Vanes	204	85	11	100	19	661	19	4	0[e]	31	294	50	0[e]	0[e]	6	3
Wt. Loss of Ring	5150	561	1119	4846	147	3656	104	67	39	235	4240	200	127	4	4	157
Total Wt. Loss	5354	646	1130	4944	166	4317	123	71	39	266	4534	250	127	4	10	160
Surface Roughness, CLA, μ":																
Vanes, Initial	3.9	15	14	18	17	24	24	20	16	23	14	20	21	14	18	19
Final	96	103	10	82	75	>200	96	17	14	123	171	97	20	17	25	10
Ring, Initial	15.8	16	16	18	16	16	28	17	16	70	8	9	12	9	12	10
Final	67	22	6	41	17	97	36	14	9	88	81	19	9	6	6	5
Viscosity, cs																
Before Test, @ 100°F	2.39	1.49	-	1.60	-	1.24	-	1.36	-	1.98	-	1.32	-	2.6	-	0.76 @ 77°F
@ 210°F	1.00	0.73	0.73	0.76	0.77	0.64	0.65	0.69	0.71	0.88	0.89	0.67	0.68	1.07	1.06	-
After Test, @ 100°F	2.40	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.80 @ 77°F
@ 210°F	-	0.73	0.73	0.77	-	0.65	-	0.71	0.71	0.89	0.89	0.68	0.68	1.06	1.07	-
Neut. [illegible] mg KOH/gm:																
Before Test	0.001	0.002	0.001	0	0.004	0.001	0	0.013	0.007	0.003	0.002	0.001	0.005	0.158	0.160	0.004
After Test	-	0.001	0.008	0.004	-	0	-	0.007	0.008	0.002	0.005	0.005	0.006	0.160	0.203	0.003

(a) Run at 125°F sump temperature was stopped at 15 minutes due to excessively low volumetric efficiency. Ring wear was 122 mg and vane wear was 14 mg.

(b) Run was stopped at 20 minutes due to excessively low volumetric efficiency.

(c) Run was stopped at 45 minutes due to excessively low volumetric efficiency.

(d) Run was stopped at 21 hours due to excessively low volumetric efficiency.

(e) Slight weight gain.

A series of pump tests were carried out on Bayol 35 at a sump temperature of 90F and outlet pressures of 100, 200, 250, 320, and 350 psig in order to investigate the effect of pressure on wear in a vane pump. The test data in Table XII is plotted in Figure 20 and shows ring wear and vane wear for 24-hour runs as a function of pump pressure. Pressure is an important factor in a vane pump, because the load of the vane on the ring surface is mainly from the back pressure of the discharge fluid which is introduced to the back end of the vanes. (The load from the centrifugal force is estimated to be only about 15 psi.) The load for the sliding contact between vanes and the ring surface is therefore a function of outlet pressure. As shown in Figure 20, wear increases as the pressure or load increases. An abrupt increase of wear occurs at a pressure of 200-250 psig. This indicates the probable transition from rubbing wear to scuffing wear. From the Talysurf data shown in Table XII, it can be seen that the surfaces of the vanes and rings were roughened as a result of wear. The degree of roughening of the surface is, however, not directionally consistent with the extent of wear. Beyond 300 psig, the roughening again decreases. It may be that the presence of wear debris in the system causes some abrasive wear to keep the rubbing surfaces from being over-roughened.

The effect of temperature on the severity of wear is not clearly defined in these data. For fuels giving severe wear, it appears that wear generally increases when going from 90F to 125F. In the case of PW-523 and AFFB-3-65, the higher temperature runs had to be terminated because of excessive wear and low volumetric efficiency. However, for those fuels giving mild wear such as RAF-176-64, 75-LN-LV or diesel fuel, the increase of temperature seems to further reduce the wear. This indicates that these fuels might contain trace components and that the antiwear effect of these becomes more pronounced at a higher temperature. The abrupt increase of wear by increasing the sump temperature from 90F to 125F indicates a sharp transition from mild to severe wear.

In comparison with Bayol 35, under the same or even milder test conditions, as shown in Figure 20 and Table XII, the currently marketed jet fuels, JP-4 and JP-5, gave less vane wear and ring wear, although the viscosity of JP-4 or JP-5 is considerably lower than that of Bayol 35 (0.54 cp for JP-4, 1.28 cp for JP-5 and 2.06 cp for Bayol 35). This experimental evidence is in line with the common belief that fuel pump wear became a serious problem when highly-refined fuels were used. This also indicates that viscosity is not the governing factor in wear severity in the Vickers pump.

With JP-5 a sticky material was deposited on the surfaces of the pump parts. The deposits became heavier at higher temperature. It appears that the wear particles may be adhering to this sticky material. It is postulated that this mixture might cause some abrasive wear so that the surface was not roughened but, in one case, even polished. The lower wear, better surface finish, or perhaps the sealing effect of this material may be the cause of the relatively higher volumetric efficiency given by JP-5 as shown in Figure 21.

TABLE XII

VICKERS VANE PUMP RESULTS FOR BAYOL 35

	(1)	(2)	(3)	(4)	(5)
Pressure, psig	100	200	250	320	350
Sump Temperature, F.	89	91	90	91	90
Outlet Temperature, F.	91	96.8	97.7	108	115
Pumping Rate, gpm	1.47	1.06	0.94	0.63	0.43
% Volumetric Efficiency	82	59	52	35	24
Wear					
Wt Loss of Vanes, mg	23	126	181	178	204
Wt Loss of Ring, mg	91	640	2966	5220	5150
Total Wt Loss, mg	114	766	3147	5398	5354
Surface Roughness (*CLA), microinches					
Vane, Initial	3.4	3.3	2.8	2.5	3.9
Final	4.7	>200	>200	109	96
Ring, Initial	8.0	13.1	18.1	15.0	15.8
Final	15.7	>200	>200	100	67

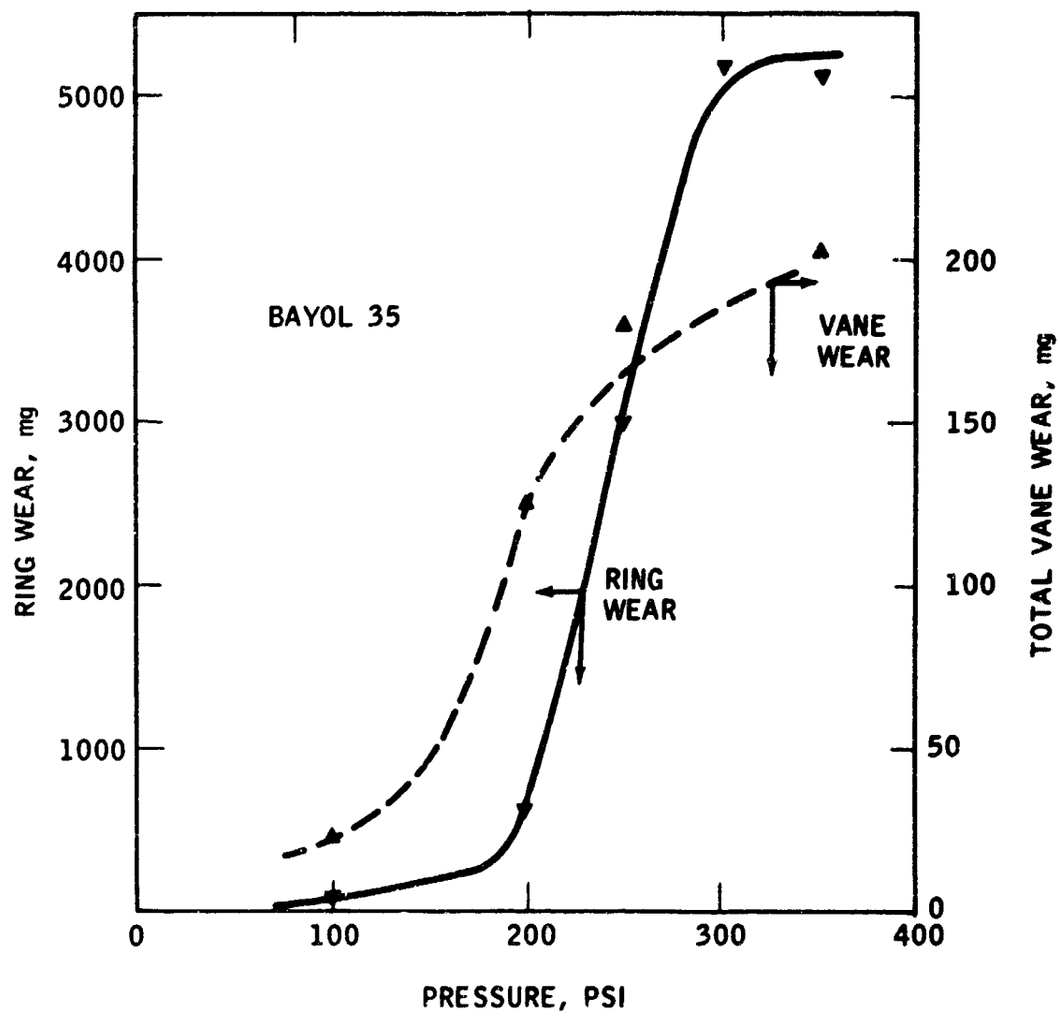


FIGURE 20 WEAR IN VANE PUMP INCREASES WITH OUTLET PRESSURE

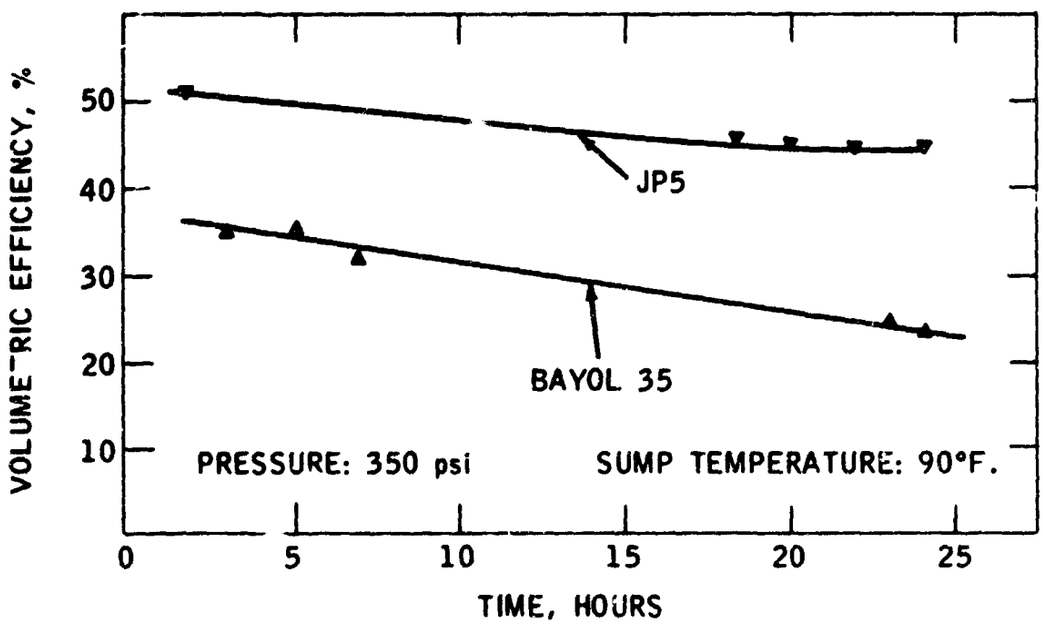


FIGURE 21 VICKERS PUMP VOLUMETRIC EFFICIENCY VS. TIME

(b) Correlation Between Trace Impurities and Pump Wear Is Indicated

The effect of viscosity and trace components in fuels on pump wear was investigated by analyzing the test data by means of Spearman's rank correlation method. Each fuel is ranked as 1, 2, 3 . . . for each variable and the variables are then compared. The coefficient of correlation γ, can be computed for two variables which are hypothesized to be correlated. The calculated coefficient, γ, is compared with the given acceptance limits to determine the significant evidence at a certain confidence level. This analysis is a rank randomization test. It is used here to detect whether the variation of wear is directionally consistent with that of viscosity or content of trace components. The equation for computation and the computed results are shown in Table XIII.

Viscosity

The viscosity of the fuels after each test was checked and showed no appreciable change. Values of viscosity at any specified temperature in pump tests were therefore interpolated from the analytical results given in Table XI. As shown in Table XIII, under these test conditions no significant correlation is detected between the severity of wear and the viscosity at the sump temperature. A further analysis was made using the viscosity at the outlet temperature which is closer to the bulk fuel temperature inside the pump. The combined test data at two sump temperatures, excluding those with very short duration, are tabulated in Table XIV. The result still fails to show a correlation between the viscosity and wear. There is, of course, a correlation between viscosity and volumetric efficiency. Excluding these runs with severe wear (<3000 mg ring wear) which caused the excessive loss of volumetric efficiency, a linear relationship between the viscosity and volumetric efficiency is indicated in Figure 22. The linear correlation coefficient was computed to be 0.91, showing significant correlation at 99% confidence level. The line of regression was thus determined and is also shown in Figure 22.

Polar Components

In general, the less-highly-refined fuels had more polar components of all kinds: aromatics, sulfur and nitrogen compounds, and organic acids. Not surpringly, a good correlation was found between wear and each of these polar constituents. This is given in Table XIII. Thus, Bayol 35 and PW-523, which had negligible sulfur content (<0.2 ppm) gave the highest wear. Diesel fuel (2300 ppm) and RAF-176-64 (560 ppm) had the highest sulfur and the lowest wear. Similarly, for acidity, diesel fuel and RAF-176-64 were the only fuels having a neutralization number above 0.005 mgKOH/g, and gave the lowest wear. Acidity increased only slightly in any of the tests, indicating that oxidation was negligible.

The best correlation appears to be with aromatic content. All fuels containing < 2% aromatics gave severe wear. Those fuels containing > 10% aromatics gave rather satisfactory performance.

