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AFAPL-TR-66-89
PART III

LUBRICITY PROPERTIES OF HIGH-TEMPERATURE JET FUELS

J. K. Appeldoorn
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ESSO RESEARCH AND ENGINEERING COMPANY

TECHNICAL REPORT AFAPL-TR-66-89, PART III
JULY 1968

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Air Force Aero Propulsion Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

124

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Air Force Aero Propulsion Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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 with Arthur F. Levenstein, Capt., USAF as project engineer under project 3048, task 304805--hydrocarbon fuels.

This report covers work conducted from 15 May 1967 to 15 May 1968. It was submitted by the authors 11 July 1968.

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

Previous studies on the friction and wear properties of jet fuels have been extended to metallurgies other than steel and to other kinds of wear, both abrasive and scuffing. Corrosive wear is found with most metals, even those that are nominally corrosion resistant, and can be controlled by using surface-active additives. Abrasive wear is triggered by corrosive wear and can be controlled indirectly by eliminating corrosive wear or directly by polar additives. Unlike corrosive wear, scuffing is most severe in dry inert atmospheres. Antiwear additives are usually also antiscuff agents.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (CONT.)

LIST OF TABLES

I. INTRODUCTION

This report concludes a three-year research study on the causes for the differences in the lubricity of jet fuels. Lubricity, as defined herein, is a fuel property; specifically, that fuel property other than viscosity which accounts for differences in friction, wear, and scuffing.

Field Problem

Jet fuel lubricity was not a problem in operational aircraft at the time this program started. However, a survey of pump and engine manufacturers showed that there were some potential problems. For example, in one experimental engine, sticking and wear of an axial piston pump had been encountered when using a highly refined fuel at high temperatures. This problem could be cured by adding about 0.1% of a special lubricity additive.

During the first six months of this program a serious field problem did develop. Jet aircraft operating from a particular base were encountering sticking of a fuel control valve. The JP-4 supplied to this base was very highly refined and contained no corrosion inhibitor in accordance with a recent change in the USAF Specification. The jet fuel was therefore strongly suspect.

The goal of this program, however, was broader than a correlation with a single problem in the field. Rather it was a complete study of jet fuel composition: to determine what components present in jet fuels account for good lubricity, what additives might be used to get still better lubricity, and how fuel lubricity is influenced by other variables such as temperature, atmosphere, and metallurgy.

Apparatus

The first step was to find a test that could reproduce field experience. Most lubricity testers have been designed for lubricants and rate all fuels as equally bad. Several different apparatus were examined. The Ball-on-Cylinder Test was found to be most satisfactory but a Vane Pump Test and the 4-Ball Wear Tester were also widely used. The Ball-on-Cylinder device measures wear, friction and the amount of metal-to-metal contact, all of which are useful in evaluating fuels and fuel additives. This apparatus could correctly distinguish between fuels of good and poor lubricity and showed that the degree of refining and the additive content is far more important than physical properties such as viscosity.

Curiously, although field problems were often more involved with some kind of friction, rather than wear, the best correlation was obtained with laboratory data on wear. It appears that, in this case at least, both friction and wear are the product of the same source, namely an adhesion between the rubbing surfaces. It is obvious that this correlation should not be carried too far. However, it is evident that wear in laboratory tests, with suitable precautions and with some obvious exceptions, can predict frictional behavior in the field.

Atmosphere

A study of the variables that might affect jet fuel lubricity showed that dissolved oxygen and water were critically important. A simple inerting of the atmosphere in the Vane Pump Test, for example, reduced wear by a factor of > 10,000. This wear proceeds by a corrosion mechanism and a mathematical model was constructed which showed good agreement with experimental data. All subsequent tests were carried out in a controlled atmosphere, each apparatus being modified accordingly. Generally the four extremes were used: dry air, wet air, dry inert, and wet inert.

Aromatic Content

Surprisingly, the most important component for imparting lubricity to jet fuels is the aromatic hydrocarbons, especially condensed-ring aromatics (naphthalene derivatives). This behavior had not been reported in the literature. Mixtures of paraffins and aromatics give lower friction, less wear and better scuff resistance than either component alone. Good jet fuels were invariably found to contain appreciable quantities of aromatics.

Paradoxically, the condensed ring aromatics alone are not good in a dry, inert atmosphere. They scuff at extremely low loads. The excellent behavior of aromatic-paraffin blends is therefore a true synergism.

Other Components

Sulfur and nitrogen components had relatively little effect on lubricity. A survey of 10 jet fuels from the field showed no correlation between sulfur or nitrogen content and lubricity. Also, the addition of all types of sulfur and nitrogen compounds (sulfides, disulfides, amines, etc.) did not improve lubricity to any extent. Similarly, the removal of naturally occurring acetic components by caustic treat caused no serious loss in lubricity. Olefinic hydrocarbons had some effect but it was relatively minor. Hence, only the aromatic content is an important component so far as lubricity is concerned.

Additives

Corrosion inhibitors which are normally added to jet fuels were found to be exceptionally effective lubricity agents, even at very low concentrations. Their removal from fuels in the field (a move taken to improve the water separation properties) appear to be an important factor leading to the sticking problems mentioned previously. These materials are surface-active agents so that their effect on lubricity is not surprising.

On the other hand, anti-oxidants and metal deactivators had almost no effect. Anti-icing agents (ether-alcohols) had some effect but not nearly as much as the corrosion inhibitors and only at much higher concentrations.

Special lubricity additives were found to be even better than the corrosion inhibitors. Some of these were effective at concentrations as low as 5ppm. Even as simple a material as oleic acid was found to be very effective.

Temperature

Friction, wear and scuffing all increase at higher temperature. Some of this comes from the lowered viscosity, some from an increased rate of corrosive wear but some appears to be due to the temperature per se. Highly-refined fuels are more sensitive to the effect of temperature than conventionally-refined fuels.

A serious difficulty was encountered in measuring the effect of temperature in an air atmosphere. The fuel would oxidize during the test and the oxidation products would act as anti-wear agents. The addition of an anti-oxidant minimized this effect somewhat but at temperatures above 240F, wear generally decreased rather than increased. This made it almost impossible to test additives at high temperatures since the fuel alone was fairly good.

Metallurgy

Most of the work reported above was done with hard chrome steel. Some limited data were obtained on AISI 440C stainless steel. The conclusions, however, were qualitatively the same as for the chrome steel.

Summary

The work thus far has identified the important fuel variables governing jet fuel lubricity. Only the aromatic content and the surface-active additives are significant. However many of the operational variables are as important as the fuel variables, particularly the presence of dissolved oxygen and water. There appears to be a strong interaction between hydrocarbon type, additive content, atmosphere and probably metallurgy as well.

The present report will focus on three major areas: scuffing, metallurgy, and abrasive wear. Scuffing is an entirely different phenomenon from corrosive wear; therefore those variables that influence wear were re-examined to determine their effect on scuffing. Several new metallurgies were examined, particularly those that are corrosion resistant. The nature and importance of abrasive wear was also determined. In addition, the Micro-Ryder rig was evaluated as a possible lubricity tester.

II. EVALUATION OF MICRO-RYDER AS A TOOL FOR STUDYING JET FUEL LUBRICITY

A. Introduction

Because of wide appeal of a gear test for evaluating the load-carrying capacity of fuels and lubricants, it was desirable to evaluate jet fuels in this type of test. Previous results have shown that the standard Ryder gear test is not altogether satisfactory. A program was therefore set up to evaluate the Micro-Ryder gear test as a jet fuel lubricity tester. Our conclusion is that this test device is not suitable for jet fuel testing.

The Micro-Ryder is just what the name implies. It is a smaller version of the standard Ryder gear. Several of the drawbacks for the larger Ryder are not found in the smaller Ryder. For example, the slave gears are loaded by means of air pressure rather than gear oil; thus, test fuel cannot be contaminated. Also, much smaller quantities of test fluid are needed (35cc vs several gallons); thus, certain pure hydrocarbon types and lubricity additives which have been found useful in jet fuels may be very easily tested in the Micro-Ryder. It remained for this study to investigate the reproducibility of the Micro-Ryder as well as its sensitivity toward jet fuels of various lubricity characteristics.

B. Modifications To Micro-Ryder

As mentioned, the Micro-Ryder is a smaller version of the standard Ryder gear test machine. In order to use the Micro-Ryder for fuels testing, several modifications had to be made. Due to the extreme severity for fuels, tests of 2-minute duration were run at each load, rather than the standard 10 minutes. In addition, the equipment was modified to measure air pressures of several millimeters of mercury. This modification was made because, for the range of air pressures indicated on the machine, the gear loading was too high; a large amount of scuffing occurred at the lowest load, 1 psi. Tests were also run in an argon atmosphere as well as in room air.

C. Experimental Results

The Micro-Ryder was not able to detect the difference in lubricity of two non-additive fuels. Figure 1 shows data on a highly refined fuel, Bayol 35, and a conventionally refined fuel, RAF-176-64. This figure is a plot of the percent scuff as measured by microscopic examination of the gear teeth versus the applied load in lbs/inch of tooth width. Normally, one rates Ryder gear data by noting the load at which 22.5 % scuff occurs. As seen in the figure, Bayol 35 and RAF-176-64 appear equivalent at the 22.5% scuff point. At higher loads, the conventionally-refined fuel actually looks worse than the highly-refined fuel. These findings are in direct contrast to those found previously with other wear testers. Bayol 35 had been shown to be much poorer than RAF-176-64 in lubricity. This is shown in Table I, which compares the scuff load at 22.5% scuff in the Micro-Ryder test with wear data from other testers used in this program. In the ball-on-cylinder device, 4-Ball wear test, and Vickers vane pump, Bayol 35 was definitely inferior to RAF-176-64. In the Micro-Ryder test it was not.

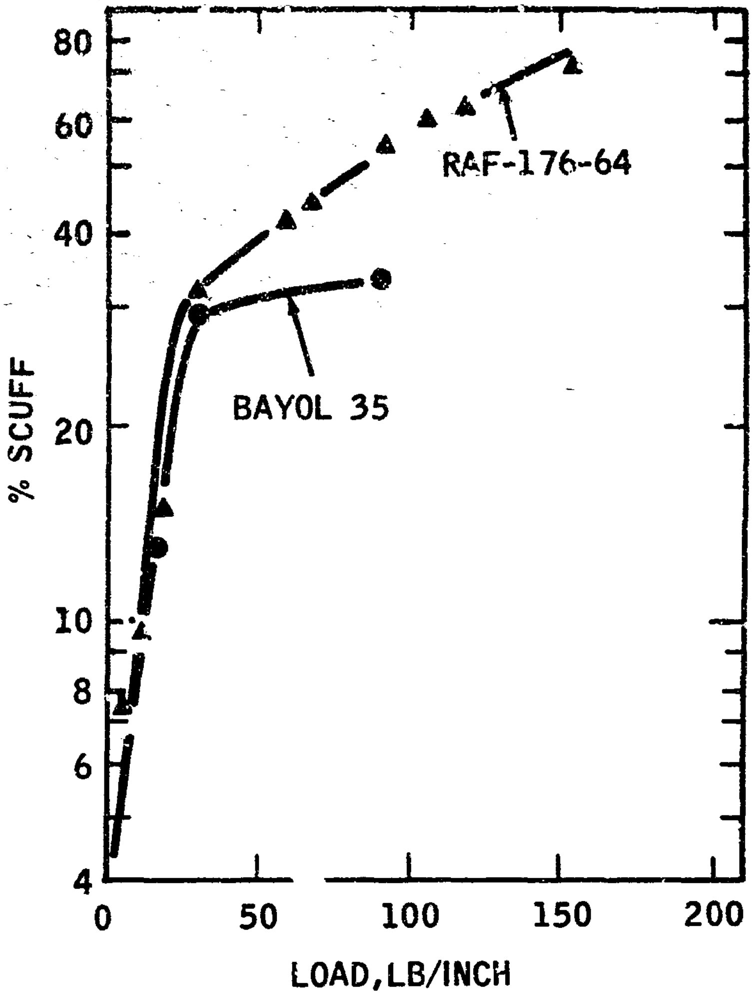

FIGURE 1 - MICRO-RYDER GEAR TESTS ON BAYOL 35 AND RAF-176-64 JET FUELS (77F, ROOM AIR, 2-MINUTE INTERVALS)

TABLE I

COMPARISON OF WEAR TESTERS WITH MICRO-RYDER

	Bayol 35	RAF-176-64
Ball-on-Cylinder WSD, mm	0.63	0.38
4-Ball Test WSD, mm	0.80	0.61
Vickers Vane Pump Vane WL, mg	204	0
Micro-Ryder Test Scuff Load, #/inch	27	18

The effect of a lubricity additive in the Micro-Ryder test was also examined. Figure 2 gives data on 0.1% of ER-3 to Bayol 35 using room air atmosphere. The effectiveness of ER-3 is readily seen in the Micro-Ryder, as Bayol 35 plus the additive exhibits about eight times the load-carrying capacity of Bayol 35 alone. This comparison is made at the 22.5% scuff point. This result is in agreement with previous data obtained on the standard Ryder gear earlier in the program.

The effect of atmosphere (Figure 3) also is in agreement with previous findings, i.e., better performance with Bayol 35 is found in inert gas environment.

At first, it was planned to use the Micro-Ryder to measure gear scuffing at high temperatures in both air and inert atmospheres. In order to estimate the severity of the Micro-Ryder at elevated temperatures, a low viscosity liquid, normal heptane, was tested at room temperature. Heptane at room temperature has a viscosity of 0.43cp, which is the viscosity of Bayol 35 at 300F. Thus, just the viscosity effect alone can be estimated by comparing heptane with Bayol 35 in an argon atmosphere. This is shown in Figure 4. Two points are to be made here. First, if a test were run at 300°F in an argon atmosphere with Bayol 35, the data would exhibit the trend shown by the heptane curve in Figure 4. That is, with no oxidation occurring (argon atmosphere) only the viscosity effect would show up at the higher temperature. The second point is that the Micro-Ryder is even more severe for the lower viscosity fluid. At less than 0.5psi applied load, the scuffing rose immediately to 22.5% with heptane. Therefore, testing jet fuels such as Bayol 35 at higher temperatures would make the severity of the Micro-Ryder worse than it is at room temperature.

D. Conclusions

The Micro-Ryder test is too severe for fuels testing. The failure of the Micro-Ryder to rate Bayol 35 and RAF-176-64 correctly may be due to running tests at loads below which it was designed. At these low loads, the test is apparently insensitive to fuels of various lubricity characteristics. On the other hand, additive and atmosphere effects agree with previous findings.

No additional work with the Micro-Ryder is planned since it is apparently too severe for fuels testing. However, the viscosity data indicate that the Micro-Ryder might be suitable for testing fluids in the lubricating oil range, that is, higher viscosity fluids.

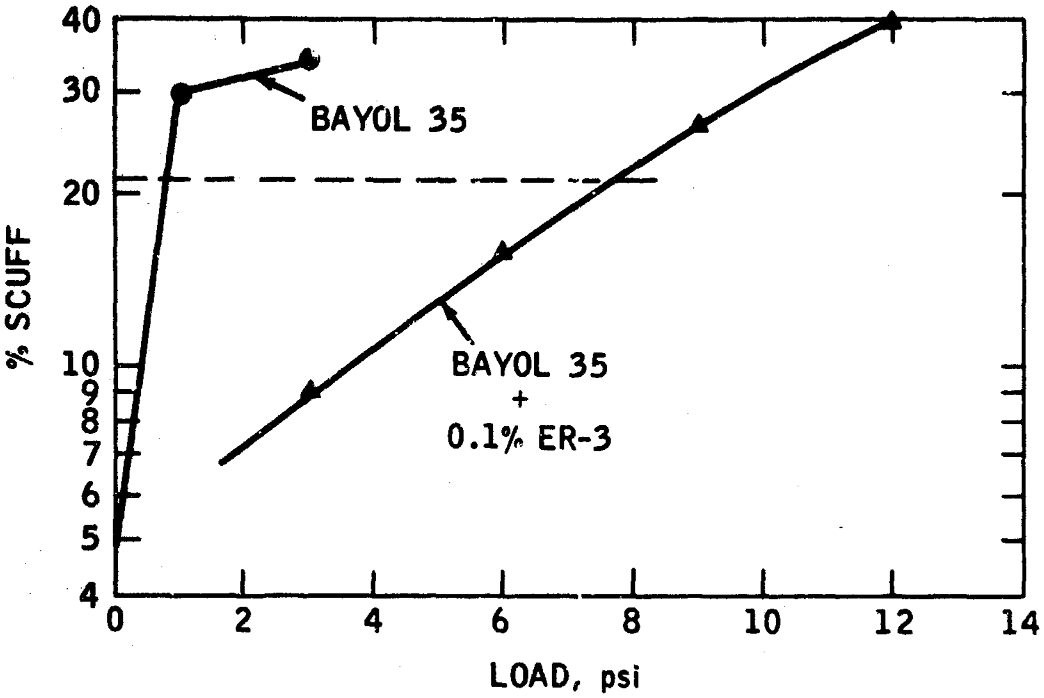

FIGURE 2 - EFFECT OF ADDITIVE IN MICRO-RYDER TEST
(77F, ROOM AIR, 2-MINUTE INTERVALS)

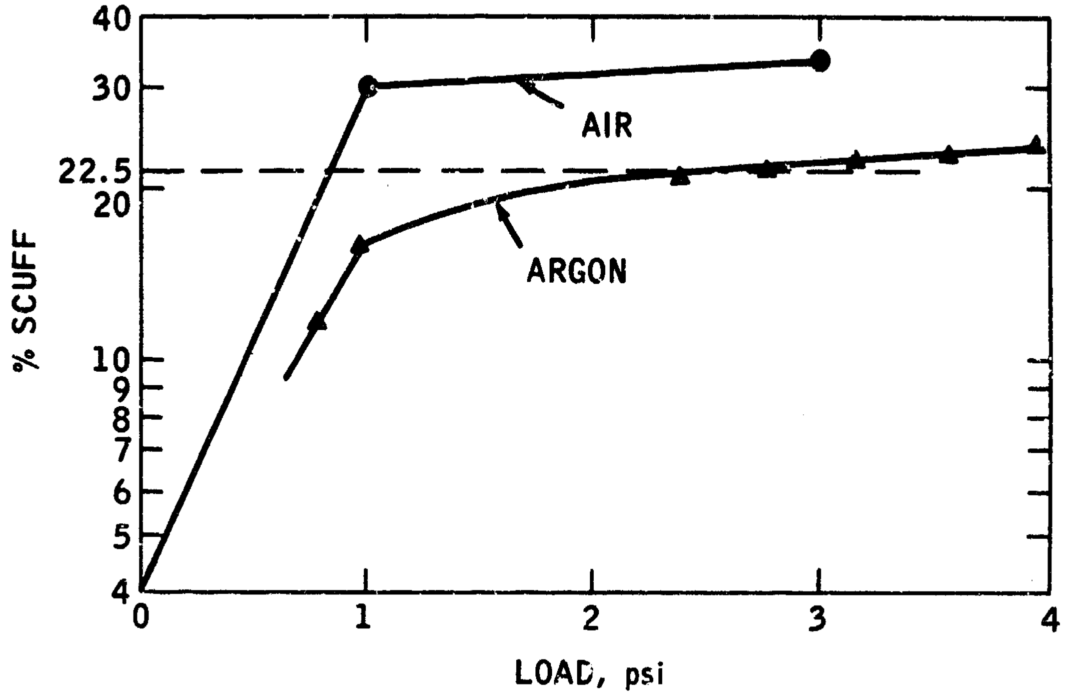

FIGURE 3 - EFFECT OF ATMOSPHERE IN MICRO-RYDER TEST
(77F, BAYOL 35, 2-MINUTE INTERVALS)

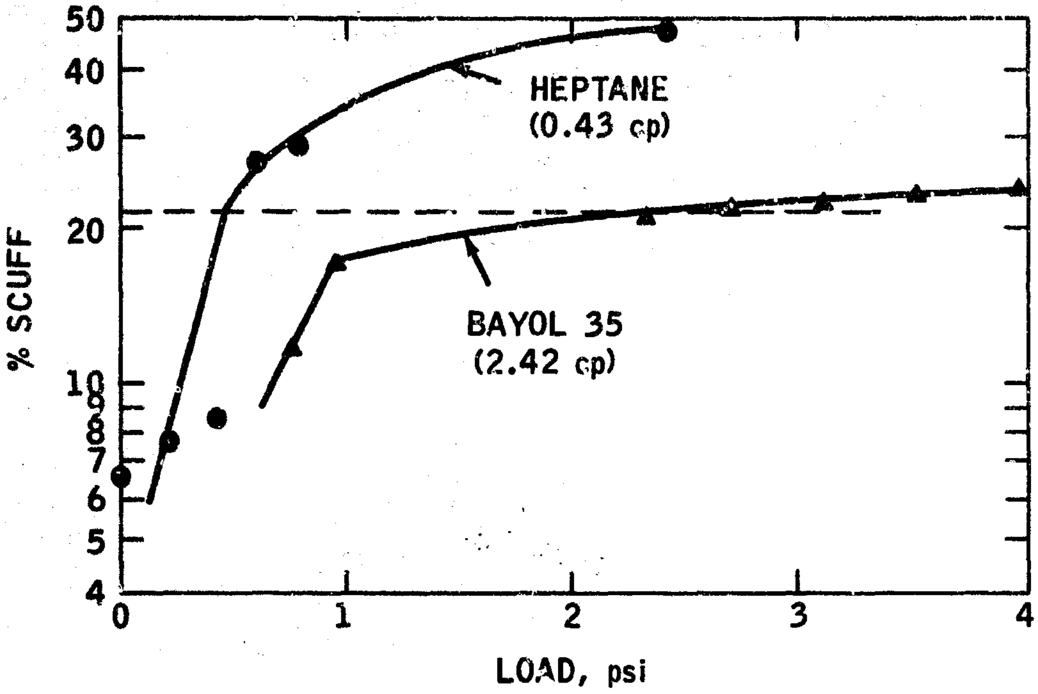

FIGURE 4 - EFFECT OF VISCOSITY IN MICRO-RYDER TESTS (77F, DRY ARGON, 2-MINUTE INTERVALS)

III. SCUFFING OF STEEL

In most of the previous work, the test conditions were selected so that scuffing would not occur. Scuffing is an entirely separate phenomenon from ordinary wear and obeys its own set of rules. It results from a combination of test conditions (high load, high speed, and high temperature) that cause the surface films to fail. When the films crack or rupture, fresh metal touches fresh metal, resulting in severe adhesion, high friction, and high wear. It should not be assumed that whatever factors will alleviate ordinary wear will also alleviate scuffing. In fact, it will be shown that the effect of inerting the atmosphere has diametrically the opposite effect on scuffing that it has on wear.

In this section, the various parameters that have been shown to have some effect on wear will be re-examined to determine their effect on scuffing. These will include (1) oxygen and moisture content of the atmosphere, (2) hydrocarbon composition of the fuel, (3) sulfur compounds, (4) additives and impurities, and (5) temperature. The data in this section will be limited to hard 52100 steel. Other metallurgies will be discussed in the next section.

The following general conclusions can be drawn:

- Unlike wear, scuffing is most severe in dry inert atmospheres and least severe in wet air.
- Wet air can sometimes lead to scuffing because of the abrasive nature of the iron oxide particles formed.
- No scuffing with paraffinic fuels was obtained in the ball-on-cylinder test even with bone-dry argon. However, scuffing with condensed-ring aromatics in argon was more pronounced at low humidity.
- Condensed-ring aromatics when blended with paraffins decrease scuffing, just as they decrease wear.
- Olefins, especially diolefins, have some antiscuff behavior in blends.
- Sulfur compounds decrease scuffing in dry argon but not in wet air.
- Lubricity additives are also good antiscuff additives, but are required in higher concentrations to give scuff protection.
- Scuffing is more severe at high temperature, unless prior hydrocarbon oxidation has occurred.

Scuffing is not always self-evident when it occurs. In the four-ball tester it was determined as follows: A series of tests at increasing loads were run and the resulting wear scar diameter plotted against load. Scuffing is evidenced by a sudden increase in scar size: The load at which this occurs is the scuff-load. Usually scuffing was accompanied by an erratic friction trace and a loud chattering noise. At very high friction, the motor's overload trip would stop the test. This is termed "seizure."

In all cases the tests were run under a controlled atmosphere, usually either dry argon or wet (saturated) air. A temperature of 240F was chosen to give the most severe conditions without encountering excessive evaporation of the fuel sample.

In the ball-on-cylinder tester, high temperatures and high loads were also used. To avoid damage of the friction-measuring device, the spring was blocked so that no friction reading was taken; scuffing was recognized by noise or "chattering".

In addition, when scuffing occurred, the wear track on the cylinder showed a considerable depth. In tests where ordinary wear occurred, the wear track showed only a flattening of the surface asperities. Talysurf profiles of the cylinder thus made it easy to distinguish between wear and scuffing.

A. Effect Of Atmosphere

Previous tests under non-scuffing conditions had shown that atmosphere has a profound effect. Wear is low in dry argon, intermediate in wet argon or dry air, and highest in wet air. This appears to be a classical example of corrosive wear, for the volume of wear was almost a linear function of the amount of oxygen available in the atmospheres. Inerting the atmosphere always had a beneficial effect. This was particularly noticeable in the vane pump test, where running in dry nitrogen reduced the wear from a prohibitive level to essentially nil.

In scuffing, however, the presence of oxygen and moisture can be expected to be beneficial. Because they do attack the metal surface, they help prevent the rupture of the surface film, and they rapidly heal any ruptures that do occur. Scuffing is therefore most likely in dry inert systems.

1. Four-Ball Tests

The ambiguous effect of oxygen and moisture is illustrated in Table II. A series of 4-ball tests were run on two high-purity fuels, increasing the load until scuffing occurred. All four atmospheres were studied. The two fuels behaved similarly. In both dry argon and wet argon, scuffing occurred at loads of 2-3kg; in dry air, scuffing did not occur until 20kg (although wear at lower loads was higher than in argon). In wet air, scuffing occurred at less than 1 kg, but this appears to be from a different cause. In wet air, corrosive wear is so severe that the iron oxide particles abrade the surface, exposing fresh metal, and initiating scuffing.

This is seen more clearly by examining the scuffing tendencies of commercial (less highly-refined) fuels under the same conditions. Table III presents data on RAF-176-64 (Jet A fuel) and JP-5. Again scuffing is most severe in dry argon and least in dry air. The table below summarizes the results on both kinds of fuels.

TABLE II

SCUFFING OF HIGHLY-REFINED FUELS

(Four-Ball Tests, 240F, 1200rpm, 15min, 52100 Steel)

WEAR SCAR DIAMETER, mm

	PW-523				Bayol 35			
Load, kg	Dry Argon	Wet Argon	Dry Air	Wet Air	Dry Argon	Wet Argon	Dry Air	Wet Air
0.5	0.20			0.72				
1	0.20	0.23	0.48	0.78	0.28	0.23	0.58	0.88
2	0.58	--	--		0.91	--	--	
3		S	0.48			1.02	0.58	
5			0.50				0.58	
10			0.63				0.65	
15			0.61				0.57	
20			S				S	
COEFFICIENT OF FRICTION								
0.5	0.15							
1	0.19	0.10	*		0.22	0.17	*	*
2	*	--	--		*	--	--	
3		**	0.13			*	0.16	
5			0.14				0.09	
10			0.16				0.14	
15			0.16				0.14	
30			**				**	

* Friction erratic.
** Friction off-scale.
S: Seizure--overload trip stopped test.

TABLE III

SCUFFING OF COMMERCIAL FUELS

(Four-Ball Tests, 240F, 1200rpm, 15min, 52100 Steel)

WEAR SCAR DIAMETER, mm

	RAF-176-64			JP-5		
Load, kg	Dry Argon	Dry Air	Wet Air	Dry Argon	Dry Air	Wet Air
3	0.28	0.30	0.35	0.27	0.39	0.55
6	S	--	--	0.90	--	--
15		0.50	0.52		0.50	0.65
20		0.59	S		0.53	S
25		S			0.60	
30					S	

COEFFICIENT OF FRICTION

	RAF-176-64			JP-5		
Load, kg	Dry Argon	Dry Air	Wet Air	Dry Argon	Dry Air	Wet Air
3	0.10	0.15	0.16	0.13	0.19	0.14
6	**	--	--	**	--	--
15		0.14	0.13		0.15	0.16
20		0.14	**		0.14	**
25		**			0.16	
30					**	

* Friction erratic.
** Friction off-scale.
S: Seizure--overload trip stopped test.

	Scuff Load, kg		
	Dry Argon	Dry Air	Wet Air
PW-523	2	20	<1
Bayol 35	2	20	<1
RAF-176-64	6	25	20
JP-5	6	25	20

Note that the commercial fuels have better scuff resistance than the highly-refined fuels, just as they had better antiwear properties. Note also that the biggest difference between these fuels was in their performance in wet air: The highly-refined fuels scuffed even at 1 kg; whereas the commercial fuels did not scuff until 20kg. This is believed to be because the polar impurities in commercial fuels reduce corrosive wear (as previously shown), which is postulated as initiating the scuffing in wet air.