It should be borne in mind, however, that these results do not establish a cause-and-effect relationship between a polar constituent and wear, however reasonable it may seem. Thus, although certain acids can reduce wear, it does not necessarily follow that all acids can do so. Similarly, although sulfur compounds are widely used as EP additives in lubricants, it does not mean that the sulfur compounds found in jet fuel have antiwear properties. The various components comprising "polar impurities" must be isolated in future investigations.

TABLE XIII

RANK CORRELATION FOR TEST DATA FROM VICKERS PUMP TESTS

Acceptance Limits: $\gamma_{s,0.01} = 0.833$, $\gamma_{s,0.05} = 0.64$

	Sump Temperature °F	$^{*}\gamma_s$	Evidence of Significance
Wear vs. Viscosity	90	0.12	No
Wear vs. Viscosity	125	0.03	No
Wear vs. ppm S	90	0.66	Significant at 95% A.L.
Wear vs. ppm S	125	0.76	Significant at 95% A.L.
Wear vs. Neut. No.	90	0.81	Significant at 95% A.L.
Wear vs. % Aromatics	90	0.85	Significant at 99% A.L.
Wear vs. % Aromatics	125	0.89	Significant at 99% A.L.

$$^{*}\gamma_s = 1 - \frac{6}{n(n^2-1)} \sum d^2$$

where d = the difference of numerical ranks of two corresponding variables.

n = number of fuels ranked.

(G. W. Snedecor's "Statistical Methods," p. 164)

TABLE XIV

VISCOSITY vs VOLUMETRIC EFFICIENCY AND WEAR

	Outlet Temperature F	Viscosity cp	Volume Efficiency %	Wear, mg Ring	Wear, mg Vane
Diesel Fuel	94	2.30	61	4	0
RAF-173-61	103	1.60	57	235	31
Bayol 35	115	1.55	24	5150	204
Diesel Fuel	136	1.36	43	4	6
JP-5	94	1.23	43	561	85
RAF-173-61	144	1.10	16	4240	294
RAF-176-64	96	1.10	48	39	0
PW523	110	1.10	26	4944	100
75 LN-LV	104	0.91	37	200	50
AFFB-3-65	106	0.90	26	3656	661
JP-5	134	0.88	30	1119	11
75 LN-LV	136	0.78	26	127	0
RAF-176-64	142	0.77	18	39	0
JP-4	104	0.47	18	157	3

Spearman Rank Correlation

Acceptance Limit: $\gamma_{s,\ 0.05} = 0.456$

$\gamma_{s,\ 0.01} = 0.645$

Viscosity vs. Ring Wear, $\gamma_s = 0.11$, No Correlation.

Viscosity vs. Vane Wear, $\gamma_s = 0.25$, No Correlation.

Viscosity vs. Vol Efficiency, $\gamma_s = 0.62$, Significant at 95% A.L.

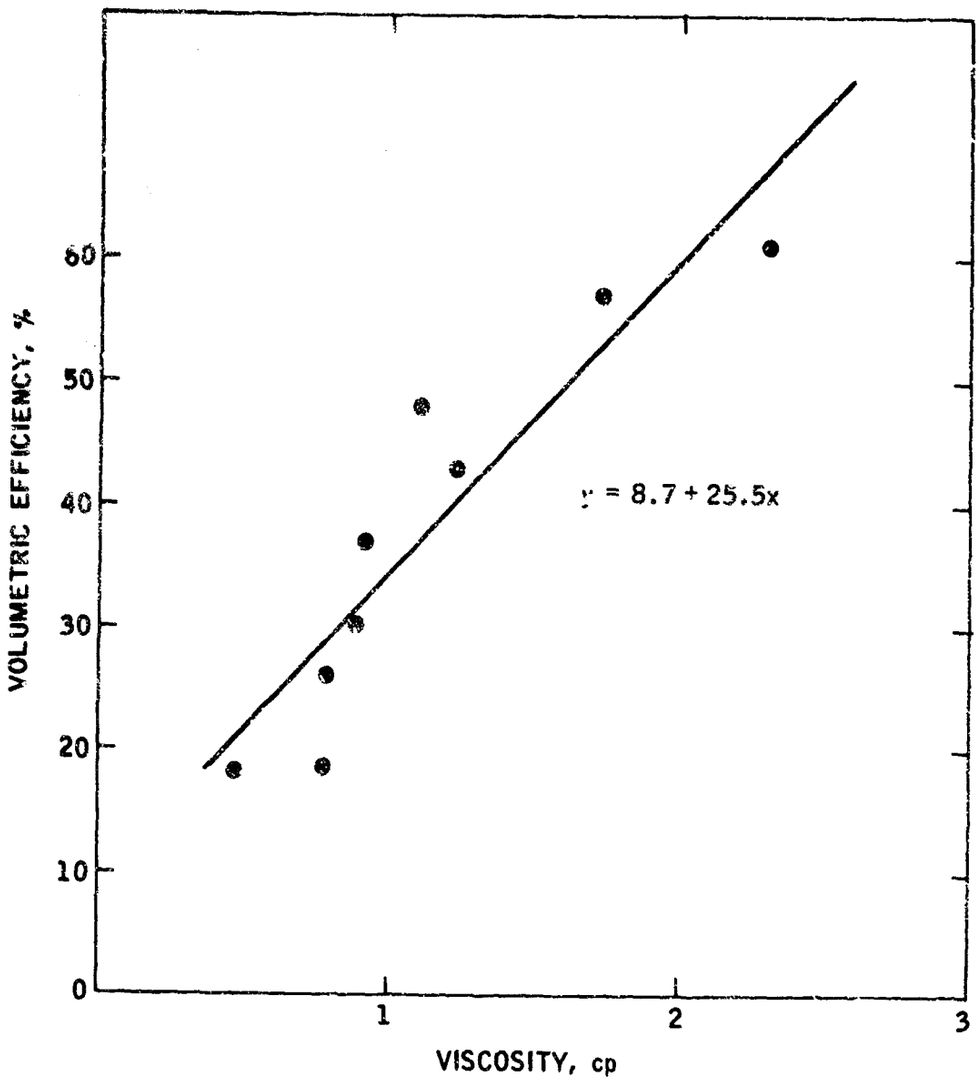


FIGURE 22 VICKERS PUMP VOLUMETRIC EFFICIENCY VS. VISCOSITY

(c) Friction in Pump Varies for Different Fuels

A difference of pump outlet temperature for various fuels tested at the same sump temperature and pressure was evident. The variation of the temperature gradient between the inlet and outlet of the pump indicates the difference of friction for various fuels in pump operation. The power loss (ΔP_F) due to friction was estimated by an energy balance using such test data as the sump temperature (T_s), outlet temperature (T_o), pumping pressure (P), fuel density (ρ), pumping rate (V):

frictional power loss	=	heat absorbed by fluid per unit time	+	rate of heat loss to surroundings

$$\Delta P_F = V\left[C_p \rho (T_o - T_s) \quad J - 144\ P\right] + J\,(h_c + h_r)\,A\,(T_o - T_a) \qquad (1)$$

C_p is the specific heat of various fuels and is obtained from the generalized chart on page 93 of Maxwell's "Data Book on Hydrocarbons."

J is the heat-energy conversion factor.

$(h_c + h_r)$ is defined as the combined coefficient for convection and radiation (Perry's Handbook of Chemical Engineering, Third Edition, p. 474).

A is the exposed area for heat loss.

T_a is the ambient temperature.

The friction force, F, can then be evaluated from

$$F = \frac{\Delta P_F}{U} \qquad (2)$$

where U is the linear velocity of rotation. The load of the vanes on the ring surface is mainly from the back pressure of the discharged fuel. Since in the discharge cycle the pressure is counterbalanced, only the six vanes in the suction cycle are loaded. Based on this information, the total load and then the coefficient of friction can be evaluated.

These computed values of friction are tabulated in Table XV. The coefficient of friction ranges from 0.05 to 0.41. These results indicate that the friction is generally high when severe wear occurs. However, there are exceptions. 75 LN-LV fuel and JP-4, for instance, gave a friction coefficient >0.3. The wear for both fuels was rather low. It appears that the anti-scuffing effect prevails as long as a surface protective film is present on the rubbing area, but this film is not necessarily effective in reducing friction.

There seems to be a general tendency for friction to increase at a higher temperature for most fuels with the one exception of 75 LV-LN which had lower friction at the higher temperature. It is interesting to note that this same effect was observed for additive fuels, as noted later. This again indicates that the frictional behavior of fuels containing additives is quite unpredictable, even though they all show a pronounced anti-wear effect.

TABLE XV

FRICTION DATA FOR VICKERS PUMP TESTS

p = 350 psig

	Sump Temperature, F	Power Loss Due to Friction ft-lb/sec	Friction lb	Coefficient of Friction
Diesel Fuel	90	84.0	7.2	0.07
	125	251.0	21.6	0.22
Bayol 35	90	460.7	39.6	0.41
RAF-173-61	90	260.0	22.3	0.23
	125	276.0	23.8	0.25
PW-525	90	395.7	34.0	0.35
JP-5	90	59.0	5.1	0.05
	125	192.0	18.3	0.19
RAF-176-64	90	146.2	12.5	0.13
	125	210.0	20.0	0.21
[illegible] LN-LV	90	367.4	31.5	0.32
	125	165.0	16.0	0.17
AFFB-3-65	90	289.2	24.8	0.26
JP-4	84(1)	287.4	24.7	0.30

(1) At 300 psig pressure.

(d) The Ring Surface Softened
After Severe Wear

The two rubbing surfaces of the pump cartridge are made of deep-hardened alloys with a hardness of Rockwell "C" 60 and a high resistance to wear. The vane is made of a molybdenum base tool steel having a high resistance to softening at high temperature. The ring was made of deep hardened bearing steel having a low resistance to softening at high temperature (>300F). The hardness of the wear surface of the vane was measured after the test and found to have undergone little change. In contrast, a decided change in the hardness of the rings was noted. It was also found that the hardness at various spots on the wear surface varied over a wide range. A macro etching procedure was employed to identify the variation of hardness on the metal surface, using a Nital solution (4% HNO_3 in alcohol). As an illustration, a micrograph of a segment of the etched ring from a pump test using AFFB-3-65 fuel is shown in Figure 23. The dark area is the softened region, having a Rockwell "C" 40-52 hardness, while the light area shows only a small change of hardness(Rockwell "C" 57-60). The reason for this nonuniformity of hardness is unknown. The values of hardness for wear surfaces of rings from pump tests using various fuels are listed in Table XVI. It is interesting that the severity of wear can be estimated from the lowest value of hardness: A ring surface softened to 45 Rockwell C or less indicates severe wear; one softened to 55 Rockwell C indicates mild wear. When there was very little wear (e.g., diesel fuel tested at 90F, sump temperature), the hardness of the ring was practically unchanged. It is known that this alloy does not soften appreciably below a temperature of 300F, which is considerably higher than the bulk fuel temperature in any tests. This is good evidence that a local high temperature on the rubbing surfaces was developed due to the metal-to-metal contact. It is therefore postulated that in severe wear the ring surface was softened by the high local temperature and then scoring occurred due to the difference of hardness between the ring and the vane which could retain its hardness at such a high temperature. The presence of a surface protective film minimized the metal-to-metal contact, so that the ring was softened to a lesser extent. This might contribute to the reduction of wear.

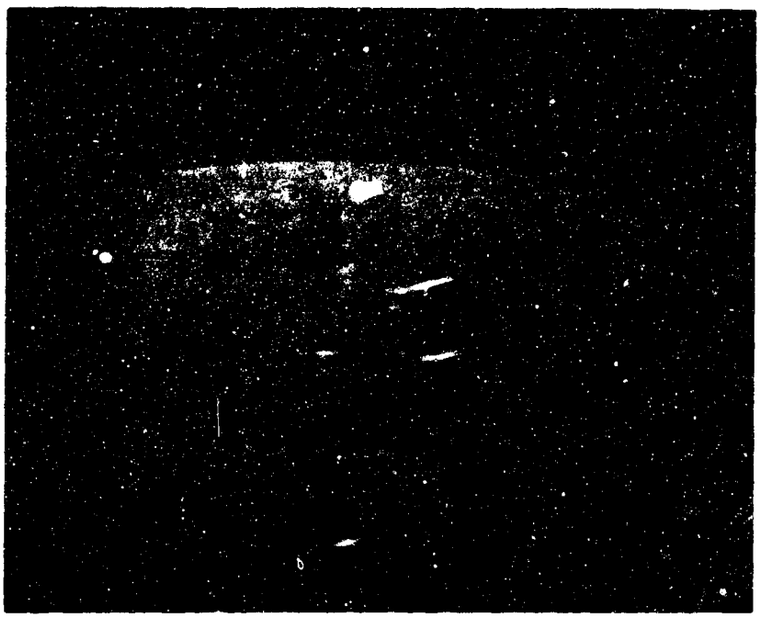


FIGURE 23 ETCHED RING SEGMENT --
VICKERS PUMP TEST WITH AFFB-3-65 (X5)

TABLE XVI

HARDNESS OF RINGS AFTER PUMP TESTS

	Sump Temperature, °F	Hardness, Rockwell "C" Dark Area(1)	Hardness, Rockwell "C" Light Area(1)	Ring Wear mg
Bayol 35	90	44-47	56-60	5150
PW-523	90	39-50	56-59	4944
RAF-173-61	125	44-50	55-60	4240
AFFB-3-65	90	44-52.5	57.5-60	3656
JP-5	125	44-51	53-57.5	1119
JP-5	90	51-56	57-59	561
RAF-173-61	90	51-56	58-59	235
75 LN-LV	90	54-60(2)		200
JP-4	84	54-59.5(2)		157
75 LN-LV	125	55-59.5(2)		127
RAF-176-64	90	53-58	58.5-59	67
Diesel Fuel	90	57-59(2)		4
Diesel Fuel	125	55-59.5(2)		4
New Ring	-	58-59.5(2)		-

(1) Etched area.