2. Ball-on-Cylinder Tests

A similar comparison was made between PW-523 and RAF-176-64 in the ball-on-cylinder device. However, as will be discussed later, scuffing in dry argon could not be obtained in this device, even at high loads, high temperatures and with high-purity fuels, as shown in Table IV.

It was possible to obtain wear-initiated scuffing (similar to that in the four-ball machine under wet air) at 1000g load in both dry air and wet air. This was evidenced by the sharp increase in wear noted in Table IV and also by the occurrence of chattering.

On the other hand, the commercial fuels showed no scuffing at any temperature or load, as shown in Table V. Further evidence of the difference between the two fuels is given by the Talysurf traces in Figure 5. When scuffing (chattering) does not occur, the wear track shows little more than a flattening of asperities. When it does occur, as with PW-523 in dry air and wet air, the track is gouged out to a considerable depth. It is possible to calculate the wear volume (V) of this track from its depth (s) and width (W) and the radius of the cylinder (R), assuming its cross-section to be a circular segment:

$$V = 2/3\ Ws.2\pi R = \frac{4}{3}\pi RWs$$

$$= 93Ws\ \text{(in cu. mm.)}$$

The computed wear volume on the cylinder for those runs showing chattering is also presented in Table V. It is about 1 cu. mm. The wear volume on the ball can be calculated from the wear scar diameter (d) and the radius of the ball (r), and is approximately ($\pi d^4/64r$). For a wear scar of 1 mm the wear volume is only 0.1cu. mm. Thus, when scuffing occurs, the majority of the wear is on the cylinder.

TABLE IV

EFFECT OF LOAD ON WEAR AT 300F

(Ball-on-Cylinder Tests, 240 rpm, 32 min, Steel-on-Steel)

Fuel: FW-523

Load, g	Wear Scar Diameter, mm Dry Argon	 Dry Air	 Wet Air
60	0.22	0.36	0.42
120	0.27	0.52	0.62
240	0.32	0.50	0.65
480	0.37	0.53	0.77
1000	0.35 (0.31)	0.98* (1.01*)	1.08* (1.05*)

---

* Chattering occurred.

TABLE V

EFFECT OF TEMPERATURE ON WEAR

(Ball-on-Cylinder Tests, 1000g, 240 rpm, 32 min, Steel-on-Steel)

Fuel	Temp., °F	Dry Argon		Dry Air		Wet Air	
		Wear Severity	WSD, mm	Wear Severity	WSD, mm	Wear Severity	WSD, mm
PW-523	160	Mild	0.28	Severe* (1.2)	1.05	Severe* (1.7)	1.09
	240	Mild	0.28	Severe* (2.2)	1.17	Severe* (2.6)	1.22
	300	Mild	0.31 (0.35)**	Severe* (1.3)	1.01 (0.98)**	Severe* (1.2)	1.05 (1.08)**
RAF-176-64	160	Mild	0.30	Mild	0.39	Mild	0.48
	240	Mild	0.42	Mild	0.41	Mild	0.57
	300	Mild	0.35 (1.02)** (0.38)** (0.45)**	Mild	0.51 (0.43)**	Mild	0.55 (0.93)**

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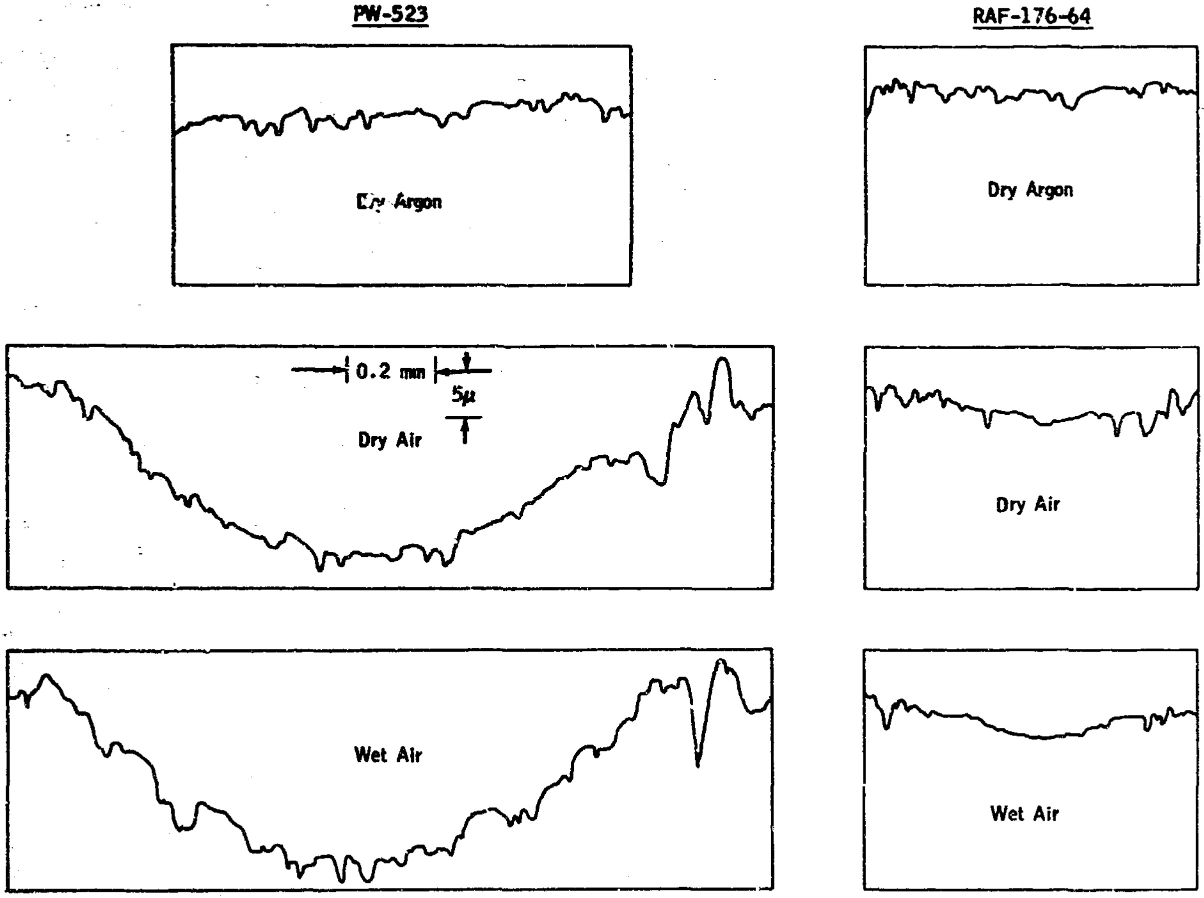
* Chattering during run and very obvious scuffing marks on the cylinder. Data in parentheses are computed wear volume in mm^3 on the cylinder based on Talysurf profile measurements.

** Duplicate run.



BALL-ON-CYLINDER TESTS (1000g, 240 rpm, 240F, 32 min., 52100 STEEL)

FIGURE 5 - TALYSURF PROFILE OF WEAR TRACK ON CYLINDER UNDER SCUFFING AND NON-SCUFFING CONDITIONS

The scuffing behavior of PW-523 is contrasted to the normal wear behavior of RAF-176-64 in Figure 6, which plots the wear data of Table V.

3. Bone-Dry Atmospheres

The dry gases normally used in these tests contain 20-30ppm water, as received from the compressed gas cylinders. It was felt that even this small quantity of water could have some effect, so a program was carried out under "bone-dry" conditions--<1 ppm water in the atmosphere.

The bone-dry conditions were obtained using a heatless dryer (1). The dryer consists of two columns of desiccant (silica gel) used alternately. Compressed gas (30-150 psi) passes through one column where its moisture is completely removed. A small part of this dried gas is then expanded and passed through the second column. Because the drying efficiency depends on the volume of gas used and not its weight, this expanded gas regenerates the silica gel to its previous condition. A timer switches the gas from one column to the other every 30 seconds, so that one column is working while the other is regenerating. Thus, complete dryness is obtained without heating and without using cryogenic temperatures. The gas leaves the drier at less than 1 ppm water. This amounts to 95% water removal from an already very dry gas.

A gas-mixing system was constructed so that any desired mixture of oxygen and nitrogen could be obtained, and at any desired moisture level. Oxygen was analyzed in the gas phase by a Beckman Oxygen Analyzer. Water was analyzed in the gas phase by a Gilbarco Sorption Hygrometer. This instrument was satisfactory at very low water contents (<10 ppm); higher water content was determined from the mixing volumes of dry and moist gas.

To measure the dissolved water directly, some preliminary work was done with a new water analyzer developed by the Analytical Research Division of Esso Research (2). It consists of a gas chromatograph coupled to a crystal hygrometer. This work showed that serious errors exist in the literature on the solubility of water in hydrocarbons and that the Karl Fischer method is not dependable in many cases. It appears that the new technique is exceptionally well suited to jet fuels. But it was felt that a full-scale investigation of water solubilities, the speed at which dissolved water will equilibrate with the atmosphere, and the perturbing effect of surfactants, was beyond the scope of this contract.

The water content in the fuel (liquid phase) should follow Henry's Law, and therefore be calculable knowing the partial pressure of water in the surrounding atmosphere and the saturation content of water in the hydrocarbon.

For the friction and wear tests, the ball-on-cylinder machine was again utilized in this study. The sample cell was sealed to eliminate back diffusion from the atmosphere provided the sample gas flow rate was high enough. AISI 52100 steel balls and cylinders were used for most of the runs. The balls were initially of Rockwell Hardness 63 R_c. Some were heat-treated to give a hardness of 26 R_c. The cylinders are ~30 R_c. For several runs a Timken roller bearing race of ~60 R_c hardness was utilized. This was not only harder but also rougher (30 μ" CLA vs 12 μ" CLA for the regular cylinder) so that differences observed could be caused by either the hardness or the roughness or both.

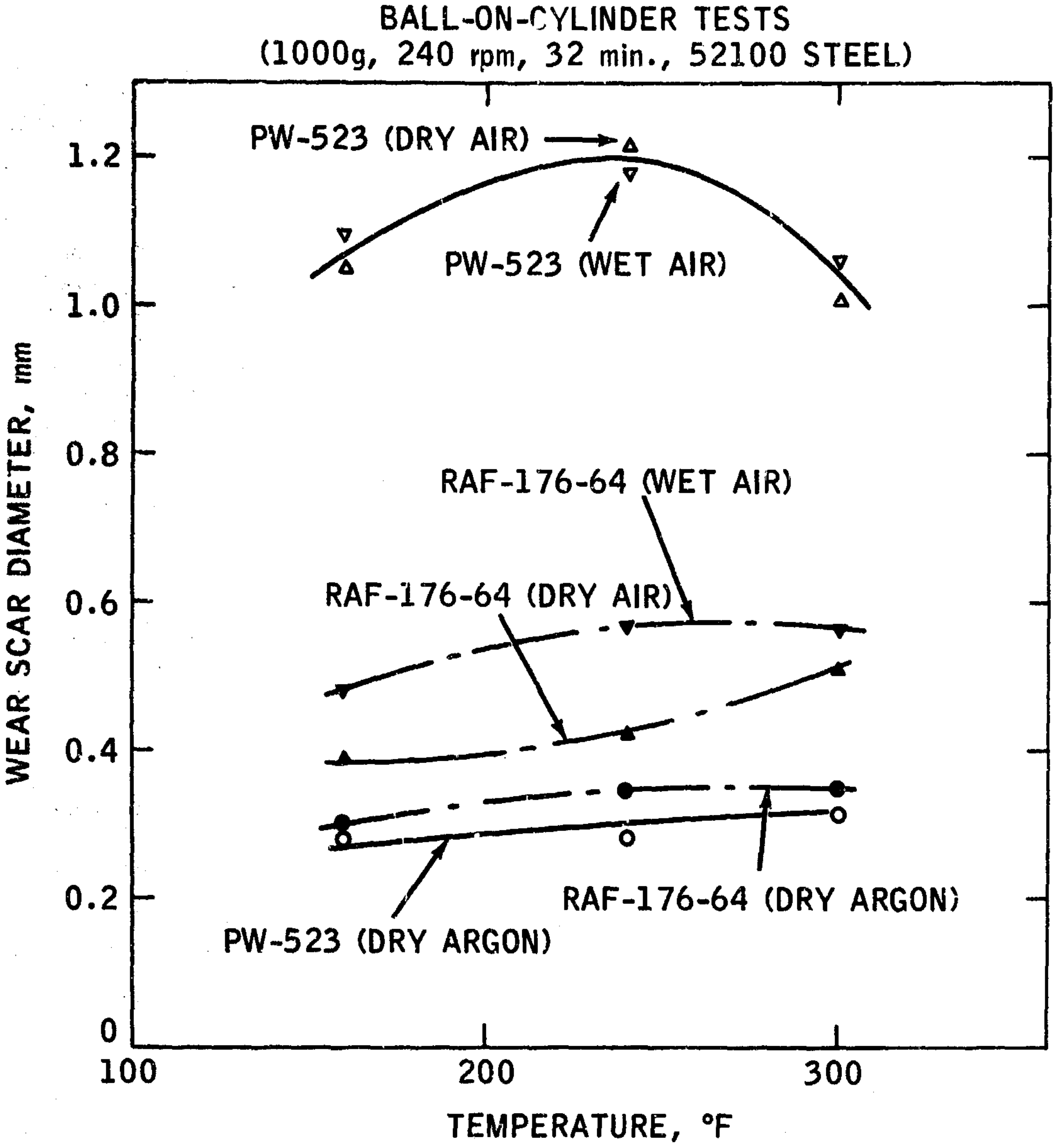


FIGURE 6 - EFFECT OF TEMPERATURE ON TWO FUELS IN VARIOUS ATMOSPHERES

a. Paraffinic Hydrocarbons

Although paraffinic fuels did not scuff in dry argon, there was some feeling that scuffing would occur under bone-dry conditions. Accordingly, tests were run with dodecane, which is a high-purity hydrocarbon of jet-fuel viscosity. However, as shown in Fig. 7 (dashed line) no scuffing occurred. The measured oxygen concentration in the atmosphere was <0.01 (the lower limit on the oxygen analyzer) which, assuming Henry's Law to hold, would give <0.1 ppm dissolved oxygen.