(2) Dark and light areas are not distinguishable.

2. EFFECT OF TRACE COMPONENTS, VISCOSITY AND TEMPERATURE

a. Effect of Trace Compounds

(1) General Considerations

Whatever lubricating properties are possessed by commercial jet fuels are often attributed to the presence of compounds. These include almost all species present in a blend aside from paraffinic and naphthenic entities. Thus, compounds containing hetero atoms (e.g., S, N, O) as well as olefinic and aromatic materials are included in this category. The test results for additives down to the 15 ppm concentration level presented earlier in this report certainly indicate that the presence of minute amounts of polar constituents in hydrocarbon fuels favorably affect their lubricity properties.

One phase of this study is therefore to determine the effect of various polar compounds. Two approaches are being followed: (1) Various aromatics, sulfur, nitrogen and oxygen compounds are added to a pure hydrocarbon to note their effect. The sulfur and nitrogen compounds are those known to exist in petroleum crudes from analytical work carried out by API Research Projects 48 and 52. The oxygenated compounds cover those that may result from air-oxidation of the fuel. (2) The fuels are extracted to separate the polar compounds, and attempts made to identify the most active constituents. Some exploratory work has been started along both these lines.

(2) Effect of Added Nitrogen and Sulfur Compounds on Cetane Lubricity

A list of the compounds tested, together with their molecular structures and boiling point, is shown in Table XVII. These include sulfides, disulfides, mercaptans, ring sulfur compounds, aliphatic and aromatic amines and ring-nitrogen compounds.

(a) Ball-On-Cylinder Results

The ball-on-cylinder machine was used to study the lubrication characteristics of the organic sulfur and nitrogen-containing compounds listed in the above table. Solutions of sulfur and nitrogen compounds in cetane were prepared at 1% S or N (by weight) in all cases in which the solubility was high enough. The pertinent data at the end of the test are summarized in Tables XVIII and XIX.

No reduction in % metallic content was noted, indicating that none of these compounds formed an insulating layer on the rubber surfaces. Likewise, wear in all cases was as high or higher than with cetane alone. Certain of the compounds did reduce friction however, giving lower values and less erratic traces. These were the two mercaptans, dibutyl sulfide, and phenothiazine.

Phenothiazine is only very slightly soluble in hydrocarbons and therefore was present only in a very low concentration. Therefore, some of the other compounds were tested at concentrations lower than 1%. These tests, summarized in Table XIX, merely confirm that the compounds have no effect on metallic content, tend to be pro-wear and reduce friction only slightly.

Two of the compounds were also tested at lower concentrations. These data are given in Table XIX.

Table XVII

Nitrogen and Sulfur Compounds Added

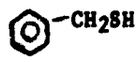
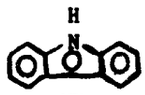
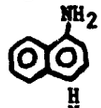
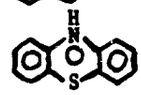
Compound	Structural Formula	B.P., °C. (760 mm.)
Benzothiophene		221°C.
Benzyl Mercaptan		194°C.
Butyl Disulfide	C_4H_9-S-S-C_4H_9	226°
Dibutyl Sulfide	C_4H_9-S-C_4H_9	182°C.
Octyl Mercaptan	$C_8H_{17}SH$	198°
Carbazole		355°C.
Naphthylamine		300° (Sub.)
Phenothiazine		371°
Quinoline		237°
Tri-n-butylamine	$(C_4H_9)_3N$	216°

TABLE XVIII

WEAR AND FRICTION IN BALL-ON-CYLINDER APPARATUS FOR CETANE CONTAINING SULFUR AND NITROGEN COMPOUNDS

(240 rpm., 240 g., 32 min.)

Compound	% Metallic Contact	Coefficient of Friction	Wear Scar Diameter (mm)
Benzothiophene	92	0.13	0.26
Benzyl mercaptan	93	0.11	0.26
Butyl disulfide	94	0.14	0.26
Dibutyl sulfide	97	0.11	0.24
Octyl mercaptan	96	0.12	0.24
Carbazole*	95	0.11	0.27
Naphthylamine*	95	0.13	0.19
Phenothiazine*	91	0.11	0.26
Quinoline	92	0.13	0.26
Tri-n-butylamine	96	0.16	0.28
Cetane (average of three runs)	93	0.13	0.21

* Solubility limitations prevented the preparation of a 1% solution; phenothiazine, which contains both S and N, was run as a saturated solution (less than 1% S or N) while carbazole and naphthylamine were run as slurries. In all three cases, solubility was marginal (i.e., much less than 1%).

TABLE XIX

EFFECT OF SULFUR AND NITROGEN COMPOUNDS - CONCENTRATION DEPENDENCE

Compound	(% Wt. S)	% Metallic Contact	Coefficient of Friction	Wear Scar Diameter, mm
Dibutyl sulfide	1%	97	0.11	.26
	0.22%	94	0.15	.19
	0.022%	94	0.13	.20
Octyl Mercaptan	1%	96	0.13	.24
	0.22%	93	0.13	.23
	0.022%	90	0.13	.20

(b) Four-Ball Tests

Some Sulfur Compounds Improve Scuff-Load

The same compounds have been tested on the four-ball normal wear tester at loads up to 80 kg. It appears that, at these more severe conditions, certain sulfur compounds reduce scuffing wear, although they have no effect on rubbing wear. These include benzyl and octyl mercaptan, dibutyl sulfide, and butyl disulfide.

Figure 24 is a linear plot of wear scar diameter vs. load for 1% sulfur solutions of butyl disulfide and octyl mercaptan in cetane compared to cetane itself. The reduction in wear scar diameter is especially marked at high loads when scuffing occurred with the base fuel. The butyl disulfide solution also shows less wear than pure cetane at light loads. Table XXI lists the wear scar diameters for all solutions at given loads.

It appears that the type sulfur compound which could be effective in these regimes is either of the mercaptan sulfur or disulfide type. This is not unexpected since these materials would be more reactive to metal surfaces than monosulfides or ring sulfur.

Two Nitrogen Compounds Decrease Wear but Not Scuffing

Several nitrogen compounds that could be trace components in jet fuels were also tested, again at 1% N concentration. Two such compounds, naphthylamine and quinoline, were found to increase the scuff load beyond 35 kg. as shown in Table XX below. However, none of the nitrogen compounds improved scuffing wear at loads greater than 35 kg., as did the sulfur compounds mentioned above. Complete data are given in Table XXII.

Table XX

Four-Ball Wear Scar Diameters - Nitrogen Compounds In Cetane

(1800 rpm, 77°F., five-minute tests)

Additive in Cetane	Wear Scar Diameter, mm 35 kg	50 kg
None	0.90	1.70
Naphthylamine	0.33	2.10
Quinoline	0.32	1.90

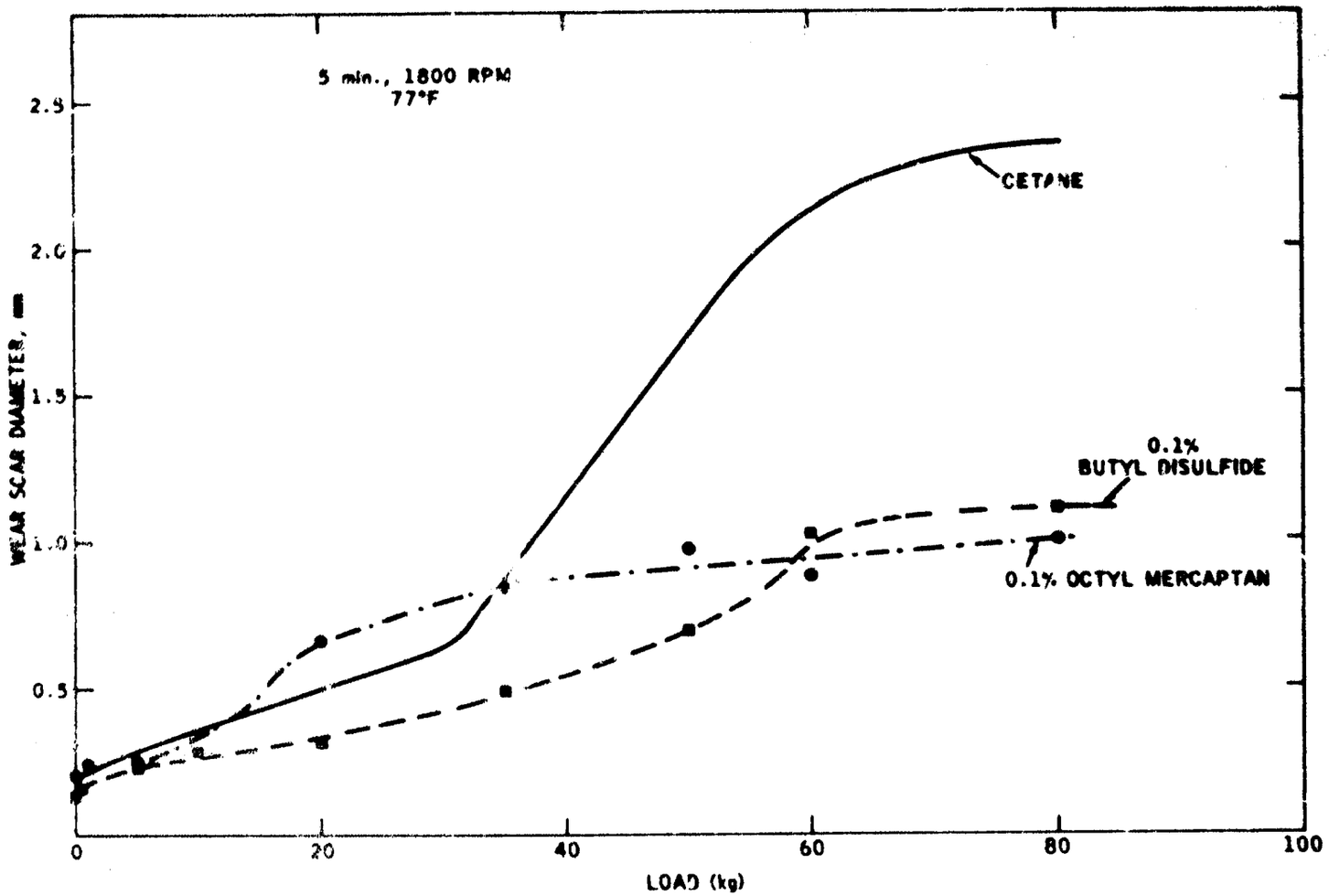


FIGURE 24 WEAR SCAR DIAMETER VS. LOAD FOR SULFUR-CONTAINING COMPOUNDS ON FOUR-BALL TESTER

TABLE XXI

FOUR BALL WEAR SCAR DIAMETER vs. LOAD FOR 1% SULFUR-CONTAINING SOLUTIONS

(5 min., 1800 rpm, 77°F)

	Wear Scar Diameter, mm									
Additive in Cetane — Load:	0.[illegible]	0.5	1.0	5.0	10	20	35	50	60	80
Benzothiophene	0.18	0.26	0.30	0.41	0.51	0.59	0.69	1.73	1.71	2.21
Benzyl Mercaptan	0.21	0.29	0.40	0.50	0.53	0.62	0.80	0.90	1.16	1.40
Butyl Disulfide	0.14	0.16	0.19	0.24	0.29	0.32	0.49	0.69	1.07	1.11
Dibutyl Sulfide	0.22	0.22	0.30	0.47	0.51	0.62	0.94	0.95	1.15	2.08
Octyl Mercaptan	0.20	0.19	0.24	0.24	0.33	0.66	0.84	0.97	0.87	0.99
None	0.20	0.22	0.23	0.30	0.35	0.55	0.90	1.70	2.13	2.36

TABLE XXII

FOUR BALL WEAR SCAR DIAMETER vs. LOAD FOR 1% NITROGEN-CONTAINING SOLUTIONS

(5 min., 1800 rpm, 77°F)

		Wear Scar Diameter mm									
Additive in Cetane	Load:	0.1	0.5	1.0	5.0	10	20	35	50	60	80
Carbazole		0.13	0.22	0.23	0.33	0.38	0.52	0.61	1.83	1.95	2.11
Naphthylamine		0.14	0.17	0.16	0.21	0.24	0.29	0.33	2.10	1.92	2.43
Phenothiazine		0.23	0.30	0.34	0.47	0.50	0.59	0.68	1.81	1.75	2.18
Quinoline		0.16	0.18	0.18	0.20	0.23	0.29	0.32	1.90	1.89	2.33
Tri-n-Butylamine		0.17	0.21	0.23	0.32	0.37	0.55	1.51	1.94	2.11	2.80
None		0.20	0.22	0.23	0.30	0.35	0.55	0.90	1.79	2.13	2.36

(d) Effect on Lubricity of Removal of Polar Species

In highly-refined fuels this "polar" component is quite small, usually less than 1%, except for aromatics. The problem of investigating the effect of such materials on fuel lubricity can be considered in the following manner. First, the polar component can be removed from the fuel and the lubricity properties of the treated and untreated fuels compared to determine the importance of such a treatment. Second, in the event that a significant difference is uncovered for the nonpolar fuel, the actual isolation and identification of the polar compounds and/or the blending of suitable polar materials into treated fuel will allow a direct determination of the fuel lubricity components.

In the experiments done to date, the hydrocarbon was passed through a three-foot high, one-inch I.D. column packed with silica gel. The column was packed and quickly covered with the hydrocarbon to be treated. Percolation was continued until one liter had been added to the column. This column-treated material was used in various friction and wear tests, after which the polar component adsorbed at the top of the column was eluted with a 50% methanol-50% acetone solution. The acetone-methanol was driven off under vacuum and mild heating to free the "polar component" fraction.

In the initial experiments in this series, the performance of diesel fuel was evaluated. The diesel fuel has been shown to contain the highest amount of sulfur and nitrogen of the fuels to be tested in this program and is also highest in acidity.

After silica gel percolation, analyses were made to determine the effect of the treatment on the chemical composition of the fuel. These include sulfur and nitrogen content and infrared and NMR spectra of the original material, the percolated fuel, and the polar material desorbed from the column.

Table XXIII below shows the effect of column treatment on sulfur and nitrogen content:

TABLE XXIII

Silica Gel Removes Sulfur and Nitrogen Compounds

	Original Diesel Fuel	Silica Gel-Treated Diesel Fuel	Column Eluate
Sulfur Content, ppm	2,300	0.6	15,700
Nitrogen Content, ppm	14	1	18

The above data indicate that the sulfur has been effectively concentrated in the polar component (a sevenfold concentration of the original fuel would yield a value of 16,000 ppm in the eluate if it were completely removed). In the case of nitrogen, the situation is not clear since the method of nitrogen analysis also utilized a column treatment to concentrate the nitrogen. These analyses are being repeated. However, the analyses do indicate that the more polar nitrogen compounds have been removed from the treated fuel.

An accurate material balance on the diesel fuel has not been obtained due to experimental difficulties. The method of evaporating the eluting solvent from the polar component may have resulted in the loss o some of the lighter materials in this fraction. Future experiments will be designed so as to avoid this difficulty.

Ball-on-cylinder tests have been run on the original diesel fuel and each of the two fractions. These results are given in Table XXIV.

TABLE XXIV

Ball-on-Cylinder Results for Extracted Diesel Fuel

(240 rpm, 32 min.)

Treatment	Load, g:	Coefficient of Friction 60	240	1000	Wear Scar Diameter, mm 60	240	1000
None		0.12	0.13	0.14	0.21	0.25	0.30
Silica-Gel Extracted		0.22	0.20	0.16	0.24	0.30	0.42
Eluate		0.08	0.13	0.12	0.36	0.47	0.48

The results are somewhat surprising. The friction results are normal, with the polar eluate giving less friction than the whole fuel and the purified fraction giving more friction and very erratic traces. But, the wear scars do not show a similar trend: Both the extracted material and the eluate gave more wear than the whole fuel. One reasonable explanation of this is as follows: The absence of polar impurities in the extracted portion causes high friction and wear; the concentration of these polar impurities in the eluate gives low friction because the impurities react with the surface to give an easily smearable layer; this layer is easily worn away, however, giving higher wear. This is reinforced by data on the metallic contact which was considerably lower for the column eluate than the whole fuel, both at 60 and 240 g loads. This indicates some kind of surface reaction which may account for the higher wear. The behavior of the extract to give low friction but higher wear is similar to that of certain additives in JP-4, as will be discussed in Section V-4.

The second experiment in the series involved the silica-gel treatment of n-cetane followed by tests similar to those described above. The cetane was of ASTM purity (Humphrey Chemical Company, 97.5% C_{16}) and was passed through the same column described previously. (An intense yellow band developed at the top of the column during treatment.) The first 100 cc of treated cetane were immediately run in the ball-on-cylinder machine; the rest of the cetane was taken off using n-pentane, and finally the yellow band which had developed at the top of the column was eluted with the 50% acetone-50% methanol solution. The yield of "polar" component in the cetane was approximately 0.8%. The yellow column eluate was concentrated and separated into two layers. Both samples were analyzed via their UV spectra. The top layer was identified as a primarily long chain ketone, similar to 2-methyl-3 decanone, the longest chain ketone of known spectrum. It is quite conceivable that this material is a C_{16} ketone, an intermediate in oxidative breakdown of n-cetane. The lower layer was very similar to this material with the only obvious difference being the presence of water. It is assumed that these two layers are a long chain ketone solution and the long chain ketone itself.

The ball-on-cylinder test conditions using cetane and treated cetane are similar to those described previously for diesel fuel. (Due to the small amount of material, no lubricity tests were made on this eluted "polar" component.) The major differences are (1) the lubricity tests were made immediately upon passage through the silica-gel and (2) the effect of bubbling pure nitrogen gas through the system under test was investigated. In one case the treated cetane was pre-equilibrated with N_2 in a conventional gas bubbler while in the other test N_2 was simply passed through the solution while the ball-on-cylinder test was in progress. As shown in Table XXV, there seems to be little advantage to this pre-equilibration.

TABLE XXV

Ball-on-Cylinder Results for Extracted Cetane

(32 min., 77°F., 240 rpm)

	Coefficient of Friction			Wear Scar Diameter, mm		
Load, g:	60	120	240	60	120	240
Cetane	0.09	0.16	0.16	0.20	0.26	0.40
Silica-Gel (1) Treated Cetane	0.13	0.25	0.19	0.22	0.61	0.83
Cetane	0.15	0.16	0.16	0.21	0.26	0.40
Silica-Gel (2) Treated Cetane-N_2	0.14	0.15	0.16	0.21	0.41	0.68
Silica-Gel (3) Treated Cetane-N_2	0.13	0.15	0.16	0.22	0.40	0.70
Silica-Gel (4) Treated Cetane	0.14	0.15	0.17	0.31	0.37	0.74

(1) Ball-on-cylinder test run immediately after column treatment.

(2) Test made after one hour equilibration of cetane with N_2 followed by N_2 bubbling during run.

(3) Test made while bubbling N_2 into solution without pre-equilibration.

(4) Test made on treated cetane 24-48 hours after column treatment.

Two cetane runs are reported since two different cylinders were used in this series. With the exception of an unusually low coefficient of friction at 60 g for the first cylinder, the results indicate good reproducibility of the lubricity data.

One obvious conclusion is that wear is greater in the silica-gel treated solutions at loads in excess of 60 g. Surprisingly, there is little change in the coefficient of friction throughout this series with the only significant difference seen in the silica-gel treated material which was run immediately after column treatment.

The solution yielding the greatest amount of wear is the one tested immediately after column treatment. This result could mean that the presence of trace amounts of water and/or dissolved oxygen may be a critical factor since these species might be expected to equilibrate with the solution through contact with the atmosphere. Other possible lubricity agents, such as aromatics and compounds containing hetero atoms, would not contribute in this manner. It is pertinent to emphasize that the increase in wear with the silica-gel treated materials over the untreated cetane is much greater than the differences between the silica-gel treated samples, indicating the potentially large role which aromatics and hetero-atom containing materials might play. Along with analytical analyses on the column-treated materials, a series of experiments are planned to evaluate the effect of dissolved oxygen on the lubricating ability of the cetane. Since the levels of interest, both in the case of oxygen and water, are less than 100 ppm, new methods of determination may be devised.

b. Effect of Viscosity and Temperature

(1) Effect of Viscosity

Several pure hydrocarbons of chromatographic quality were selected for studying the effect of viscosity on wear characteristics. Two of them, heptane and dodecane were tested at 97F. Heptane at 97F (36C) has an absolute viscosity of 0.355 cp which matches that of JP-5 at 300F (149C). The viscosity of dodecane is only slightly lower than that of JP-5 at all temperatures. At the test temperature of 97F, dodecane has an absolute viscosity of 1.15 cp as compared to 1.20 cp for JP-5. This is 3.25 times as viscous as heptane at 97F or JP-5 at 300F.

The 4-ball wear data are plotted in Figure 25. Both curves are well behaved, showing an initial stage of almost constant scar size and a normal wear region with a slope of 0.25. The more viscous fluid, dodecane, shows a smaller initial wear scar and a distinctly lower wear rate of 1.16×10^{-4} mm^3/min than the less viscous fluid, heptane. The wear rate for heptane is 5.06×10^{-4} mm^3/min. This observation illustrates that viscosity alone is an important factor.

(2) Effect of Temperature - 97 to 183F

Temperature has both direct and indirect effects on the wear of a lubricated system. One of the significant indirect factors is the decrease in viscosity due to the increase in temperature. Thus, in making a critical study of the effect of temperature on wear, it becomes necessary to separate the influence of viscosity change associated with temperature change from the effect of temperature per se. This separation was accomplished by choosing pure hydrocarbons of chromatographic quality in a homologous series and selecting their corresponding test temperatures in such a way that they all have the same viscosity at their test temperatures.

The three normal paraffins, heptane, octane and nonane have the same viscosity of 0.355 cp at 97F (30C), 141F (60.5C) and 183F (84C) respectively. Figure 26 shows that the four-ball wear rates for these three hydrocarbons at their selected temperatures fall practically on one single wear scar size vs. time curve. Thus, variation in temperature from 97 to 183F with viscosity maintained constant, seems to have no significant effect on the four-ball wear for paraffinic hydrocarbons from the same homologous series.

(3) Effect of Temperature - 300F

For further increase in test temperature above 183F, oxidation was expected to cause changes in the test fluid. An atmosphere control attachment was designed, fabricated and installed on the four-ball wear tester. Argon was used to keep the test fluid under inert atmosphere during the heating period as well as during the test runs.

Dodecane was tested at 288F (142C). At this test temperature, dodecane has the same viscosity as JP-5 at the pump inlet temperature of 300F. Test runs were not extended beyond 15 min because of excessive evaporation loss at the test temperature. This also meant the need of a pressurized system for tests at temperatures above 300F. In testing dodecane at 288F, the number of test runs for each fluid were reduced to two because heating-up and cooling-down periods greatly lengthened the time requirement for each test.