The tests were repeated using the softened steel balls, with the same result. (Fig. 7, solid line.) No scuffing occurred under low-oxygen/bone-dry conditions. Some differences were noted at high oxygen concentrations; the hard steel ball gave more wear than the soft steel in pure oxygen. (Somewhat anomalous results were obtained in wet air, where the soft ball (Fig. 7, point ■) gave more wear than the hard ball (point ▲). According to these data, hard steel is more sensitive to oxygen than to water whereas the reverse is true for soft steel.)

Some further tests were carried out using the harder Timken bearing in place of the normal cylinder. Again no scuffing was obtained at 1 kg. At 4 kg, however, scuffing did occur under bone-dry conditions and at oxygen concentrations below 1%. These data are given in Figure 8. Only the combination of high load and hard surfaces, and absence of water and oxygen, brought about this kind of scuffing. The table below summarizes the data.

Ball	Cyl.	Load (kg)	W.S.D. (mm)	Coefficient of Friction
Soft	Soft	1	.34-.38	.09-.07
Hard	Soft	1	.32	.17
Soft	Soft	4	.44	.12
Hard	Soft	4	.41	.12
Hard	Timken (Hard)	4	1.63	.46

It again should be mentioned that the Timken bearing has about twice the roughness of the normal cylinder and that this could also have some effect. At any rate, the ball-on-cylinder test can be run under conditions sufficiently severe to bring about scuffing with paraffinic fuels in the absence of water and oxygen.

b. Aromatic Hydrocarbons

1-Methylnaphthalene and the other condensed ring aromatics show opposite behavior from the paraffins. These aromatics have been shown to scuff at extremely low loads at low oxygen and water contents. Bone-dry conditions would be expected to aggravate the situation. Such was found to be the case, as shown in Fig. 9, which is a plot of wear vs. oxygen concentration at various humidities.

It can be seen that as water concentration decreases, it takes more and more oxygen to prevent scuffing. This is summarized in the following table:

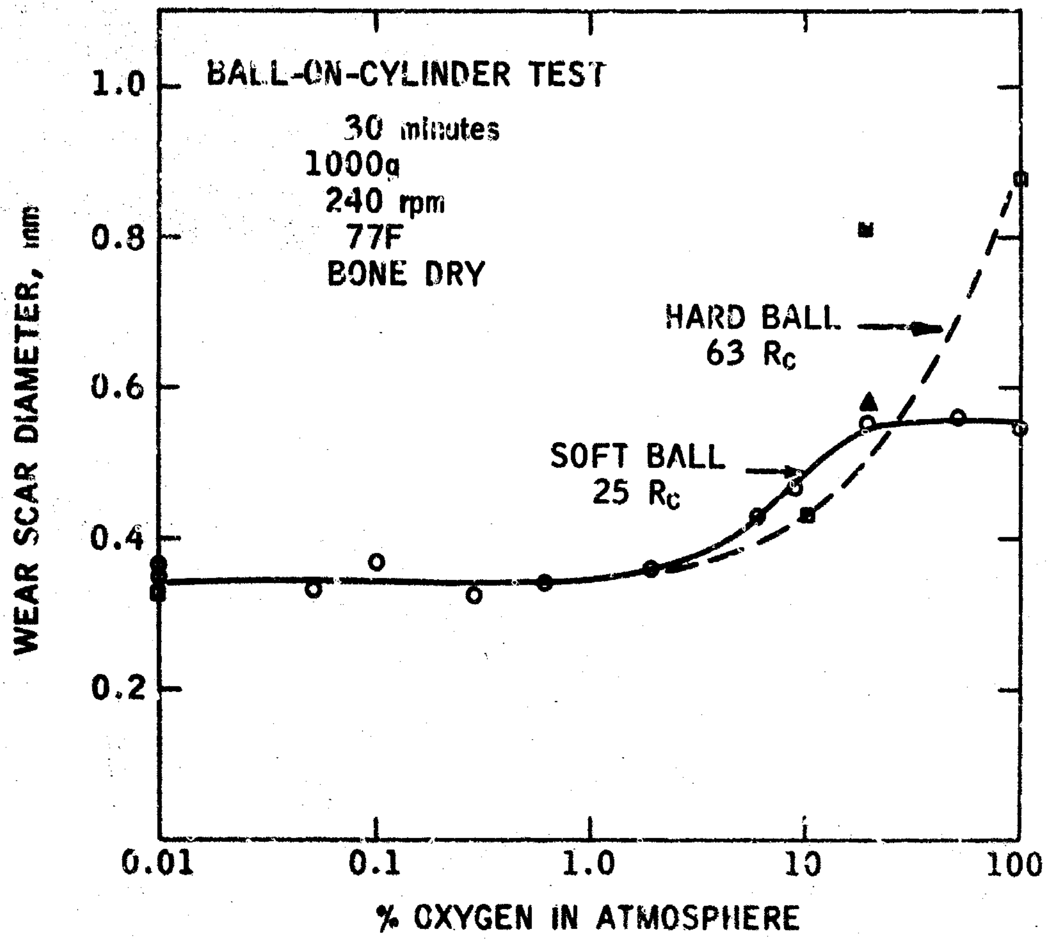


FIGURE 7 - WEAR VS OXYGEN FOR DODECANE - NORMAL HARDNESS CYLINDER

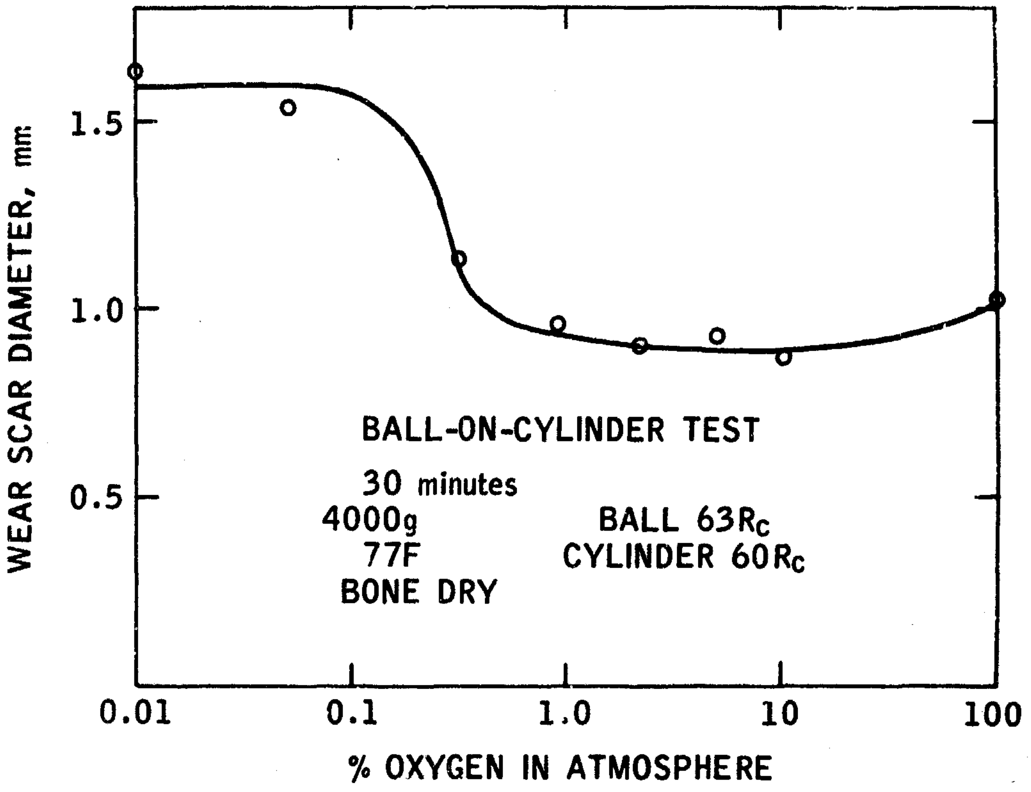


FIGURE 8 - WEAR VS OXYGEN FOR DODECANE - HARD CYLINDER

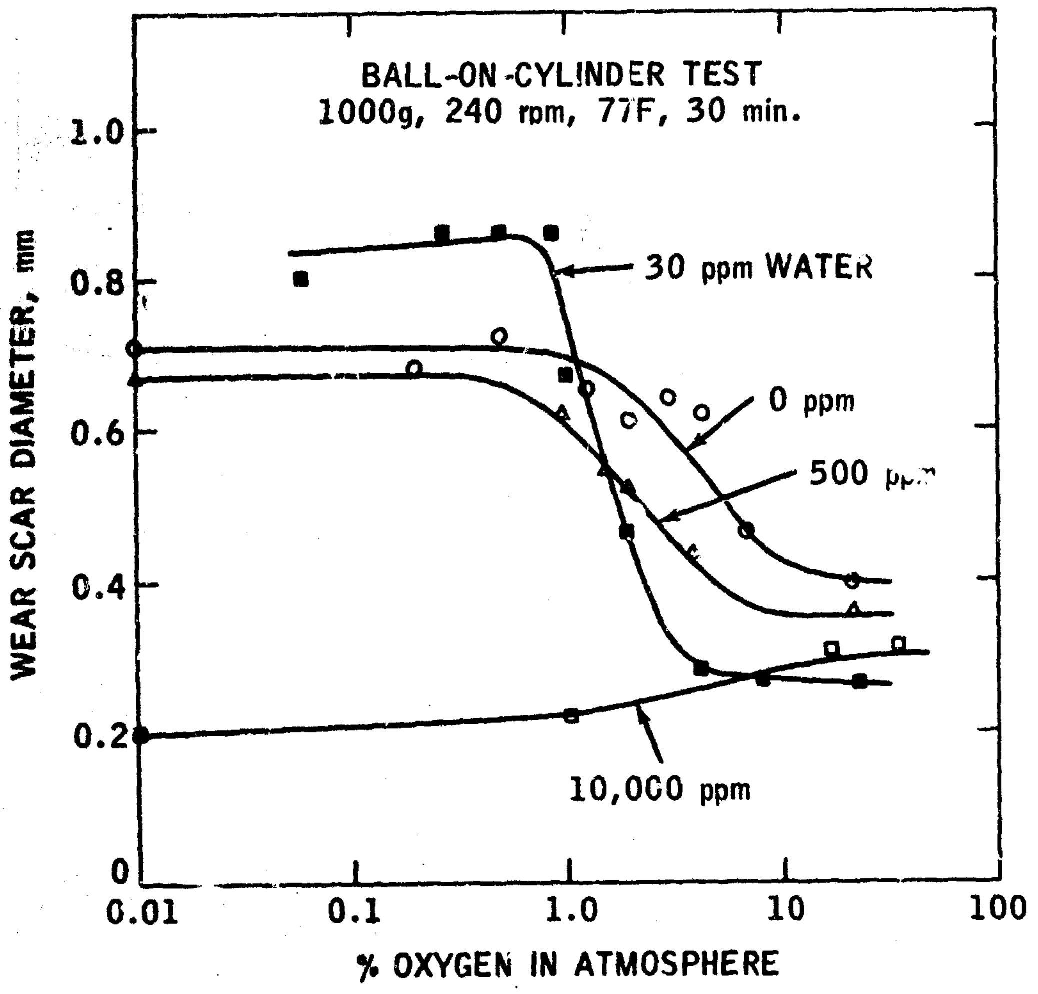


FIGURE 9 - WEAR VS OXYGEN FOR 1-METHYLNAPHTHALENE -- NORMAL HARDNESS CYLINDER

Scuffing of 1-Methylnaphthalene

ppm Water	% O_2 to Prevent Scuffing
0	7
30	4
500	2
10,000	0.01

The data at 30 ppm were those reported earlier. The later data show less of a difference in the final wear scar between scuffing and non-scuffing. The reason for this is unknown, but it does not affect the overall conclusions.

All the above data were taken with a load of 1 kg and the hard ball. An attempted use of the soft balls for this lubricant resulted in no scuffing even under conditions of pure N_2. This is in agreement with the data from the Vickers pump test, where no scuffing was found with methylnaphthalene in nitrogen. More intense conditions, such as obtained with the four-ball tester, are needed to get scuffing conveniently.

B. Hydrocarbon Type

1. Condensed Ring Aromatics Scuff At Very Low Loads

It was previously reported that the condensed-ring aromatics, 1-and 2-methylnaphthalene, scuffed at very low loads in dry argon. This finding has now been extended to other aromatics--phenanthrene, naphthalene and diphenyl,-- which are solids at room temperatures. Naphthalene and phenanthrene were run in ball-on-cylinder tests at 300F, along with 1-and 2-methylnaphthalene and Bayol 35 as reference. All the condensed-ring aromatics scuffed badly (Table VI), as evidenced by large wear scars on the balls, noisy chattering during the test, and deep wear tracks on the cylinder. As before, the addition of moisture (wet argon or wet air) eliminated the scuffing. Fig. 10 shows the difference in the Talysurf traces of the wear tracks for 2-methylnaphthalene in the three atmospheres. The run in dry argon shows the unmistakable deep wear track associated with scuffing, whereas the tracks in wet argon and wet air are barely discernible.

Diphenyl, which is not a condensed ring aromatic, behaves in an intermediate fashion. In the ball-on-cylinder test in dry argon at 175F, diphenyl scuffed at 240g, better than the 60g for 1-methylnaphthalene, but worse than the more-than-1000g for Bayol 35 (Table VII). This behavior does not extend to the single-ring aromatics: At 77F, benzene did not scuff up to the 4000g limit of the machine, whereas iso-octane (2,2,4-trimethylpentane) scuffed at 800g. Note that iso-octane was better than 1-methylnaphthalene in spite of its much lower viscosity and higher volatility.

In the vane pump, however, 1-methylnaphthalene would not scuff in dry nitrogen even at a load (outlet pressure) of 400psi (Table VIII). There was almost no wear and very little roughening of the surface. Apparently, the unit loads obtained in the vane pump are very modest compared to those in the ball-on-cylinder test, and much lower than those in the four-ball test.

TABLE VI

WEAR OF POLYNUCLEAR AROMATICS AT 300F

(Ball-on-Cylinder Tests, 1000g, 240 rpm, 32 min, 52100 Steel)

	Dry Argon		Wet Argon		Wet Air	
Aromatics	Wear Severity	WSD, mm	Wear Severity	WSD, mm	Wear Severity	WSD, mm
Naphthalene	Severe* (8.1)	1.45	--	--	Mild	0.69
Phenanthrene	--	2.70	--	--	--	--
Bayol 35	Mild	0.35	--	--	--	0.91
1-Methylnaphthalene	Severe* (5.0)	1.87	Mild	0.61	Mild	0.48
2-Methylnaphthalene	Severe* (8.1)	1.44	Mild	0.92	Mild	0.45

* Chattering during runs and very obvious scuffing marks on the cylinder. Data in parentheses are computed wear volume in mm^3 on the cylinder based on Talysurf profile measurements.