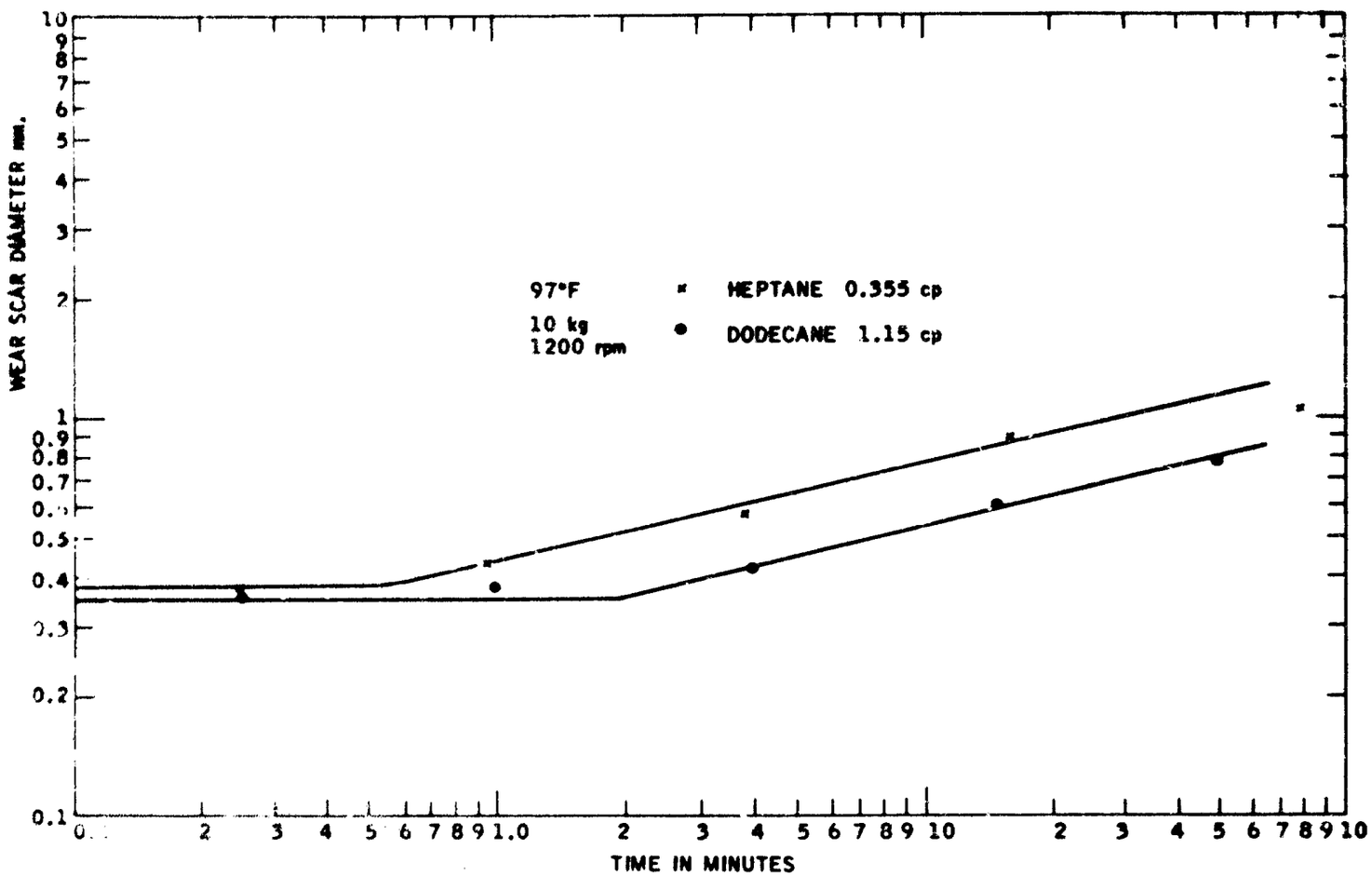


FIGURE 25 EFFECT OF VISCOSITY ON WEAR IN THE FOUR-BALL MACHINE

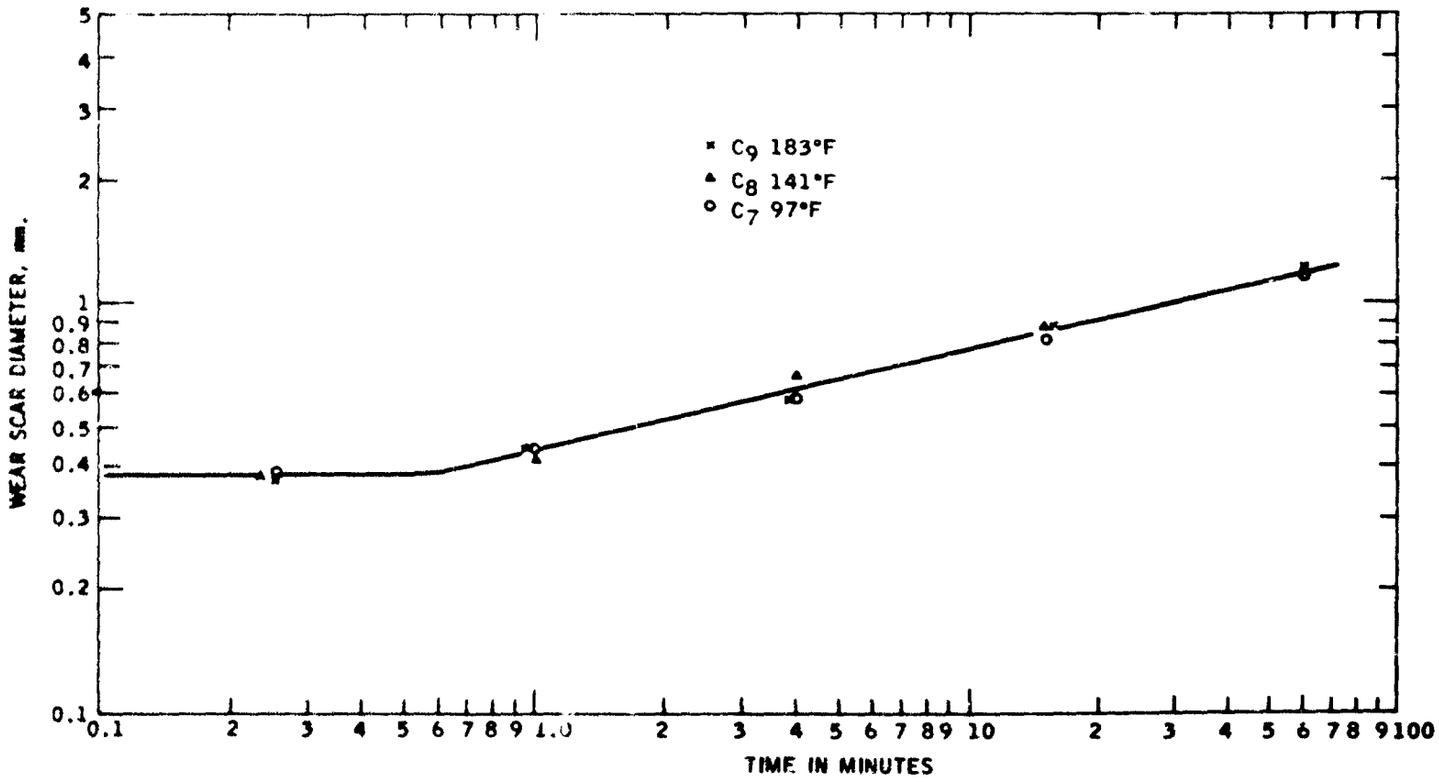


FIGURE 26 EFFECT OF TEMPERATURE ON WEAR IN FOUR-BALL MACHINE 97-183F

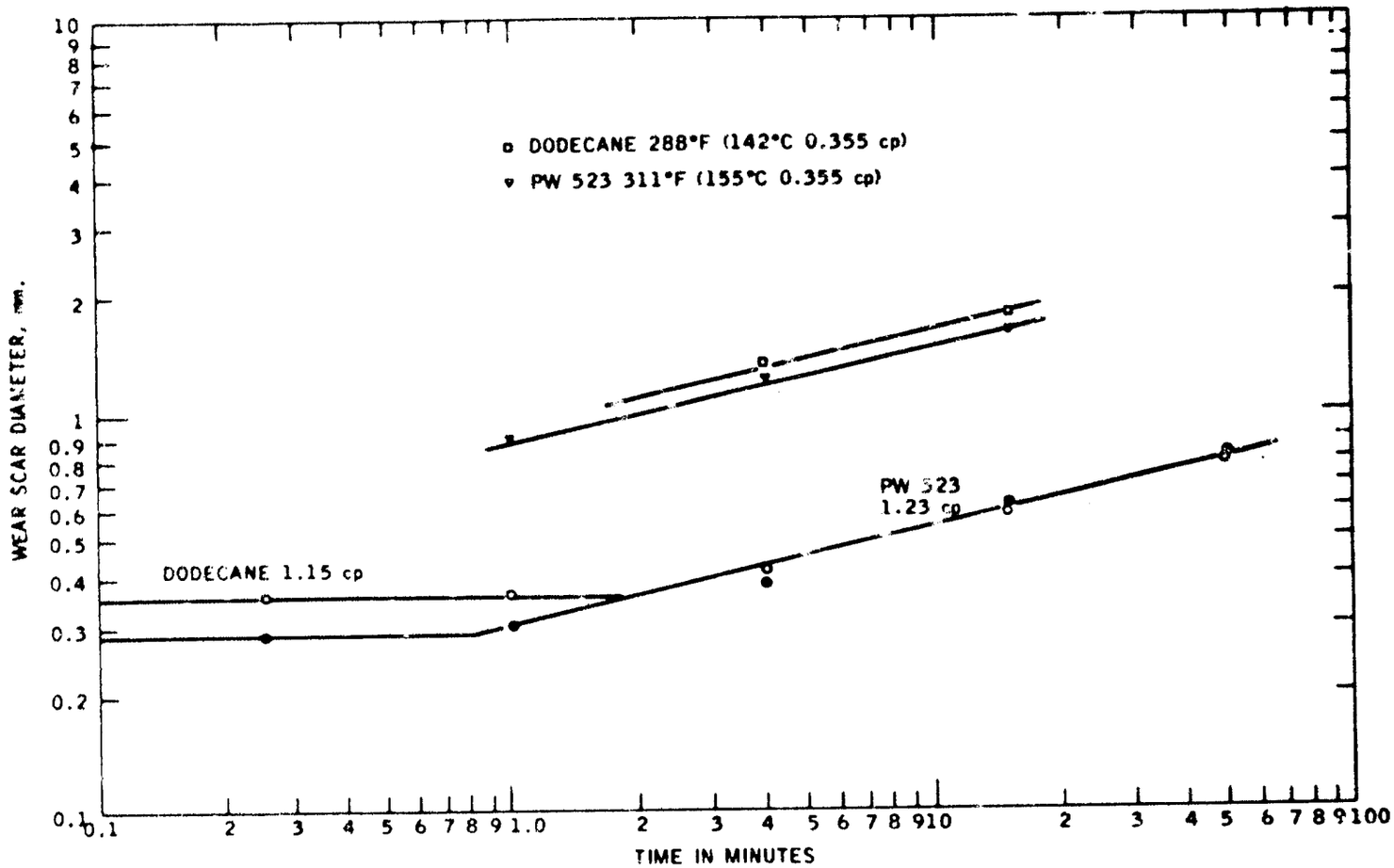


FIGURE 27 EFFECT OF TEMPERATURE ON WEAR IN FOUR-BALL MACHINE - 300F

The uppermost curve in Figure 27 shows the two points for dodecane at 288F on a log d vs. log t plot. They fall on a straight line of 0.25 slope with a wear rate of 111.7×10^{-4} mm^3/min, which is much higher than its wear rate at 97F: 1.16×10^{-4} mm^3/min. The 100-fold increase in wear rate represents the total temperature effect, which includes the indirect effect through the decrease in viscosity. As already shown, the decrease in viscosity alone caused an increase in wear rate from 1.16×10^{-4} to 5.06×10^{-4} mm^3/min. Thus the effect of temperature increase from 97F (36C) to 288F excluding the viscosity effect, is a 22-fold increase in wear rate.

(4) Comparison Between Pure Paraffinic Hydrocarbon and Commercial Fuels

PW-523 is a mixture of C_{11} to C_{14} hydrocarbon with relatively high n-paraffin content. It is the purest one of the ten fuels currently being tested on this program.

Because it is extremely highly refined it was tested at 97F (1.23 cp), and at 311F (0.355 cp) and compared with chromatographic quality dodecane at 97F (1.15 cp) and at 288F (0.355 cp).

Figure 28 shows the comparison of four-ball results at 97F. Both fluids have practically same wear rate of 1.163×10^{-4} mm^3/min. At the higher temperature, PW-523 causes a slightly lower wear rate of 93.7×10^{-4} mm^3/min vs. 111.7×10^{-4} mm^3/min. The four-ball data obtained so far show that the extremely highly refined PW-523 is comparable to the chromatographic quality dodecane in four-ball performance.

The composition of JP-5 on the basis of gas chromatographic analysis is quite similar to that of PW-523. It does, however, contain quite high amounts of s-impurities. At the high test temperatures, the wear rate for JP-5 is 8.5×10^{-4} mm^3 min which is only about 1/12 of the wear rate for PW-523 and dodecane. The difference is not so large at 97F. JP-5 has a wear rate of 0.60×10^{-4} mm^3/min as compared to 1.16×10^{-4} mm^3/min for PW-523 and dodecane.

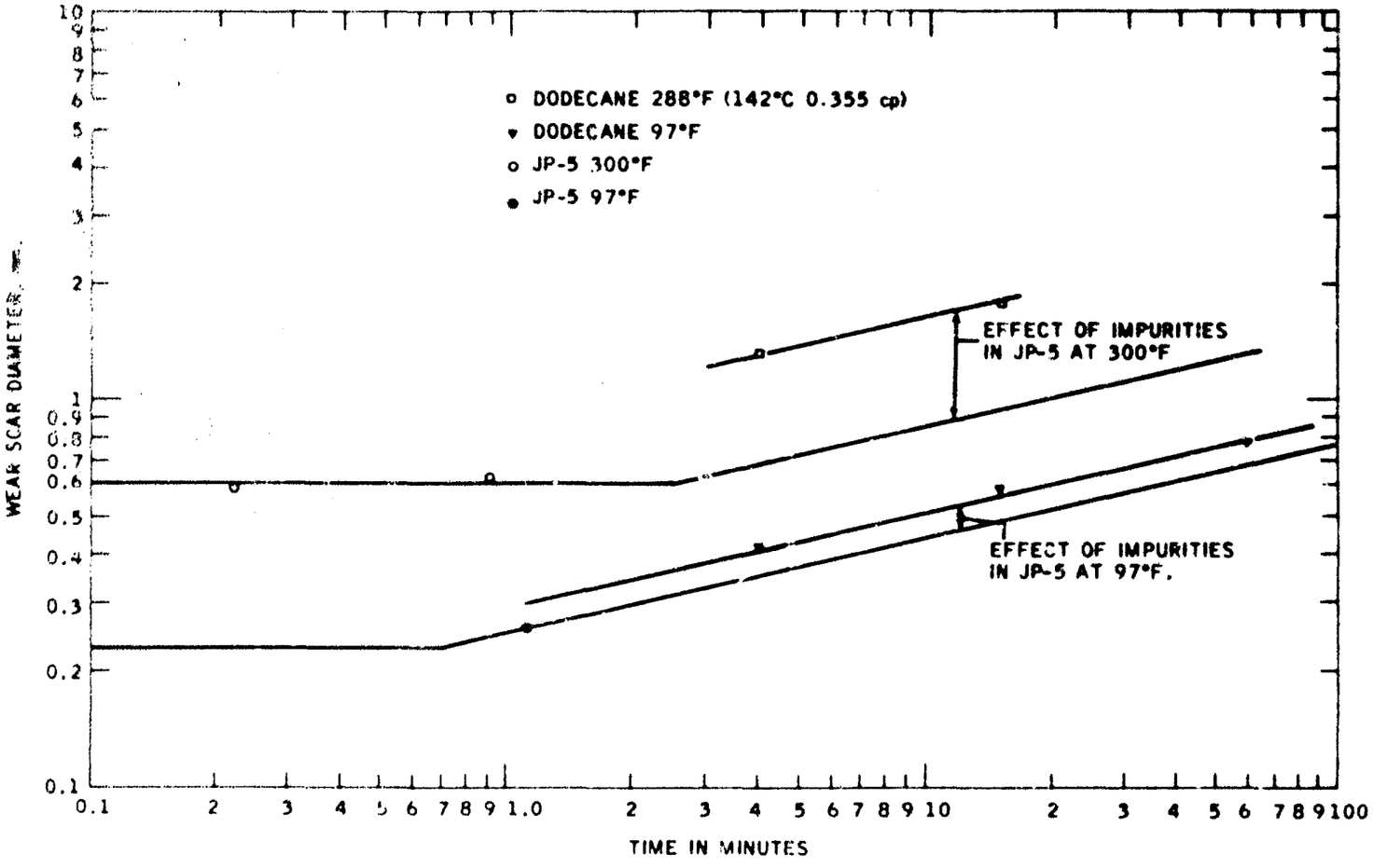


FIGURE 28 COMPARISON OF FOUR-BALL WEAR SCARS FOR DODECANE AND (PW-523)

3. EFFECT OF COMMERCIAL ADDITIVES

a. General

In contrast to the effects of viscosity, hydrocarbon type, and trace components--all of which are relatively minor--the effects of antiwear additives are profound. As little as 15 ppm can have a major effect on friction and wear. In this section are described the evaluation of several antiwear additives in a variety of test devices. The main purpose of these preliminary experiments was to determine the sensitivity of the various test devices to the antiwear additives with respect to both scuffing and rubbing wear. The experimental results are given below, following a brief description of the antiwear agents used.

Further work with corrosion inhibitors, including tests at the 15 ppm concentration level, were carried out using the ball-on-cylinder device as part of the investigation of the field control-valve problem that is discussed in Section V-4, following.

b. Antiwear Agents Used

(1) Tricresyl Phosphate (TCP) - TCP is a well-known antiwear additive that forms iron phosphate on the rubbing surfaces, which apparently accounts for its lubricating properties.