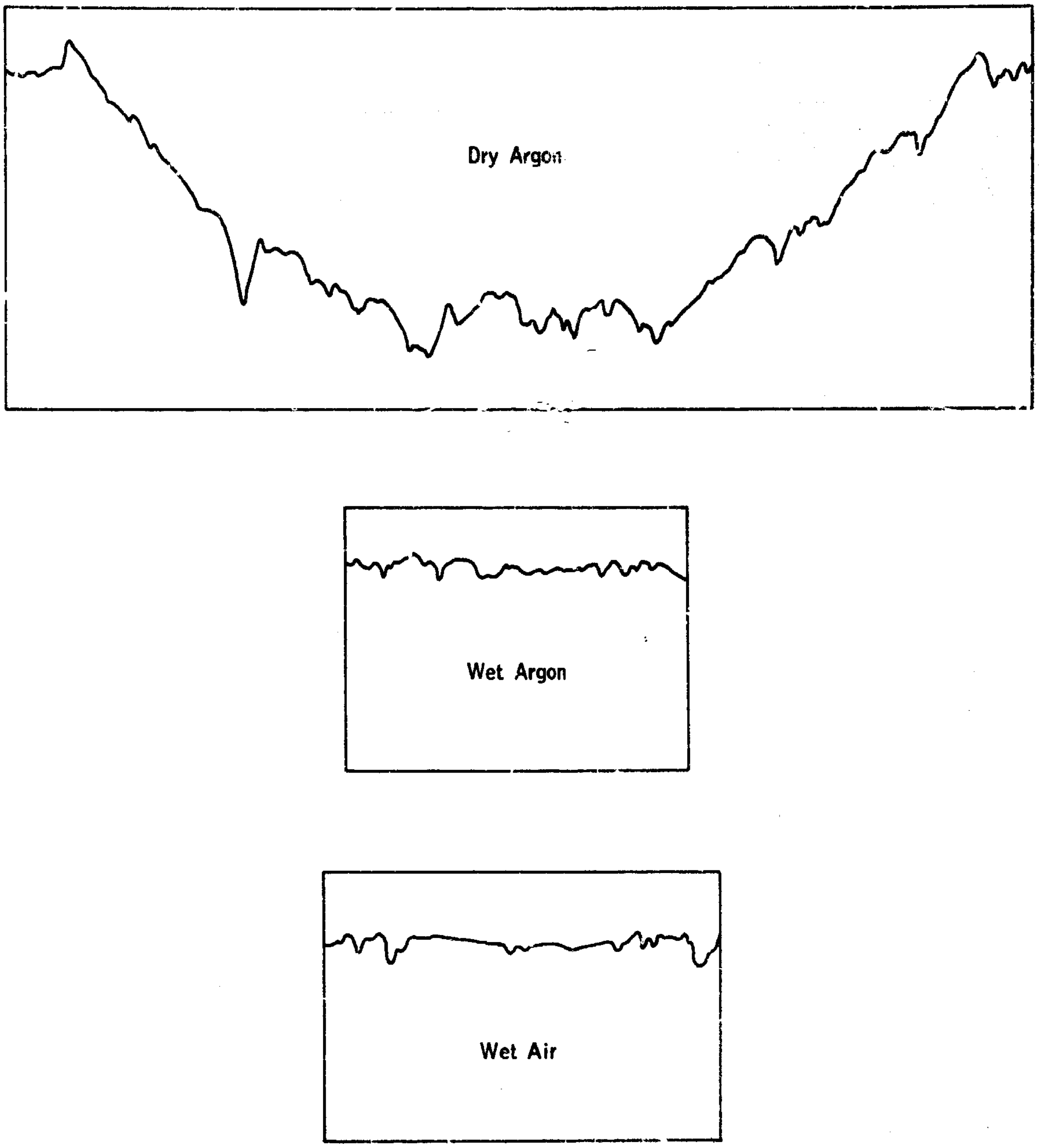


FIGURE 10 - TALYSURF PROFILE OF 2-METHYLNAPHTHALENE IN BALL-ON-CYLINDER TESTS
(1000g, 240 rpm, 300F, 32 min, 52100 Steel)

TABLE VII

SCUFFING OF AROMATICS

(Ball-on-Cylinder Test: Dry Argon)

Hydrocarbon	Scuff Load, g 77F	 175F
1-Methylnaphthalene	400	60
Diphenyl	--	240
Bayol 35	>4000	>1000
Benzene	>4000	--
2,2,4-Trimethylpentane	800	--

TABLE VIII

VICKERS VANE PUMP TESTS ON 1-METHYLNAPHTHALENE IN NITROGEN

Pressure, psig	400	370
Pumping Rate, gpm	0.39	1.07
Volume Efficiency, %	22	59
Wear, mg		
Wt. Loss of Vanes	1	1
Wt. Loss of Ring	0	2
Surface Roughness, µ inch		
Vanes, Initial	8	7
Vanes, Final	9	7
Ring, Initial	15	11
Ring, Final	14	11

2. Condensed-Ring Aromatics Reduce Scuffing In Blends With Paraffins

Previous work had shown that condensed-ring aromatics when added to a paraffinic fuel would reduce wear under non-scuffing conditions. Their ability to reduce scuffing has been found to be equally dramatic. Fig. 11 shows the result of four-ball tests carried out in wet air. The addition of 1-methylnaphthalene to the paraffinic Bayol 35 gives an increase in scuff load from 6kg to 60kg. Furthermore, this effect is noted at all atmospheres and is truly synergistic as noted in Table IX. Even in dry argon, where pure 1-methylnaphthalene is so prone to scuffing, when blended with Bayol 35 it increases the scuff load five-fold.

This antiscuff property of aromatics is a characteristic of all aromatics, although not all aromatics are equally effective. Also, they are effective even at 1% concentration as shown in Table X. In these tests, the four-ball machine was run at increasing loads until the friction was so high that the overload-trip would shut off the motor. It was found that 1% of 1-methylnaphthalene increased the "seizure" load from 10kg to 50kg, that tetralin (tetrahydronaphthalene) was about as good, and that quinoline (a condensed-ring heterocyclic nitrogen compound) was even better. In contrast, the condensed-ring aliphatic, decalin (decahydronaphthalene), had no effect whatsoever.

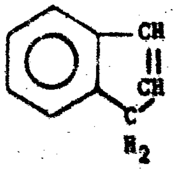
The same antiscuff effect was found at higher temperatures (Table XI). In dry argon, Bayol 35 scuffed at 3kg. The addition of 5% 1-methylnaphthalene or indene increased the scuff load to 10kg. In wet air, the effect was even greater. Bayol 35 scuffed at 1 kg, whereas the aromatic blends increased this to 20kg.

These data give further support to our earlier findings that the heavy aromatics in commercial fuels are responsible for their good lubricity, and that their removal in making highly-refined fuels is responsible for the poorer friction and wear properties of these fuels.

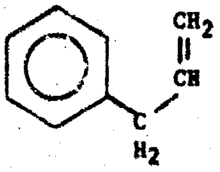
3. Olefins

Olefins have also been found to have some effect on wear, although the effect is not nearly as striking as that of the condensed-ring aromatics. The monoolefins, such as dodecene-1, are relatively ineffective, but the diolefins are much better.

The same pattern holds for their antiscuff behavior. A series of four-ball tests were carried out in dry argon and wet air at 77F and 240F on 5% olefin blends in Bayol 35. Results are given in Tables XII and XIII, and summarized in the table below. The best of the olefins is allyl benzene, which gave a scuff load of 30+kg under all conditions. The chemical structure of this compound closely resembles that of indene, which was shown in the preceding section to be very good also.



Indene



Allylbenzene

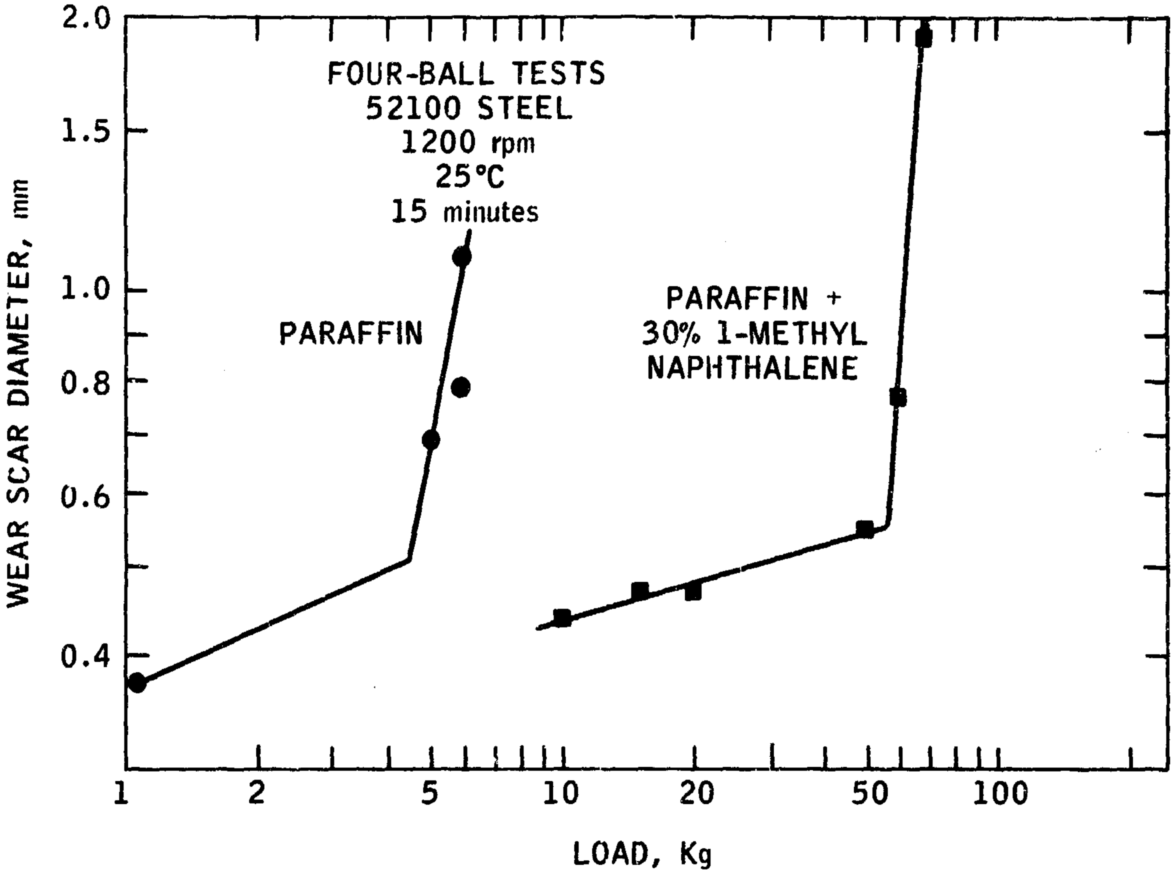


FIGURE 11 - AROMATICS INCREASE LOAD-CARRYING CAPACITY OF PARAFFINS--FOUR-BALL TESTS

TABLE IX

SYNERGISM OF AROMATIC/PARAFFIN BLENDS IN SCUFF PROTECTION

(Four-Ball Tests, 1200rpm, 77F, 15min, 52100 Steel)

% 1-Methylnaphthalene in Bayol 35	Scuff Load, kg		
	Dry Argon	Dry Air	Wet Air
0	12	9	6
30	60	60	60
100	<3	6	25

TABLE X

AROMATICS PREVENT SCUFFING AT 1% CONCENTRATION

(Four-Ball Tests: 1200rpm, 77F, wet air, 52100 Steel)

Aromatic in Bayol 35	Seizure Load*, kg
None	10
1% 1-Methylnaphthalene	50
1% Tetralin	45
1% Quinoline	>50
1% Decalin	10

* Load at which overload-trip shut off motor because of excessive friction.

TABLE XI

SCUFFING TENDENCIES OF AROMATICS

(Four-Ball Tests, 1200RPM, 240F, 15 Min.)

Base Fuel: Bayol 35

	Dry Argon						Wet Air						
Load, kg:	1	3	5	8	10	13	1	3	5	8	10	15	20
Wear Scar Diameter ***													
None	0.28	0.71	S	-	-	-	0.83	S	-	-	-	-	-
5% 1-Methylnaphthalene	-	-	0.33	-	0.75	S	-	-	0.40	-	0.43	0.58	S
5% Indene	-	-	0.28	0.30	S	-	-	-	0.27	-	0.39	0.50	S
Coeff. of Friction													
None	0.22	*	**	-	-	-	*	**	-	-	-	-	-
5% 1-Methylnaphthalene	-	-	0.15	-	0.12	**	-	-	0.16	-	0.13	0.14	**
5% Indene	-	-	0.12	0.11	**	-	-	-	0.12	-	0.12	0.13	**

* Erratic friction and chattering noise.

** Friction off-scale and seizure occurred.

S: indicates seizure.

TABLE XII

EFFECT OF OLEFINS ON WEAR

(Four-Ball Tests, 1200rpm, 77F, 15min)

	Wear Scar Diameter, mm												Coefficient Of Friction											
	Dry Argon						Wet Air						Dry Argon						Wet Air					
Load, kg:	5	10	15	20	25	30	5	10	15	20	25	30	5	10	15	20	25	30	5	10	15	20	25	30
Olefin (5wt%) In Bayol 35																								
None	0.28	S*					0.78**						0.09	***										
Allyl Benzene	0.32	0.33	0.36	0.34	0.47	S*	0.48	0.48	0.49	0.53	0.60	0.68	0.14	0.12	0.10	0.11	0.13	***	0.18	0.15	0.15	0.14	0.13	0.12
α-Methyl Styrene	0.20	0.25	S*	-	-	-	0.49	0.49	0.56	S*	-	-	0.11	0.10	***	-	-	-	0.13	0.11	0.10	***	-	-
2-5 Dimethyl-2-4 hexadiene	0.23	0.31	S*	-	-	-	0.47	0.51	S*	-	-	-	0.11	0.11	***	-	-	-	0.16	0.13	***	-	-	-
2-5 Dimethyl-1-5 hexadiene	0.27	0.28	0.35	S*	-	-	0.37	0.42	0.45	0.48	S*	-	0.13	0.10	0.10	***	-	-	0.17	0.16	0.15	0.15	***	-
Vinyl Cyclohexene	0.27	0.28	S*	-	-	-	0.43	0.43	S*	-	-	-	0.11	0.10	***	-	-	-	0.18	0.15	***	-	-	-

* "S" indicates seizure.
** Scuffed at 6kg load.
*** Friction off-scale.

TABLE XIII

EFFECT OF OLEFINS ON WEAR

(Four-Ball Tests, 1200rpm, 240F, 15min)

	Wear Scar Diameter, mm												Coefficient Of Friction											
	Dry Argon					Wet Air							Dry Argon					Wet Air						
Load, kg:	3	5	10	15	30	3	5	10	15	20	25	30	3	5	10	15	30	3	5	10	15	20	25	30
Olefin (5wt%) In Bayol 35																								
None	0.71					S*							-					**						
Allyl Benzene	0.25	0.30	-	0.43	0.47	0.23	0.47	-	0.52	0.60	0.53	0.62	0.15	0.1	-	0.13	0.12		0.11		0.15	0.15	0.15	0.12
α-Methyl Styrene	0.25	0.30	S*		-		0.45	0.67	0.63	S*	-	-	0.12	0.13	**	-	-		0.14	0.13	0.13	**	-	-
2-5 Dimethyl-2-4 hexadiene	0.27	0.30	S*		-	0.52	0.57	0.70	S*	-	-	-	0.13	0.11	**	-	-		0.13	0.13	**	-	-	-
2-5 Dimethyl-1-5 hexadiene	0.27	0.30	S*		-	0.42	0.48	0.60	0.67	0.58	0.70	0.77	0.11	0.10	**	-	-	0.15	0.14	0.15	0.14	0.14	0.14	0.15
Vinyl Cyclohexene	0.27	0.28	S*		-	0.44	0.67	0.60	S*	-	-	-	0.16	0.13	**	-	-	0.15	0.16	0.12	**	-	-	-

* "S" indicates seizure.
** Friction off-scale.

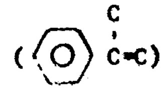
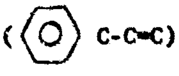
Scuffing Of Olefin Blends

Olefin (5 wt%) in Bayol 35	Four-Ball Scuff Load, kg 77F Dry Argon	 77F Wet Air	 240F Dry Argon	 Wet Air	Relative Oxidation Rate
None	10	<5	<3	<3	[illegible]
Dodecene-1	-	-	5	3	[illegible]
Allylbenzene	30	>30	>30	>30	4
α-Methylstyrene	15	20	10	15	1160
2-5-Dimethyl-1-5 hexadiene	20	20	10	>30	2.6
2-5-Dimethyl-2-4-hexadiene	15	15	10	15	26
Vinylcyclohexene	15	15	10	15	350

It had been previously felt that the lubricity of the olefins was correlated with their ease of oxidation, and in a sense this is true. But the correlation between scuff load and oxidation rate is rather poor, as shown from the last column of the above table. The oxidation rates were estimated by Boland's empirical rule (3). Also, the olefins were effective under dry argon, where oxidation would be impossible. Hence the lubricity of olefins is due to something more than their susceptibility to oxidation.

On the other hand, the above table shows that in air the olefin blends give higher scuff loads at 240F than at 77F, whereas in argon they are better at 77F than at 240F. That is, the olefins are able to overcome the pro-scuff effect of temperature, provided air is present. This does look like an oxidation effect.

There is an interesting relationship between resonant and non-resonant isomers. Note in the table below that 2,5-dimethyl 1-5 hexadiene (non-resonant) is better than 2,5-dimethyl 2-4 hexadiene (resonant) and that allylbenzene is better than α-methylstyrene.

Olefins (5% In Bayol 35)	Scuff [illegible] At 240F, kg In Argon	 In Wet Air
None	3	1
2-5 Dimethyl-2-4 hexadiene (C-C=C-C=C-C)	10	15
2-5 Dimethyl-1-5 hexadiene (C=C-C-C-C=C)	10	> 30
α-Methyl Styrene ()	10	15
Allyl Benzene ()	30	> 30

A more detailed comparison of the test results for 5% allylbenzene and α-methylstyrene is shown in Fig. 12.

A further study on the effect of oxidation on wear and scuffing is reported in Table XIV. Ball-on-cylinder tests were made on dodecane (alkane), dodecene (olefin), and indene (aromatic) at 240g load. These hydrocarbons were redistilled chemical reagents; the dodecane was further purified by passing through the silica gel column before the test. A series of tests was carried out on each hydrocarbon in the following sequence: (1) a ball-on-cylinder test in argon or air at 77F, (2) heat to 300F in argon, (3) a ball-on-cylinder test on the same sample in argon or air at 300F, (4) cool to 77F in argon, and (5) a repeat ball-on-cylinder test at 77F in argon or air.

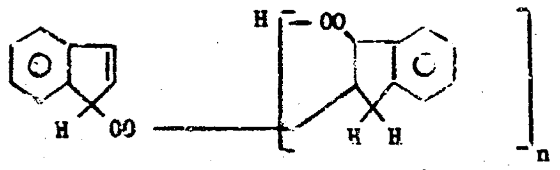
In air, dodecane gave higher wear at 77F than at 300F. This clearly indicates the oxidation effect as evidenced by the lower wear in the repeat run at 77F and the increase of Neut. No. in the sample after tests. In argon, indene gave high wear at 77F and caused scuffing at 300F--in a nonoxidizing atmosphere the wear became more severe at a higher temperature. It is also noteworthy that the oxidation of indene at 300F did not change its poor lubricity as shown in the repeat run at 77F.

It is well-known that there are two possible ways for the propagation of the alkyl peroxy radical in autoxidation of hydrocarbons, namely,

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \qquad (1)$$

$$ROO\cdot + C{=}C \longrightarrow ROOC - C\cdot \qquad (2)$$

For dodecane, Reaction (1) is the only possible step, and the product of the oxidation is mainly carbonyls such as a carboxylic acid that may adsorb on the surface to form a protective film. For indene, the propagating step has been found mainly to be Reaction (2), and the major product after oxidation is a copolymer with the oxygen (4). The oxy-polymer has been found to be:



This polymeric film may be formed in the contact region to give wear protection in the presence of oxygen. However, this does not explain why indene has such poor antiscuffing properties in the first place.

It is evident that a great deal more needs to be learned about the relationship between structure, reactivity and lubricity of hydrocarbons. The broad facts have been delineated in this work, but the reasons for their behavior are still unknown.

From the practical standpoint of jet-fuel quality this information may not be pertinent. In order to get the high thermal stability required for supersonic aircraft, the fuels must be highly refined. In particular, the olefins, sulfur compounds and nitrogen compounds--including heterocyclics--must be removed.

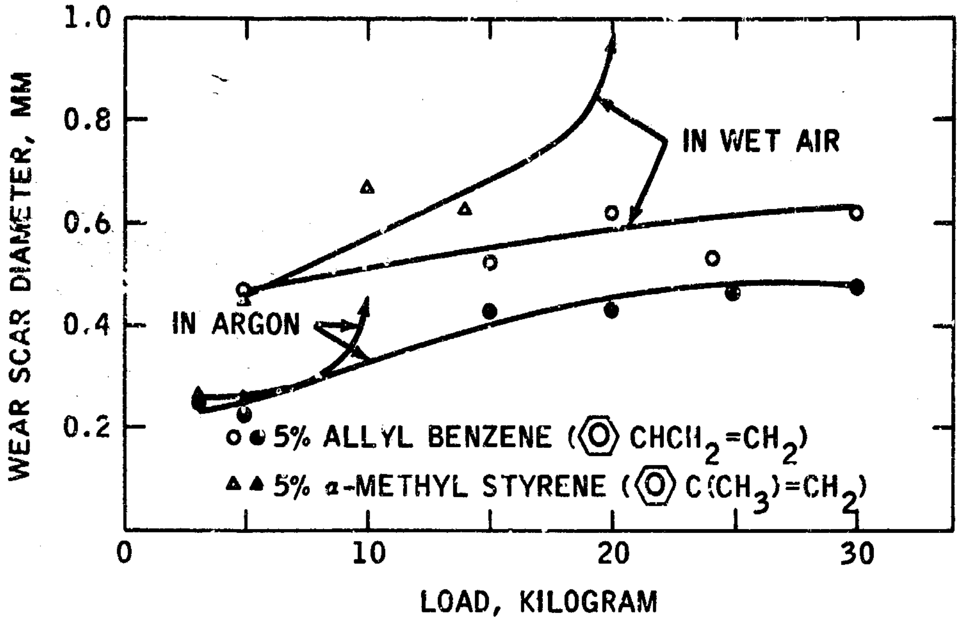


FIGURE 12 - COMPARISON OF SCUFFING LOAD BETWEEN α-METHYL STYRENE AND ALLYL BENZENE (FOUR BALL TESTS - 1200RPM, 15MIN, 240F)

TABLE XIV

EFFECT OF OXIDATION ON FRICTION AND WEAR

	Dodecane		Dodecene		Indene	
Sequence of Test	**CoFr**	**WSD, mm**	**CoFr**	**WSD, mm**	**CoFr**	**WSD, mm**
1. 77F, Argon	0.16	0.28	--	0.28	0.15	0.85
Air	--	0.67	--	0.30	0.13	0.35
2. 300F, Argon	0.14	0.30	0.11	0.35	**	0.87*
Air	0.22	0.38	0.14	0.32	0.22**	0.38
3. 77F, Argon	0.17	0.33	0.12	0.29	0.18**	0.80
Air	0.17	0.35	0.11	0.29	0.17	0.33
Final Neut No, ppm KOH	162		276		83	

---

* Test stopped at 4 minutes due to excessive friction and chattering.

** Friction reading erratic.

In this process, the condensed-ring aromatics are also taken out. The resulting fuel consists almost entirely of paraffins and cycloparaffins and has poor lubricity. Although the lubricity could be restored by adding condensed-ring aromatics without impairing the thermal stability, it is probably easier and cheaper to do this with lubricity additives. The use of condensed-ring aromatics does have the advantage of giving a higher-density fuel (more BTU/gallon) and less problems with water emulsions, but runs into the danger of poorer luminometer number.

C. Sulfur Compounds

Wear tests had previously shown that sulfur compounds of the type and in the concentration found in jet fuels were ineffective lubricity agents. To see if they were good antiscuff agents, some additional tests were run.

1. Ball-On-Cylinder Tests

Three organic sulfur compounds, thiophenol (a mercaptan), dioctyl sulfide and dibenzyl disulfide, were tested in the ball-on-cylinder rig at 1000g load using PW-523 as the base fuel. The concentration for thiophanol was 30ppm S which is above the allowable limit (10ppm) for mercaptan sulfur in jet fuels. The concentration for sulfides was 100ppm S, the sulfur content of most jet fuels. Thiophenol and dioctyl sulfide did not show any antiwear and antiscuffing effect as shown in Table XV. The disulfide showed some antiscuffing effect in that the runs at 160F (but not 240F) ran without any chattering noise and no severe wear was measured on the cylinder. However, the difference of wear scar diameters was not significant.

2. Four-Ball Tests

In the four-ball test three types of sulfur compounds (mercaptan, sulfide and disulfide), each combined with one of three different organic groups (alkyl, benzyl and phenyl), were tested at 77F in dry argon and wet air. The concentrations were 50ppm as S for mercaptans (above the maximum allowable by specification) and 200 ppm as S for sulfides (a typical concentration).

The results are presented in Table XVI and summarized below.

Effect of Sulfur Compounds On Scuffing

	Scuff Load, kg					
	In Argon			In Wet Air		
	-SH	-S-	-SS-	-SH	-S-	-SS-
Alkyl	10	10	10	10	5	5
Benzyl	15	10	10	15	5	5
Phenyl	15	10	10	10	5	5
Base Fuel	--------5---------			--------3---------		

TABLE XV

EFFECT OF SULFUR COMPOUNDS ON SCUFFING

(Ball-on-Cylinder Tests, 1000g, 240 rpm, 32 min, 52100 Steel)

Base Fuel: PW-523

Additive	Temp. °F	Dry Argon		Dry Air		Wet Air	
		Wear Severity	WSD, mm	Wear Severity	WSD, mm	Wear Severity	WSD, mm
None	160	Mild	0.28	Severe* (1.2)	1.05	Severe* (1.7)	1.09
	240	Mild	0.28	Severe* (2.2)	1.09	Severe* (2.6)	1.17
50 ppm S as Thiophenol	160	Mild	0.42	Severe* (0.64)	0.92	Severe* (0.9)	0.94
	240	Mild	0.41	Severe* (1.05)	1.10	Severe* (1.7)	1.20
100 ppm S as Dioctyl Sulfide	160	Mild	0.28	Severe* (0.97)	1.06	Severe* (1.7)	1.14
	240	Mild	0.35	Severe* (1.6)	1.14	Severe* (2.3)	1.22
100 ppm S as Dibenzyl Disulfide	160	Mild	0.39	Mild	0.86	Mild (0.07)	0.92
	240	Mild	0.28	Severe* (1.3)	1.05	Severe* (1.6)	1.02

---

* Chattering during runs and very obvious scuffing marks on the cylinder. Data in parentheses are computed wear volume in mm^3 on the cylinder based on the Talysurf profile measurements.

TABLE XVI

EFFECT OF SULFUR COMPOUNDS ON WEAR

(Four-Ball Tests, 1200rpm, 77F, 15min)

	Wear Scar Diameter, mm								Coefficient Of Friction							
	Dry Argon				Wet Air				Dry Argon				Wet Air			
Load, kg:	1	5	10	15	1	5	10	15	1	5	10	15	1	5	10	15
% Additives In PW-523																
50ppm Mercaptans,																
Octyl	0.20	0.30	S*	-	0.60	0.72	0.78	S*	0.06	0.11	***	-	0.06	0.16	0.18**	***
Benzyl	0.17	0.27	0.32	S*	0.47	0.70	0.78	0.85	0.08	0.14	0.11	***	0.07	0.14	0.16	***
Phenyl	0.20	0.27	0.29	S*	0.50	0.70	0.85	S*	0.07	0.11	0.10	***	0.07	0.17	0.33**	***
200ppm Sulfides,																
Dibutyl	0.20	0.32	S*	-	0.53	0.81	0.80	S*		0.10	***	-		0.55**	0.34**	***
Benzyl	0.18	0.31	S*	-	0.58	0.98	S*	-	0.21	0.10	***	-	0.06	0.47**	***	-
Phenyl	0.18	0.33	S*	-	0.45	0.88	S*	-	0.08	0.08	***	-	0.08	0.52	***	-
200ppm Disulfides,																
Dibutyl	0.20	0.30	S*	-	0.57	0.97	-	S*	0.15	0.09	***	-	0.08	0.51**	-	***
Benzyl	0.18	0.34	S*	-	0.58	1.00	1.02	S*	?	0.10	***	-	0.06	0.54**	0.42**	***
Phenyl	0.27	0.28	S*	-	0.57	0.72	0.92	S*	0.20	0.11	***	-	0.09	0.17**	0.28**	***
None	0.20	0.85			0.47	0.81			0.15	0.10**			0.15	0.57**		

* "S" indicates seizure.
** Erratic friction and chattering noise.
*** Friction off-scale.