(2) Zinc Dialkyldithiophosphate (ZnDDP) - This is a common mild-EP additive widely used in motor oils. It has the formula $[(RO)_2 PSS]_2 Zn$ and is made by reacting an alcohol with P_2S_5 and then neutralizing the resulting acid to form the zinc salt. In this case the alcohol was a C_4-C_8 mixture. The mechanism of this additive has not been determined, but it apparently decomposes thermally and then reacts with iron at the rubbing surfaces.

(3) Bright stock is a highly-refined paraffinic residuum with a viscosity of 1000 cp at 77°F.

(4) The remaining additives to be studied in the program are all of a proprietary nature and will henceforth be coded as ER-1, ER-2, ER-3, etc. This coding will remain the same throughout the contract work, and as new additives of a proprietary nature are added to the program, new numbers will be assigned.

c. Ball-on-Cylinder Tests - Additives Reduce Wear, Friction, and Metallic Contact But Not all Simultaneously

The ball-on-cylinder machine, has been used to evaluate various antiwear agents as 0.01%-1% solutions in cetane. Since cetane has relatively poor load-carrying ability, the test loads were limited to 240 g. The metallic system consists of a 52100 steel ball and cylinder combination with all runs made at room temperature and 240 rpm. The values reported were taken at the end of 32 minutes. The coefficient of friction, percent metallic contact, and the wear scar diameter for these runs to date are summarized in Table XXVI.

The general conclusion that can be reached based on these data include the following:

- For additives ER-1 and TCP a significant reduction in % metallic contact is noted at all loads.

- The ER-1 solutions reduce the coefficient of friction over the base case at all loads.
- ER-3 causes a reduction wear scar diameter over the base case at all loads; at 1% concentration it caused a reduction in the coefficient of friction.

It is interesting that none of the additives were good in reducing all three of the measured values--friction, wear and metallic contact. This illustrates the importance of establishing proper correlations between laboratory and field tests. This test is particularly useful in investigating the low-load regime.

TABLE XXVI

Ball-on-Cylinder Test Results for Additive Solutions

240 g, 240 rpm, 32 min., 77°F.

% Add. in Cetane	% Metallic Contact				Coeffic.- Frict.				WSD, mm			
Load:	30	60	120	240	30	60	120	240	30	60	120	240
None	49	68	87	94	.10	.13	.13	.14	.20	.22	.24	.26
0.1 ER-3	50	75	87	91	.08	.10	.11	.11	.17	.18	.19	.21
0.2 ER-3	53	72	91	97	.15	.13	.11	.11	.19	.21	.20	.22
1.0 ER-3	45	71	84	92	.08	.08	.09	.09	.17	.18	.19	.20
0.1 ER-1	13	21	27	55	.09	.09	.10	.10	.18	.22	.26	.30
0.2 ER-1	13	30	47	41	.08	.22	.09	.09	.18	.24	.25	.27
1.0 ER-1	10	11	17	27	.06	.09	.09	.09	.20	.23	.25	.28
1.0 Bright Stock	53	77	81	95	.19	.13	.15	.17	18	.22	.25	.27
0.2 TCP	0	0.6	0.6	1.2	.21	.11	.13	.14	.18	.22	.24	.26
0.2 ZnDDP	62	88	99	100	.2	.15	.16	.15	.17	.21	.24	.29

d. Four-Ball Tests - Additives Have Little Effect on Scuff Load but Decrease Wear at Low Loads

A series of commercial antiwear agents were tested as 0.1% solutions in n-cetane at room temperature in the four-ball normal wear tester. Those tested so far are TCP, ZnDDP, ER-1, ER-2, and ER-3. All tests were of five minute duration at three different speeds and loads up to 80 kg.

The load conditions are such that a normal wear situation is present at the lowest load (10 kg) while a severe catastrophic regime is present at the heaviest load (80 kg). Runs at 100 kg load were attempted but wear was not reproducible, the liquid became quite hot and the spindle speed was questionable. Hence, loading was limited to 80 kg. The wear scar diameters for the runs at 600, 1200, and 1800 rpm are tabulated in Table XXVII.

The chief purpose of this series of tests is to determine the scuff load or seizure load, that is, the load at which normal wear changes to scuffing wear. In general, there was no significant improvement in the scuff loads for any of the additives. This fact is significant because these additives are known to be effective in Ryder gear tests and in field pump experience.

On the other hand, most of the additives did reduce wear in the low-load range of 10-30 kg. This reduction was most apparent at the lowest speed (600 rpm). ER-2, ER-3, and ZnDDP appeared to retain their antiwear activity to higher loads than TCP or ER-1. Table XXVII illustrates this point.

TABLE XXVII

Four-Ball Wear Test Results for Additive Solutions

Wear Scar Diameter, mm

% Additive in Cetane	10 kg	20 kg	30 kg	50 kg	80 kg
600 rpm, 5 min, Room Temp.					
0.1% ZnDDP	0.23	0.27	0.32	0.39	1.23
0.1% TCP	0.28	0.32	0.34	0.74	0.87
0.1% ER-1	0.27	0.31	0.34	0.96	0.83
0.1% ER-2	0.24	0.29	0.32	0.59	0.84
0.1% ER-3	0.24	0.31	0.36	0.39	0.78
None	0.33	0.43	0.53	0.60	0.76
1200 rpm, 5 min. Room Temp.					
0.1% ZnDDP	0.25	0.31	0.40	1.01	1.06
0.1% TCP	0.30	0.34	0.69	0.66	2.00
0.1% ER-1	0.29	0.37	0.68	0.81	1.84
0.1% ER-2	0.27	0.29	0.31	0.59	2.14
0.1% ER-3	0.24	0.28	0.36	0.54	1.96
None	0.37	0.53	0.57	0.67	2.10
1800 rpm, 5 min, Room Temp.					
0.1% ZnDDP	0.29	0.29	0.68	1.06	1.87
0.1% TCP	0.33	0.60	0.55	0.74	2.40
0.1% ER-1	0.30	0.37	0.62	1.87	2.09
0.1% ER-2	0.28	0.31	0.47	2.10	2.07
0.1% ER-3	0.25	0.28	0.33	1.94	2.38
None	0.35	0.55	0.60	1.70	2.30

e. Ryder Gear Tests - Lubricity Additives
Greatly Improve Load-Carrying Ability

Three jet fuel lubricity additives have been evaluated in the Ryder test at 0.1% concentration in Bayol 35. These were run at 5#/10 minute increments. All showed a pronounced improvement in load-carrying ability as shown in Table XXVIII.

TABLE XXVIII

Additives in Ryder Gear Tests

% Additive in Bayol 35	Scuff Load, #/Inch Single Test	Average
None	339,678	508
0.1% ER-1	665,953	809
0.1% ER-2	1368,720	1044
0.1% ER-3	1299,1126	1212

Although there is an appreciable scatter between sides for ER-1 and ER-2, it is apparent that all additives significantly increase the load-carrying capacity of the base fuel. It also seems that ER-2 and ER-3 are somewhat superior, under these conditions, to ER-1.

f. Vickers' Vane Pump Tests

(1) One Percent Bright Stock in Bayol 35
Increases Load-Carrying Capacity Somewhat

It was learned from our field survey that the lubricity of the fuel might be improved by merely adding small amounts of a heavy oil to the fuel. To investigate this possibility, a series of pump tests was made using a blend of 1% (by weight) of bright stock in Bayol 35. The bright stock is a solvent-extracted, deasphalted, and dewaxed residuum of 10.3 poise at 77°F and 103 VI. A comparison of these test results with those obtained from the previous test using the base fuel is shown in Table XXIX. Under the experimental conditions of 90°F and 350 psi, the scuffing wear was eliminated. But, under more severe conditions of either higher pressure or higher temperature, scuffing wear was again observed. Previous tests indicate that addition of 1% ER-3 essentially eliminated the wear and gave satisfactory operation under all these conditions. Previous pump wear data with Bayol 35 alone at 90°F indicate that the probable transition from rubbing wear to scuffing wear occurs at a pressure of 200-250 psig. The addition of the heavy oil therefore shifts such a transition to a pressure between 350 psig and 430 psig. Since the load for the sliding contact between vanes and the ring surface is a function of outlet pressure, it may be interpreted that the addition of the heavy oil is advantageous to shift the transition load for scuffing wear.

In pump tests with 1% bright stock in Bayol 35, the volumetric efficiency was notably increased, and a varnish-like material was deposited on most parts of the pump cartridge. This deposited material, which appeared much more viscous than the bulk fuel, might contribute to the increase of the load-carrying capacity. The presence of these viscous materials on the rubbing surfaces might also account for the reduction of the internal leakage so as to improve the volumetric efficiency. It is anticipated, however, that the tendency to form deposits may lessen the chance in satisfying the thermal stability requirements.

(2) Additives Show Pronounced Antiwear Effect

(a) E.P. Additives

The well-known antiwear additives, ZnDDP and TCP, were tested in the Vickers' vane pump at a concentration of 0.1% (by weight) in Bayol 35. The test conditions were the same as or more severe than that under which a very severe wear occurred with Bayol 35 alone. The results, shown in Table XXIX, indicate that both additives prevented wear almost entirely in all cases. The surface finish was improved and volumetric efficiency was high.

In the pump tests with TCP and ZnDDP, a thin film was coated on the sliding surface of each vane and could not easily be removed by mild abrasion and heating in solvents. Figure 29 shows the photomicrographs of these surfaces together with those of a new vane and a vane used in a pump test using the base fuel, Bayol 35. With Bayol 35 alone the occurrence of gross wear is evident; the wear tracks and fragments adhering to the surface are clearly seen in the photomicrograph. The deposited films formed by the additives are also clearly shown. This accounts for their antiwear effect. Recent published data on TCP supports the postulation of phosphate formation on the metal surface. No similar data are available for ZnDDP, but the texture of the deposit from these two additives is quite different. The different characteristics of these deposits may cause the different extent of effectiveness of these additives shown in the pump tests.

(3) Jet Fuel Additives

Four jet fuel additives were tested in the Vickers' vane pump at 1000 ppm and/or 50 ppm concentrations (by weight) in Bayol 35. The test conditions were the same as or at a higher temperature than that under which severe wear occurred with Bayol 35 alone. As shown in Table XXX, all are effective in reducing wear with reference to the base fuel.

At 1000 ppm concentration ER-2 and ER-3 are somewhat more effective than ER-1 in that ER-1 gave higher initial wear and roughened the rubbing surfaces. This difference became more evident at lower conc entration (50 ppm) where Bayol 35 containing ER-1 gave considerably higher wear than Bayol 35 containing ER-2 and ER-3. A deposited film was observed on the contact surfaces of the vanes for all these additive fuels giving low wear, $<$ 100 mg weight loss. This could account for their antiwear effect.

TABLE XXIX

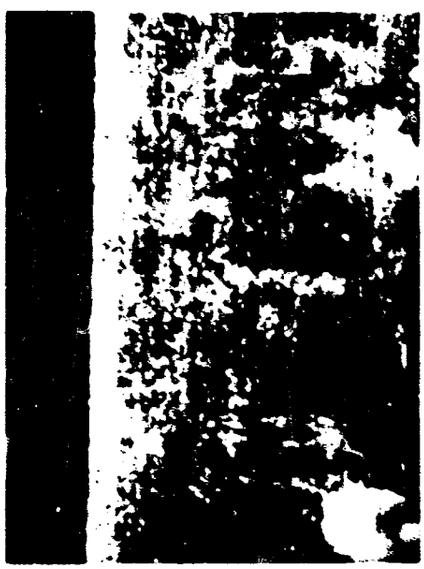
VICKERS PUMP TEST RESULTS FOR E.P. ADDITIVES

(Comparison With Base Fuel)

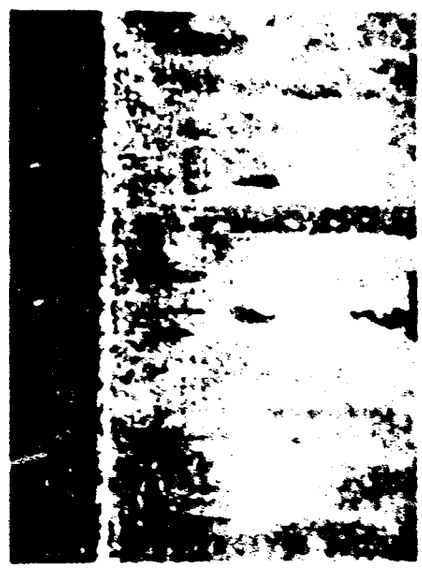
	Bayol 35	1% Bright Stock in Bayol 35			0.1% ZnDDP in Bayol 35				0.1% TCP in Bayol 35		
Pressure, psig	350	350	350	430	350	350	450	450	350	350	450
Sump Temp., °F	90	90	124	90	90	125	92	125	90	125	90
Outlet Temp., °F	115	94	138	126	93	122	110	129	91	128	93
Pumping Rate, gpm	0.43	1.07	0.31	0.26	1.02	0.87	0.27	0.46	0.87	0.43	0.81
Vol. Eff., %	24	59	17	15	57	48	15	26	48	24	45
Vanes, Initial	3.9	3.2	3.5	2.4	18.8	7.8	20.1	20.7	14.7	15.0	14.3
Final	96	80	174	>200	20.4	19.5	30.6	24.4	16.7	15.7	19.0
Ring, Initial	15.8	24	7.7	13.1	24	12	12	17	15.0	9.4	25
Final	67	36	165	132	17	8.6	37	16	9.4	10.0	16

New Vane

Vane, Used in a Pump Test
With Bayol 35 Showing Severe Wear



Vane, Used in a Pump Test
With 0.1% ZNDDP in Bayol 35



Vane, Used in a Pump Test
With 0.1% TCP in Bayol 35

FIGURE 29 PHOTOMICROGRAPHS OF CONTACT SURFACES OF VANES (51X)

TABLE XXX

VICKERS VANE PUMP TESTS FOR JET FUEL ADDITIVES

	Base Fuel (Bayol 35)	ER-1			ER-2			ER-3			ER-5
		50 ppm	1000 ppm		50 ppm	1000 ppm		50 ppm	1000 ppm		50 ppm
Pressure, psig	350	350	350	350	350	350	350	350	350	330	350
Sump, Temperature, °F	90	90	90	125	90	90	125	90	90	125	90
Outlet Temperature, °F	115	116	96	134	98	102	130	98	102	136	98
Pumping Rate, gpm	0.43	0.28	1.05	0.42	0.88	0.74	0.82	0.79	1.00	0.33	0.82
Vol. Eff., %	24	16	58	23	48	41	46	44	56	18	45
Wear, mg											
Weight Loss of Vanes	204	415	0*	22	6.4	0	6	32	0*	0*	32
Weight Loss of Ring	5150	2144	135	40	29.6	21	21	47	13	0	52
Total Weight Loss	5354	2559	135	61	36.0	21	27	79	13	0	84
Surface Roughness, CLA, μ"											
Vanes, Initial	3.9	23	16	27	20	19	21	24	20	24	23
Final	96	> 200	18	118	5	23	16	111	20	22	95
Ring, Initial	16	9	13	10	13	11	17	9	13	10	8
Final	67	125	21	48	9	17	9	19	7	6	27
Coefficient of Friction	0.41	0.28	0.16	0.16	0.20	0.29	0.10	0.19	0.38	0.13	0.19

* Slight weight gain.