It will be noted that in wet air none of the sulfur compounds was effective. All gave large wear scars at 5kg, and the sulfides and disulfides also gave high friction indicative of scuffing. This is in agreement with our conclusion based on wear data: sulfur compounds in jet fuels are not responsible for differences in lubricity observed in the field.

The data in dry argon, however, are different and are rather intriguing. All the sulfur compounds eliminated scuffing at 5kg and the wear scars were very low. Thus, these compounds are lubricity agents when oxygen and water are absent. In this respect they are similar to the condensed-ring aromatics.

The behavior of these sulfur compounds also has some interesting theoretical aspects. Unlike the lubricity additives, the sulfur compounds have very little effect in wet air. Apparently their antiscuff effectiveness cannot function when water or oxygen are present. This implies either a competition for the surface between the sulfur compounds and oxygen/water (a competition which the sulfur compounds lose) or a complex reaction involving the sulfur compound, the steel surface, oxygen and water. This latter seems more likely for, as noted earlier, the sulfur compounds are pro-wear agents under non-scuffing conditions. The same effect was noted in these experiments and is summarized in the table below.

Effect Of Sulfur
Compounds On Wear At 1 kg Load

	Wear Scar Diameter, mm					
	In Argon			In Wet Air		
Sulfur Compound	-SH	-S-	-SS-	-SH	-S-	-SS-
Alkyl	0.20	0.20	0.20	0.60	0.53	0.57
Benzyl	0.17	0.18	0.18	0.47	0.58	0.58
Phenyl	0.20	0.18	0.27	0.50	0.45	0.57
Base Fuel	--------0.20--------			--------0.47--------		

In wet air, there is a definite increase in wear particularly for the disulfides and the alkyl mercaptan.

One other peculiarity of the sulfur compounds was noted. When scuffing occurred in dry argon it was sudden and catastrophic. Friction was so high as to cause "seizure" (the overload trip to the motor would stop the test). In wet air, scuffing would occur as evidenced by high and erratic friction and a large wear scar, but "seizure" would not occur until several load increments higher. This behavior is illustrated in Fig. 13. In general, it can still be concluded that sulfur compounds play little part in the lubricity of jet fuels.

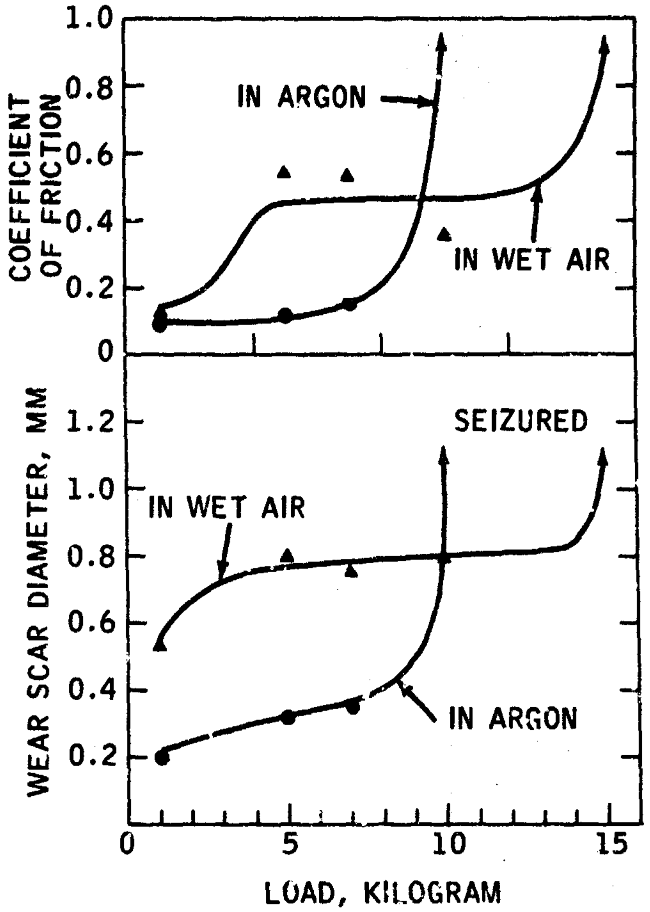


FIGURE 13 - EFFECT OF DIBUTYL SULFIDE ON SCUFFING
(FOUR BALL TESTS - 1200RPM, 15MIN, 77F)

D. Lubricity Additives

Several lubricity additives had been evaluated earlier and many were found to be quite effective in reducing wear. One of the best was oleic acid. Also evaluated were tricresyl phosphate (TCP) and zinc dialkyl dithiophosphate (ZnDDP), two well-known antiwear additives, and a series of proprietary materials coded ER-1, ER-2 etc. ER-1 has had some field experience in test engines; it has been used at relatively high concentrations, 0.1%. ER-3 was developed expressly as a jet fuel lubricity additive. It is effective at concentrations of 50ppm and even lower.

1. Four-Ball Tests

The antiscuff ability of four lubricity additives at 50ppm in PW-523 is given in Table XVII. These tests were run at 240F. In argon, only ER-3 had any appreciable effect on scuffing. It increased the scuff load from 1 kg to 4-5kg. Other additives--ER-1, ZnDDP, and oleic acid--were ineffective. In wet air, the additives were somewhat better. Fig. 14 shows that both oleic acid and ER-3 prevented scuffing out to 15kg. ER-1 and ZnDDP were much less effective. Some scuffing occurred with ZnDDP at loads as low as 2kg, but the friction never became high enough to cause seizure even at 7kg.

However, at 1000ppm (0.1%) concentration all these additives showed some antiscuff properties as shown in Table XVIII. A comparison of scuff loads for these additives at two different concentrations is given below.

Four-Ball Scuff Load, kg

(Base Fuel: PW-523)

Additives	Dry Argon 50ppm	Dry Argon 1000ppm	Wet Air 50ppm	Wet Air 1000ppm
None	1		0.5	
ZnDDP	2	10	2	20
Oleic Acid	3	10	20	> 30
ER-1	2	10	3	15
ER-3	5	30	20	> 30

It will be noted that all the additives are more effective in wet air than in dry argon. This is the same effect noted earlier with the naturally-occurring polar compounds found in commercial fuels. It is believed to be a reflection of the natural tendency of all fuels to scuff less if oxygen and water are present. Both oxygen and water form oxides, which reduce adhesion and scuffing. In addition, the simple adsorption of water also tends to diminish scuffing. The reason that non-additive fuels scuff more readily in wet air is that corrosive wear plays an important part in the scuffing process: the presence of oxygen and water causes the formation of iron oxide which in turn causes abrasive wear and scuffing. The lubricity additives suppress corrosive wear and thus allow water and oxygen to fulfill their antiscuff function. Also, the additives themselves are more reactive with the surface when a full oxide layer is present.

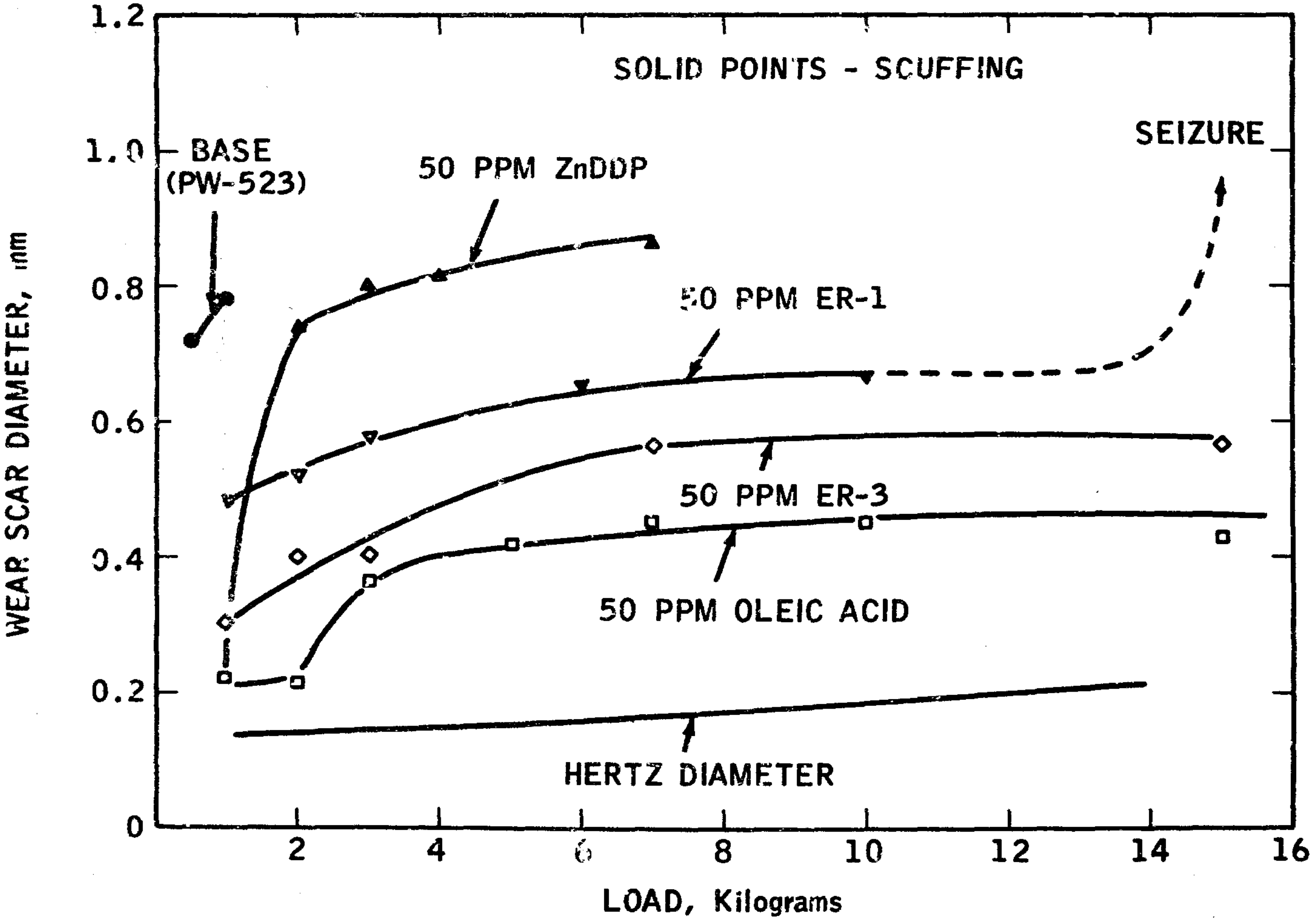


FIGURE 14 - EFFECT OF ADDITIVES ON SCUFFING LOAD IN WET AIR
(FOUR-BALL TESTS - 240F, 1200RPM, 52100 STEEL, 15 MIN.)

TABLE XVII

EFFECT OF LUBRICITY ADDITIVES ON WEAR

(Four-Ball Tests, 1200rpm, 240F, 15 Min.)

Base Fuel: PW-523

	Dry Argon						Wet Air								
Load, kg:	0.5	1	2	3	5	7	0.5	1	2	3	5	7	10	15	20
Wear Scar Diameter*															
None	0.20	0.48	0.56	-	-	-	0.72	0.78	-	-	-	-	-	-	-
50ppm ZnDDP	-	0.20	0.68	S	-	-	-	0.20	0.75	0.80	-	0.88	-	-	-
50ppm Oleic Acid	-	0.24	-	0.62	S	-	-	0.22	0.23	0.38	0.42	-	0.45	0.43	S
50ppm ER-1	-	0.20	0.53	0.58	S	-	-	0.48	0.53	0.58	0.61	-	0.66	S	-
50ppm ER-3	-	0.20	-	0.27	0.69	S	-	0.30	-	0.38	0.61	0.57	0.52	0.57	S
Coeff. of Friction															
None	0.15	**	**	-	-	-	**	**	-	-	-	-	-	-	-
50ppm ZnDDP	-	0.15	**	***	-	-	-	0.10	**	**	-	**	-	-	-
50ppm Oleic Acid	-	0.17	-	**	***	-	-	0.10	0.11	0.17	0.12	-	0.13	0.12	***
50ppm ER-1	-	0.14	**	**	***	-	-	0.11	0.17	**	**	-	**	***	-
50ppm ER-3	-	0.14	0.13	0.12	**	***	-	0.2	-	0.17	0.12	0.14	0.13	0.11	***

* "S" indicates seizure.

** Erratic friction and chattering noise.

*** Friction off-scale.

TABLE XVIII

EFFECT OF LUBRICITY ADDITIVES ON WEAR

(Four-Ball Tests, 1200rpm, 240F, 15min)

	Wear Scar Diameter, mm												Coefficient Of Friction											
	Dry Argon						Wet Air						Dry Argon						Wet Air					
Load, kg:	3	5	10	15	20	30	3	10	15	20	25	30	3	5	10	15	20	30	3	10	15	20	25	30
% Additive in PW-523*																								
0.1% ZnDDP	0.23	0.26	S**	-	-	-	0.37	0.38	0.65	S**	-	-	0.09	0.09	****	-	-	-	0.18	0.16	0.12	****	-	-
0.1% Oleic Acid	0.27	0.30	0.83	S**	-	-	0.26	0.44	0.39	-	0.48	0.51	0.11	0.08	***	****	-	-	0.14	0.08	0.08	-	0.10	0.12
0.1% ER-1	0.29	0.27	S**	-	-	-	0.48	0.63	S**	-	-	-	0.09	0.13	****	-	-	-	0.16	0.19	****	-	-	-
0.1% ER-3	0.34	-	0.42	0.39	0.38	0.62	0.33	0.38	0.36	-	0.53	0.52	0.06	-	0.06	0.09	0.10	0.11	0.10	0.13	0.11	-	0.13	0.12

* PW-523 scuffed at 1 kg in argon and 0.5 kg in wet air.
** "S" indicates seizure.
*** Erratic friction and chattering noise.
**** Friction off-scale.