4. LUBRICITY OF JP-4'S AND EFFECT OF CORROSION INHIBITORS

a. Background

During this reporting period, information was received from one of the jet engine manufacturers that malfunctioning of a fuel-control valve was occurring in the field. This trouble seemed to have started at about the time that certain changes had been made in the jet fuel at the critical location, one of the changes being that the corrosion inhibitor had been omitted.

To determine whether additives in this low a concentration could have such a pronounced effect, some initial tests were run on the ball-on-cylinder machine. The results indicated that corrosion inhibitors in concentrations as low as 15 ppm (0.0015%, 4#/1000 bbl.) could indeed reduce friction, wear, and metallic contact quite noticeably. Because of the importance of the field problem, the effect of corrosion inhibitors has been investigated in some detail. This investigation is also important to the present overall program because the level of additive was much smaller than had previously been considered to have a practical effect on lubricity. In earlier work, 2,000 ppm of lubricity additives had been found to be required for outstanding gear test performance and 600 ppm for moderately good performance.

Two new elements were introduced by the fuel-control valve problem: (1) load-carrying ability was not the issue, but rather the reduction of friction (reduced adhesion) between closely lapped metal surfaces carrying essentially no load, (2) highly-refined JP-4 fuels could be made commercially which had essentially no lubricity whatsoever. A combination of a "squeaky clean" fuel, no surface-active additive, and a mechanical system capable of high adhesion could cause serious sticking problems. The data reported here is organized as to technical format and not as obtained chronologically.

b. Non-Additive Fuels

Three JP-4 fuel samples from three USAF bases were supplied us by WPAFB. One of these bases (coded A) was from the site of the fuel-control valve trouble. This fuel was found to give substantially higher wear than the other two in the ball-on-cylinder machine, using a steel-on-steel system. Friction was also higher and much more erratic. These results are given in Table XXXI.

TABLE XXXI

Ball-on-Cylinder Results for JP-4's-I

Steel-On-Steel, 240 rpm, 32 min.

JP-4 Fuel	Wear Scar Diameter, mm			Coef. of Friction		
	60 g	240 g	1 kg	60 g	240 g	1 kg
A	.31	.49	.58	.14*	.16*	.38*
B	.23	.33	.38	.18	.15	.18
C	.22	.27	.34	.13	.15	.18

* Friction more erratic with Fuel A.

As a result of the ability of the ball-on-cylinder rig to distinguish between fuels, several other JP-4 were sent us for evaluation. Two were furnished us from one engine manufacturer that had reported some high friction and sticking with these fuels in laboratory engine tests. Three were from another engine manufacturer who had had serious flight performance reported on two of the three. Finally, four additional JP-4's from four more USAF bases were sent by WPAFB. The composition of these fuels was not known, nor were there any data on what additives, if any, the fuels contained. Although these data could probably have been obtained analytically, it did not appear that this information would be any particular advantage over the information already being obtained on the ten commercial fuels. The data are being reported here only to illustrate that major differences are found among JP-4's used in the field. In evaluating these fuels on the ball-on-cylinder test, it was found that the wear scar on the ball was an accurate reflection of the frictional behavior. This therefore became the standard method of reporting the data. However, in all cases, the friction traces were closely compared to ensure that the wear scar was in fact indicating the amount of friction. For additive fuels this correlation between wear and friction did not hold, as will be shown later.

Table XXXII gives the relative performance of these JP-4's. Fuel F was clearly the worst of the fuels, with Fuel G nearly as bad. These two fuels had the most serious problems reported from the field. Their frictional traces were extremely erratic, often going off-scale. At the higher loads the behavior was so bad that the tests had to be terminated to avoid damaging the spring in the friction-measuring apparatus.

The differences in performance cannot be ascribed to viscosity, for most of the fuels were between 0.9 and 1.0 cs. Of the two lowest viscosity fuels, one was quite poor in lubricity, the other was our Reference JP-4 which is exceptionally good. Viscosity at 77F are given in the last column of Table XXXII, and it can be seen by inspection that there is no correlation.

It is evident that current refining practices can give a fuel that is extremely pure as far as lubricity agents are concerned.

c. Oxidation Inhibitors

A distillation of Fuels A, B and C revealed that the bottoms from Fuels B and C developed a pink color in methanol. This was shown photospectrometrically to be caused by the oxidation inhibitor--N,N'-dialkylparaphenylenediamine--used in these two fuels. To determine whether this additive could have caused the difference between Fuel A and Fuels B and C, a brief study was carried out.

Using Fuel A as a base, the effect of 30 ppm of N,N'-disecondary-butylparaphenylenediamine was determined in the ball-on-cylinder rig. The results, given in Table XXXIII, show no decrease in wear scar, nor was there a difference in metallic contact. Friction was quite erratic in all runs, but somewhat smoother and at a slightly lower level with the additive.

Similar tests were carried out in cetane, using 7.5 and 30 ppm of the additive. Again there was no change in wear or metallic contact and in this case the friction traces were actually more erratic than with cetane alone.

TABLE XXXII

BALL-ON-CYLINDER RESULTS FOR JP-4'S - II
(Steel-on-Steel, 240 rpm, 77F)

JP-4 Fuel	Wear Scar Diameter, mm							Vis/77F, cs
	Series 1 (32 min)			Series 2 (64 min)		Series 3 (64 min)		
	60 g	240 g	1000 g	60 g	240 g	60 g	240 g	
A-1*						0.37	0.55	0.92
A-2*	0.24	0.33	0.46	0.25	0.36			
D		0.31	0.40					0.93
E		0.30	0.44					
F				(0.50)	**			0.99
G				(0.75)	**	0.42		0.96
H				0.26	**			0.94
I						0.33	**	0.77
J						0.29	0.39	0.92
K						0.27	0.32	1.03
L						0.32	0.40	0.94
Reference								0.76
B								0.97
C								0.92

* From same base at different times.

** Test discontinued because of excessive friction.

TABLE XXXIII

Antioxidant Has no Effect on Lubricity in Ball-on-Cylinder Tests
(Steel-on-Steel, 240 rpm, 32 min.)

Fuel	WSD, mm 60 g	240 g	1 kg
JP-4 A	0.24	0.33	0.46
A + 30 ppm N,N'-disecondary-butyl-paraphenylenediamine	0.26*	0.35*	0.48*
Cetane	0.21		
Cetane + 30 ppm same	0.2[illegible]*		
Cetane + 7.5 ppm same	0.19*		
Cetane + 7.5 ppm N,N'-disalicylidene 1,2 propanediamine	0.21**		

* Friction somewhat less.
** Friction somewhat greater.

It is apparent from the data that the lower friction of fuels B and C is not due to the presence of this antioxidant.

A metal deactivator (N,N'-disalicylidene 1,2 propanediamine) was also tested at 7.5 ppm and also was found to have no effect on lubricity. This is also shown in Table XXXIII.

d. Corrosion Inhibitors

(1) Initial Study of Two Commercial Additives

The chief suspect in the sudden rash of field problems seemed logically to be the absence of the corrosion inhibitors. These materials are strong surface-active agents, and therefore would logically be good antifriction agents. In fact, it is precisely their surfactant properties that led to their removal in the first place, for they seriously interfere with water-haze removal. Also, it is well-known that antiwear agents frequently impart rust inhibition to oils.

In the initial investigation two rust inhibitors, coded ER-4 and ER-5, were studied in detail. These two additives are entirely different in chemical composition and, as will be seen, perform quite differently as antifriction additives. Early ball-on-cylinder tests had indicated these two additives both greatly reduced friction of a highly purified fuel. This was confirmed by tests carried out by a jet engine manufacturer, where sticking of the fuel control resulted when a non-additive fuel was used, but could be unstuck if the fuels were changed to one containing one of these corrosion inhibitors. The agreement between these two test methods greatly increased the confidence in each method alone.

Ball-on-cylinder test data are summarized in Tables XXXIV and XXXV. It will be seen that both ER-4 and ER-5 reduce friction, with ER-5 being perhaps somewhat better. ER-5 also reduces the wear scar as would be expected, inasmuch as it decreases the adhesive friction. This behavior is consistent in two JP-4's and cetane.

ER-4 obviously works in a different manner than ER-5. Although it is about as good as ER-5 in reducing friction, it actually causes an increase in wear, the increase becoming greater at higher concentrations. At the same time, the metallic contact (measured by electrical resistance) decreases to zero, indicating the formation of an insulating layer between the rubbing surfaces. The higher the concentration of ER-4, the more rapidly the metallic contact decreases to zero. These data are summarized below in Table XXXVI.

TABLE XXXVI

Effect of ER-4 Concentration on Ball-on-Cylinder Results
(Steel-on-Steel, 60 g, 240 rpm)

ER-4 in Cetane	WSD, mm	Time for Metallic Contact to Decrease to 10%, minutes	Coefficient of Friction
None	0.21	--	0.17
50 ppm	0.21	18.8	0.14
500 ppm	0.25	8.5	0.14
1%	0.28	1.7	0.14

The action of ER-4 is similar to that of most EP additives. These are known to react rapidly with fresh metal to form an inorganic or partly inorganic layer, usually a sulfide, chloride, phosphate or similar compounds. This compound reduces adhesion and friction, but is soft and easily worn away. By reducing adhesion, these additives prevent scuffing but only at the expense of sacrificial wear. It is evident from the data on ER-4 that the wear scar diameter of such additives is no indication of their anti-friction activity.

The data in Tables XXXIV and XXXV show that good anti-friction behavior is obtained in most cases with as little as 50 ppm. However, with Fuel F, which is exceptionally poor in lubricity, 50 ppm was not enough to bring this fuel to the level of other JP-4's and 25 ppm of ER-5 gave a failure at 240 g load.

It is interesting that the corrosion-inhibitor ER-5 was about as good a lubricity additive as the antiwear additive ER-3. However, oleic acid was even better. On the other hand, adding 1% of a very high viscosity petroleum stock, ER-6, was completely ineffective. This material does not contain any surface-active compounds, and the test is analogous to adding heavy aviation oil to the fuel. It is obvious that in this test the surface-active properties are important.

These tests differ from the actual fuel control unit in three ways: (1) the metals are steel-on-steel whereas in the fuel control both surfaces are hard-anodized aluminum, (2) the speed is constant, whereas the piston in the fuel

TABLE XXXIV

CORROSION INHIBITORS ARE ANTIFRICTION AGENTS IN BALL-ON-CYLINDER TESTS - I
(Steel-on-Steel, 240 rpm, 77F)

		Wear Scar Diameter, mm.							
		Cetane		Ref. JP-4	Fuel B	Fuel A-2		Fuel F	
	Load, g:	60	240	60	60	240	1000	60	240
	Time, min.	32	32	32	64	16	16	64	64
Additive									
None		0.21	0.26	0.24	0.29	0.36	0.45	0.50*	**
50 ppm	ER-4	0.21	0.30	0.28	0.27	0.39	0.48		
	ER-5	0.17			0.22			0.26	0.30
	ER-3								0.34
	Oleic Acid					0.23			
25 ppm	ER-5							0.27	**
100 ppm	ER-3					0.28	0.30		
500 ppm	ER-4	0.25							
1 %	ER-4	0.28	0.46						
1%	ER-6					0.36	0.45		

* Excessive chattering.

** Test terminated because of excessive friction.

TABLE XXXV

CORROSION INHIBITORS ARE ANTIFRICTION AGENTS
BALL-ON-CYLINDER TESTS - II
(Steel-onSteel, 240 rpm, 77F)

		Coefficient of Friction							
		Cetane		Ref. JP-4	Fuel D	Fuel A-2		Fuel F	
	Load, g:	60	240	60	60	240	1000	60	240
	Time, min.	32	32	32	64	16	16	64	64
Additive									
None		0.17	0.16	0.23	(1)	(1)	(1)	(1)	**
50 ppm	ER-4	0.14	0.14	0.16	(2)	(1)	(2)		
	ER-5	0.12			(3)			(2)	(2)
	ER-3								(3)
25 ppm	ER-5								
100 ppm	ER-3					(3)	(3)	(2)	**
500 ppm	ER-4	0.14							
1%	ER-4	0.14	0.13						
1%	ER-6					(1)	(1)		

(1) Erratic friction trace

(2) Moderately smooth friction trace

(3) Smooth friction trace

** Test terminated because of excessive friction

control is subjected only to periodic motion, and (3) the area of contact is very small and the Hertz load relatively high.

In order to eliminate the first difference, 4150C aluminum cylinders and 4122C aluminum buttons were fabricated and hard anodized. These coatings are much harder than hard steels. Hard anodized aluminum has a surface layer of corundum, rating 9 on Moh's scale of hardness, which is very roughly about 85 Rockwell C.

The first attempts to get an anodized surface was with aluminum balls and cylinders that were on hand. The alloys were high in copper, and difficult to anodize. The oxide surfaces were poorly adhered. Even so, tests on these parts showed qualitative agreement with the steel-on-steel tests. In comparing the three JP-4's, Fuel A gave a bigger wear scar on the ball, showed some flaking on the cylinder track, and had high and erratic friction throughout the test. Fuels B and C gave smaller scars, and much smoother friction traces for the first 20-25 minutes when they, too, became erratic. Fuel A with 50 ppm of either ER-4 or ER-5 was considerably better in both wear and friction. These data are summarized in Table XXXVII.

TABLE XXXVII

Ball-on-Cylinder Results - Anodized Aluminum-I
(Anodized Al (AA-2017) on Anodized Al (AA-2024) 30 g, 60 rpm, 32 min.)

Fuel	WSD, mm	Friction
A-1	0.78*	High-erratic
B	0.71	Low-smooth for 25 min.
C	0.69	Low-smooth for 20 min.
A-1 + 50 ppm ER-4	0.53	Low-smooth for entire test
A-1 + 50 ppm ER-5	Not defined	Low-smooth for entire test

* Track shows flaking of anodized surface.

These tests were repeated on another cylinder with the same relative results, although at a different absolute level, due apparently to irreproducibility of the anodized surface. The frictional traces were also different; in this series the coefficient of friction rose rapidly during the first few minutes, then fell off to a steady value of 0.20. The most apparent differences between fuels were the maximum level reached in the early part of the test, as shown in Table XXXVIII.

TABLE XXXVIII

Ball-on-Cylinder Results - Anodized Aluminum-II
(Anodized Al (AA-2017) on Anodized Al (AA-2024) 30 g, 60 rpm, 32 min.)

Additive in Fuel A-2	Max. Coeff. of Friction	WSD, mm
None	1.5	0.57
1% ER-6	1.4	0.43
50 ppm ER-4	1.5, 1.4	0.53*
50 ppm ER-5	1.0	*
50 ppm Oleic Acid	0.63	*
100 ppm Oleic Acid	0.33**	*

* Scar undefined.
** Friction also less erratic.

It is worth noting that ER-4 did not give a larger wear scar, as it did with steel. Its reaction with Al_2O_3 is obviously different. ER-6, the heavy petroleum stock, again was relatively ineffective even at 1% when compared to ER-5 or oleic acid at 50 ppm. ER-3 at 100 ppm (so chosen to have the same Neut. No. as 50 ppm oleic acid) was considerably better. Obviously more work is needed here at different concentrations, surface interactions, loads and speeds.

The additive tests were repeated using low-copper aluminum alloys (4150C & 4122C) also hard anodized. The surfaces from these alloys were much smoother, blacker, and more adherent. The additive performance, however, was nearly identical to the previous tests as shown by the results in Table XXXIX.

TABLE XXXIX

Ball-on-Cylinder Results - Anodized Aluminum-III
Hard-Anodized Al (Bendix alloys, 4150C & 4122C) 32 min.

	WSD, mm			Coeff. of Friction	
Load g	30	120	240	120	240
Speed rpm	60	60	240	60	240
Additive in JP-4 A-2					
None	0.33	0.43	0.62	.126	0.142
50 ppm ER-4	0.28	0.40	0.66	.122	0.141
50 ppm ER-5	0.22	0.31	0.52	.106*	0.154*
100 ppm ER-3	0.20	0.32	0.54	.099*	0.140*

* Much smoother friction trace.

ER-4 was not a pro-wear additive, but it was not as effective in reducing friction as either ER-5 or ER-3. Again it indicates that ER-4 works with steel by reaction with the surface. With Al_2O_3 this reaction is impossible and its effectiveness is much less. This points up the fact that good performance in friction and wear is not solely a property of the fuel (lubricity), but rather is a joint property of the fuel and the surface, interacting together.

To test possible stick-slip behavior at slow speeds, still using anodized aluminum, ball-on-cylinder rig was modified by using a reduction gear in the drive mechanism, and driving through a loosely-coupled magnetic coupling. The combination of slow speed and non-rigid coupling gave very pronounced stick-slip. Motion consisted of a series of jerks 1.2 mm long, one every 8 seconds or so. Static friction was about double the dynamic friction.

This test technique showed only minor differences among fuels and additives, although what differences were found agree qualitatively with the higher speed runs. Fuel A was worse than B or C. Fuels A and B responded to ER-4 and ER-5, with ER-5 being better.

It appears that the small area of contact may be defeating the correlation of this test with fuel-control-valve performance. Lapped in surfaces of about 1 sq. cm will be experimented with.

(2) Extension Study of Miscellaneous Corrosion Inhibitors

Several other approved corrosion inhibitors have also been evaluated as lubricity additives and compared with those given in Table XXXIV. Although there are some differences among them, all appear to reduce friction and wear of a steel-on-steel system. Presumably, based on the experience of ER-4 and ER-5, they will also be effective in other systems as well. The wear measurements from the ball-on-cylinder tests are given in Table XL. Two of the additives, ER-4 and ER-7, are known to be of similar chemical composition and apparently act by reaction with the surfaces as evidenced by the increase in WSD. At 15 ppm these two additives are barely effective, reducing friction only slightly. The other additives reduce friction in proportion to their reduction of wear.

The results for isooctane given in Table XL demonstrate the effectiveness of the additives more clearly since this material is purer than the JP-4's. The JP-4 fuels undoubtedly contain polar materials that provide lubricity and tend, therefore, to mask the effects of the additives. No attempts have been made to determine the chemical composition or surface reaction characteristics of these additives. None of them appear to give as good a performance as ER-3, ER-5, or oleic acid.

TABLE XL

Lubricity of Approved Corrosion Inhibitors

Ball-on-Cylinder Tests, Steel-on-Steel
240 rpm, 32 Min Wear Scar Diameter, Min.

Additive	15 ppm in Ref.JP-4		15 ppm in Isooctane		50 ppm in JP-4 D	
	240 g	1000 g	60 g	240 g	60 g	
none	0.39	0.41	0.60	0.72 (1)	0.29	0.27
Oleic Acid	0.28	0.30	0.21			
ER-3	0.31	0.31	0.27	0.32		0.24
ER-4	0.45	0.45	0.46		0.28	
ER-5	0.30	0.33	0.28	0.32	0.22	
ER-7	0.46	0.45				0.21
ER-8	0.35	0.39			0.22	
ER-9	0.32	0.37	0.21			0.22
ER-10	0.31	0.36	0.21			0.22
ER-11	0.33	0.36				0.20

(1) Test discontinued at 20 minutes when rubbing wear gave way to scuffing wear (noted by a sudden rise in friction and audible rubbing vibration).

SECTION VI

SUMMARY AND CONCLUSIONS

A field survey of engine and pump manufacturers indicated that there is a potential problem whenever jet fuels are the only source of lubrication in pumps or controls. Problems encountered included wear, scuffing, sticking, seizure, and fatigue pitting. A literature survey confirmed that the problem existed but failed to pinpoint the causes.

The seizure of some aircraft fuel controls that occurred late in 1965 after corrosion inhibitors had been left out of the fuel blend and the elimination of this seizure problem by reintroduction of corrosion inhibitors at the 15 ppm concentration level, gave a clear indication that the presence of surface-active agents at this low concentration could have a very marked influence on the lubricity properties of jet fuels. Tests carried out under this contract on the ball-on-cylinder machine showed that this device was quite capable of distinguishing both between those fuels that had caused field seizure problems and those that had not, and also between the poor lubricity fuels and the same fuels with 15 ppm corrosion inhibitors added. Comparative wear data from the ball-on-cylinder, four-ball, and Vickers vane pump tests for the ten commercial fuels tested in this program showed that there was general agreement between these devices in the normal wear regime. Although it has yet to be demonstrated that the latter two tests can match the sensitivity of the ball-on-cylinder device to small differences in lubricity, it is clear that we do possess the test instruments necessary to evaluate jet fuel lubricity under a number of different rubbing wear conditions.

In keeping with the observation that traces of surface-active agents reduce friction significantly, the results of this program indicated clearly that the more highly refined fuels (lowest concentration of trace polar components) offered the least protection against wear, seizure, etc.

All E.P. additive and corrosion inhibitors tested contributed some form of lubricity aid to those fuels and solvents that were demonstrably lacking in lubricity properties of their own. However, some differences in the mode of action between additives was found, which may be very important in the choice of additive used to cure a given field problem. For example, two additives were found to reduce friction but increase wear in the ball-on-cylinder test when run in JP-4 fuels. Thus, while these additives may be suitable for eliminating seizure problems under conditions of occasional motion, they could be most unsuitable for conditions of continuous rubbing wear.

Five test devices are available that are potentially able to test the lubricating properties of fuels under scuffing conditions. These are the four-ball, Falex, and Ryder gear machines. The Ryder gear machine was able to detect the effect of high ($\sim$0.1%) concentrations of E.P. additives in jet fuel, but, due to the nature of the test, was not capable of detecting small differences in lubricity. The Falex scuff test was able to separate the ten commercial fuels into two broad classes. The first group consisted of the highly refined fuels that had already shown poor antiwear properties and these also showed the poorest antiscuff protection. The second group consisted of the less highly refined fuels, and these showed the better antiscuff properties just as they had shown the best antiwear properties.

It is difficult to tell at this stage of the work why it was not possible to differentiate the ten fuels in a more detailed manner. It may be because the polar materials in jet fuel do not provide antiscuff protection or because the test devices are too insensitive to detect the differences. This question may be resolved by tests under scuff conditions using the ball-on-cylinder and four-ball machines. It does seem clear, that higher additive concentrations than the 15 ppm that gave wear protection, will be needed to give scuff protection since, at this low concentration level, a deficiency of additive is likely to develop at the working metal faces if new metal is continuously being exposed.

SECTION VII

FUTURE WORK

Work over the next year is expected to be along four lines.

(1) The trace compounds present in fuels will be examined further to find which is the most effective in improving friction and wear performance. This will include both adding compounds to the fuel and separating and identifying fuel components.

(2) The effect of temperature on fuel performance and particularly on additive performance will be elucidated.

(3) The importance of dissolved oxygen and water will be determined.

(4) Attempts will be made to discover the mechanism by which additives and trace constituents reduce wear and friction.

REFERENCES

(1) Coordinating Research Council, "An Investigation of the Performance of Jet Engine Fuels for Supersonic Transport Aircraft" CRC Report LD-152, March 1965

(2) C. Campbell, Canadian Aero. J. 4, 200 (1958)

(3) T. Sakurai, J. Chem. Soc. Japan, Ind. Chem. Sect. 24, 313, 320, 363 (1951)

(4) Y. Tamai, J. Inst. Petro. 44, 207 (July 1958)

(5) S. Nagata, Y. Tomoda, and H. Haga, Technical Repts. Osaka Univ. 6, 31 (1956)

(6) R. S. Fein & K. L. Kreuz, ASLE Trans. 8, 29 (1965)

(7) M. J. Furey & J. K. Appeldoorn, ASLE Trans. 5, 149 (1962)

(8) E. E. Klaus & H. E. Bieber, ASLE Trans. 7, 1 (1964)

(9) E. E. Klaus, M. R. Fenske, E. J. Tewsbury, "Fluids, Lubricants, Fuels, and Related Materials," WADC TR 55-30 (Parts I-VIII, 1960), WADD TR 60-898 (Parts 1-2, 1963), ML-TDR-64-68 (1964), AFML-TR-65-112 (1965)

(10) R. S. Fein, ASLE Trans. 8, 59 (1965)

(11) F. G. Rounds, ASLE Trans. 7, 8 (1964)

(12) V. Hopkins & A. D. St. John, WADC TR-58-297 (1958-59)

(13) G. I. Kichkin, I. V. Rozhkov, A. V. Vilenkin, and Y. N. Kornilova, Khim. Tekh. Top. Masei 8, 60 (1963)

(14) A. P. Gryaznov & I. V. Rozhkov, Khim. Tekh. Top. Masel. 9, 57 (1964)

(15) I-M Feng and H. Chalk, Wear 4, 257 (1961)

(16) R. S. Owens, L. E. St. Pierre & R. W. Roberts, ASLE Trans. 8, 37 (1965)

(17) Z. A. Sablina and A. A. Gureyer, Khim. Tekh. Top. Masel. 7, 33 (1960)

(18) J. D. Conboy, "Investigation of Bearing Lubrication with Additive Fuels" U.S. Naval Air Material Center Report NAMC-AEL-1487, Jan. 1957, ibid NAMC-AEL-1677, Apr. 1961, ibid NAMC-AEL-1721, Mar. 1963

(19) P. M. Ku & C. W. Lawler, Proc. of Air Force-Navy-Industry Propulsion Systems Lubricants Conference, ASD-TDR-62-465, page 65 (1962)

(20) Furey, M. J., ASLE Trans. 4, 1-11 (1961).

(21) I-M. Feng, Wear 5 275 (1962).

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13. ABSTRACT

A field survey of engine and pump manufacturers indicated that there is a potential problem whenever jet fuels are the only source of lubrication in pumps or controls. Problems encountered included wear, scuffing, sticking, seizure, and fatigue pitting. A literature survey confirmed that the problem existed but failed to pinpoint the causes.

The friction and wear performance of ten commercial fuels, chosen to represent a broad range of physical and chemical properties, differed markedly. These fuels were inspected for viscosity, volatility, hydrocarbon type, and trace constituents. The strongest factor affecting lubricity appeared to be the nature of trace polar components in the fuel. The exact components responsible have not yet been determined.

The occurrence of sticking in the fuel control valve of operational jet engines led to the examination of a number of commercial JP-4's from different sources. There was a good correlation between field performance of the fuels and their performance in the laboratory tests. It was found that as little as 15 ppm of corrosion inhibitors significantly improved the lubricity in laboratory tests of those fuels that lacked lubricating properties of their own. Other lubricity additives were even more effective.

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