A second important fact from the above table is that the scuff load increases as the concentration increases. This is different from the case of corrosive wear, where only 50ppm was usually sufficient to eliminate the wear, and further increases in concentration had little effect. Again this is not surprising: scuffing is a dynamic condition in which the surface layer is continuously rubbed off and must reform before the next traverse. Higher loads cause the surface layers to be rubbed off faster, and this must be countered by a faster film formation, i.e., a higher concentration of additive available at the surface to react.

Both of these facts are illustrated in Figs. 15 and 16 which show the complete data for ER-3. In dry argon 50ppm ER-3 is only effective up to 3kg, whereas in wet air it is effective up to 15kg. Increasing the concentration to 1000ppm increases the scuff load in both dry argon and wet air.

2. Ball-On-Cylinder Tests

The effectiveness of ZnDDP, ER-1 and ER-3, were also evaluated at a concentration of 50ppm in ball-on-cylinder tests. The conditions (1000g load and 160-300F) were such that the base fuel, PW-523, would scuff. It will be seen (from Table XIX) that ER-3 prevented scuffing (chattering) at all temperatures, ER-1 at 160F and 240F but not 300F, and ZnDDP only at 160F. Essentially, the same results were obtained in both dry air and wet air. There is a good correlation between scuff load at constant temperature (as determined in the four-ball rig) and scuff temperature at constant load (as determined in the ball-on-cylinder rig).

An important observation is that high wear on the ball is not always accompanied by high wear on the cylinder. Note that at 160F, all additives gave zero cylinder wear (no scuffing), but the ball wear varied from 0.53 to 0.97. On the other hand, high wear on the cylinder is invariably accompanied by high wear on the ball. In other words, when scuffing occurs, wear is high on both surfaces, but when scuffing does not occur only the ball shows measurable wear. By examining both surfaces, it is possible to determine whether high wear on the ball is due to scuffing or to normal corrosive wear.

It is apparent that with 52100 steel all of these additives are antiscuff agents to some degree. More data on the antiscuff behavior of additives is given in subsequent sections, particularly in other metallurgies.

B. Effect Of Temperature

Several examples have already been given showing that scuffing is more severe at higher temperatures. Part of this may be because of reduced viscosity, but high temperatures would be expected to be harmful because scuffing itself is considered to be surface-temperature phenomenon.

1. Four-Ball Tests

Table XX shows scuff loads at 77F and 240F for PW-523 and its blends with additives, ER-1 and ER-3. It will be seen that the scuffing becomes more severe at higher temperatures. This is true for highly refined fuels as well as fuels containing additives.

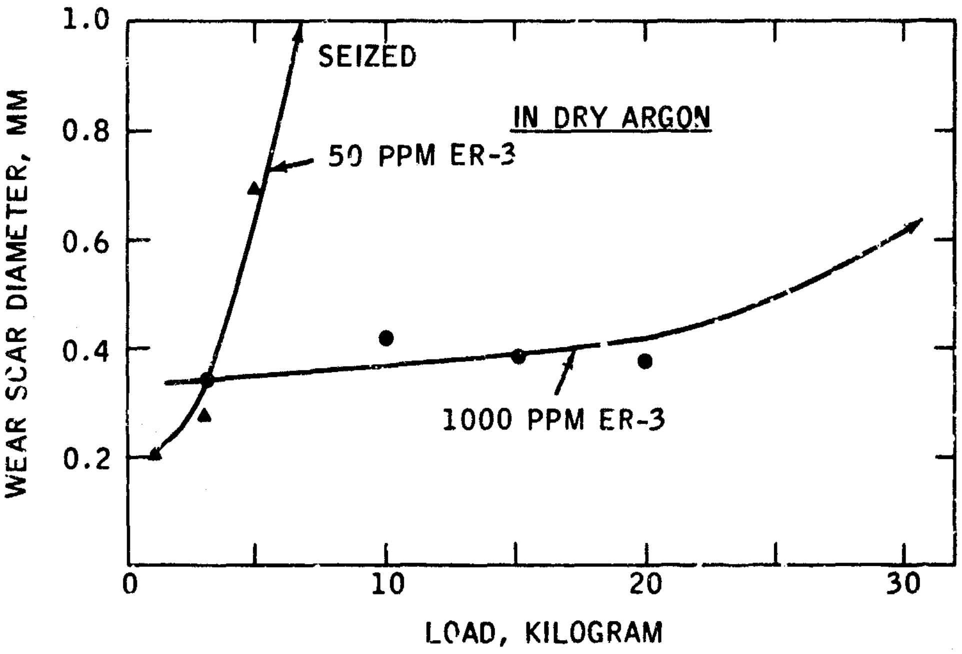


FIGURE 15 - EFFECT OF ADDITIVE CONCENTRATION (FOUR BALL TESTS - 1200RPM, 15MIN, 240F, 52100 STEEL)

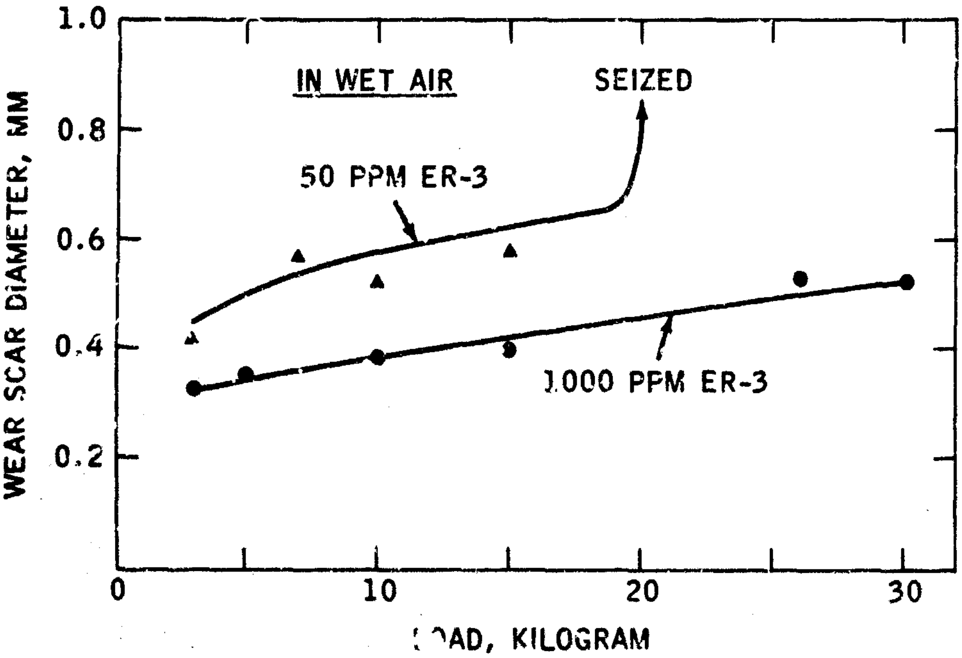


FIGURE 16 - EFFECT OF ADDITIVE CONCENTRATION
(FOUR BALL TESTS - 1200RPM, 15MIN,
240F, 52100 STEEL)

TABLE XIX

ANTISCUFFING EFFECT OF ADDITIVES

(Ball-on-Cylinder Tests, 1000g, 240 rpm, 32 min, 52100 Steel)

Additive in PW-523	Temp., °F	Dry Air Cylinder Wear, mm^3	Dry Air Ball WSD, mm	Wet Air Cylinder Wear, mm^3	Wet Air Ball WSD, mm
None	160	1.3	1.05	1.3	1.09
	240	2.6	0.87	2.1	1.17
	300	1.7	0.93	1.2	1.10
50 ppm ZnDDP	160	Nil	0.85	Nil	0.70
	240	1.3	0.91	1.3	1.00
	300	1.6	1.14	2.1	1.17
50 ppm ER-1	160	Nil	0.80	Nil	0.95
	240	Nil	0.70	Nil	0.85
	300	0.1	1.13	1.9	1.07
50 ppm ER-3	160	Nil	0.53	Nil	0.70
	240	Nil	0.45	Nil	0.58
	300	Nil	0.55	Nil	0.53
		(Nil)	(0.54)	(Nil)	(0.56)

TABLE XX

TEMPERATURE EFFECT ON SCUFFING LOAD

(Four-Ball Tests, 1200rpm, steel)

Additive in PW-523	Argon		Wet Air	
	77F	240F	77F	240F
None	5	2	3	0.5
1000ppm ER-1	25	10	25	15
1000ppm ER-3	45	30	>60	45

2. Ball-On-Cylinder Tests

The determination of scuff load in the four-ball test is a time-consuming operation, involving several separate tests. An alterantive procedure was to increase the load smoothly until scuffing occurred. The Roxana four-ball machine is ideally suited for this, for the load is applied pneumatically. However, this procedure was not satisfactory. Reproducibility was extremely poor and the scuff load was always far higher than obtained with the separate-test method.

Another approach was to run the ball-on-cylinder test at constant load but to increase the temperature until scuffing occurred. Scuffing was evidenced by high friction and severe chattering noise. This technique was not entirely successful, but it revealed some interesting facts.

The tests were carried out in dry argon only. The fuel sample was preheated to 120F, and during the test the temperature rose continuously at a rate of about 10°F/minute. If no scuffing had occurred at 350F, the test was stopped. The total test time was therefore about 25 minutes.

Fig. 17 shows the behavior of Bayol 35 in this test. At 240g, no scuffing was obtained up to 350F. At 2000g and 4000g, scuffing was complete as soon as it occurred at all. However, at 1000g the scuffing behavior was intermediate: friction rose somewhat more slowly, and then leveled off before final failure. This run was then repeated, but the test was stopped at the high friction level before failure. Fig. 18 is a photomicrograph showing the difference in the appearance of the wear scar showed welding and metal transfer. When the test was stopped before failure, there was no sign of welding or metal transfer.

A plot of scuff temperature vs. load (Fig. 19) shows that scuff temperature decreases smoothly as load increases.

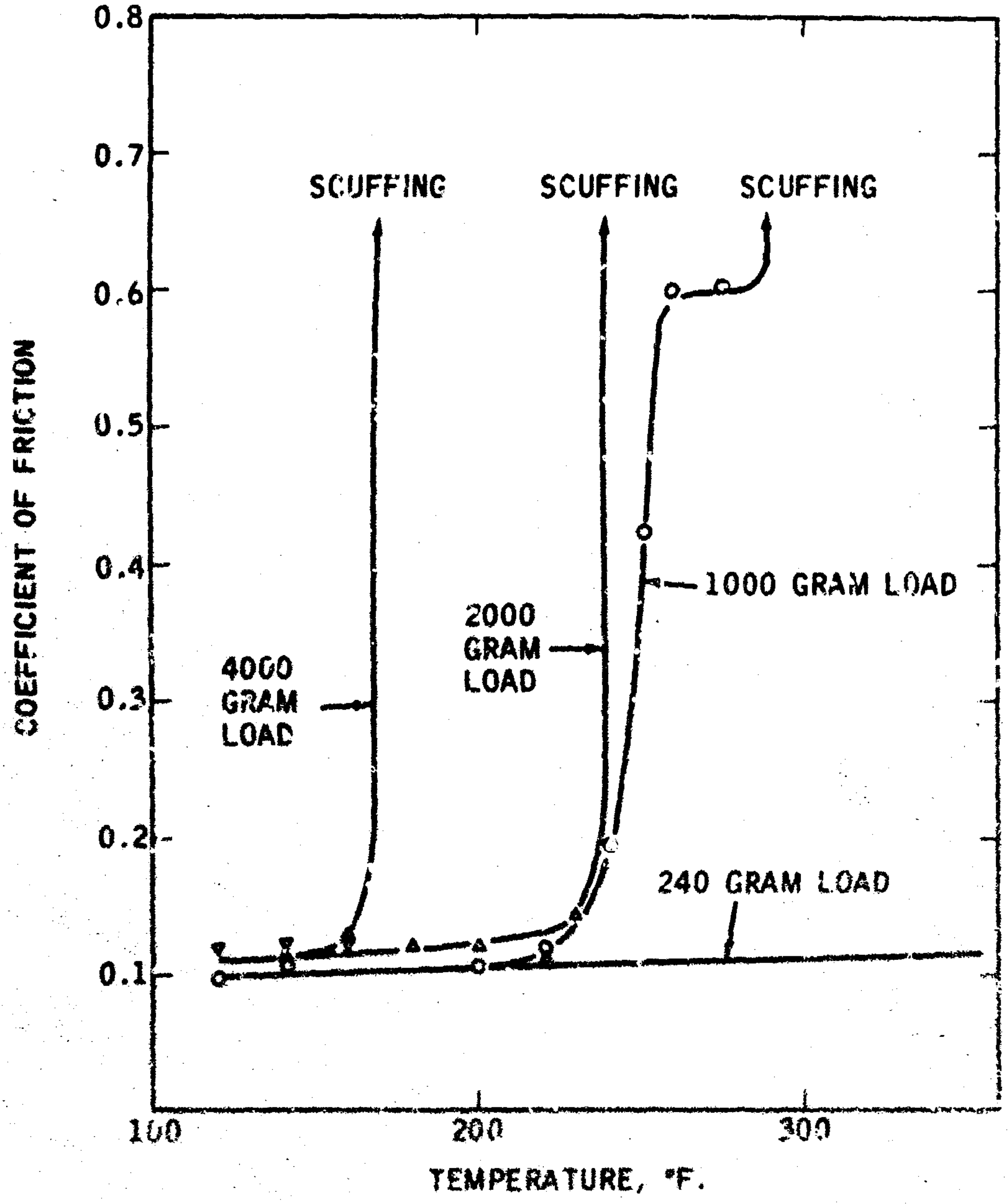
Additives were also tested in this manner, using a load of 4000g. Results are given in Table XXI. Those additives that gave a higher scuff load in the four-ball tester also gave a higher scuff temperature in the ball-on-cylinder device. ER-3 was best, showing no failure. A photomicrograph of the wear scar from this run is also shown in Fig. 18. The other additives were in the order oleic acid, ZnDDP, and ER-1. It is noteworthy that whereas ZnDDP and ER-1 showed no effect on scuff load in the 4-ball test, they did show some effect on scuff temperature. It may be that this procedure is more sensitive in picking up small differences, or it could be that this is due to a fundamental difference in the test procedures. In the scuff temperature test, the additive has a longer time to establish a protective film.

Of the hydrocarbons used as additives, methylnaphthalene showed no failure, while dodecene was entirely ineffective.

Two sulfur compounds were also examined: 170ppm of thiophenol (50ppm as S) showed some effect, but 550ppm of butyldisulfide (200ppm as S) was as good as 50ppm oleic acid. Earlier data had shown that butyldisulfide was not effective in reducing wear at room temperature.

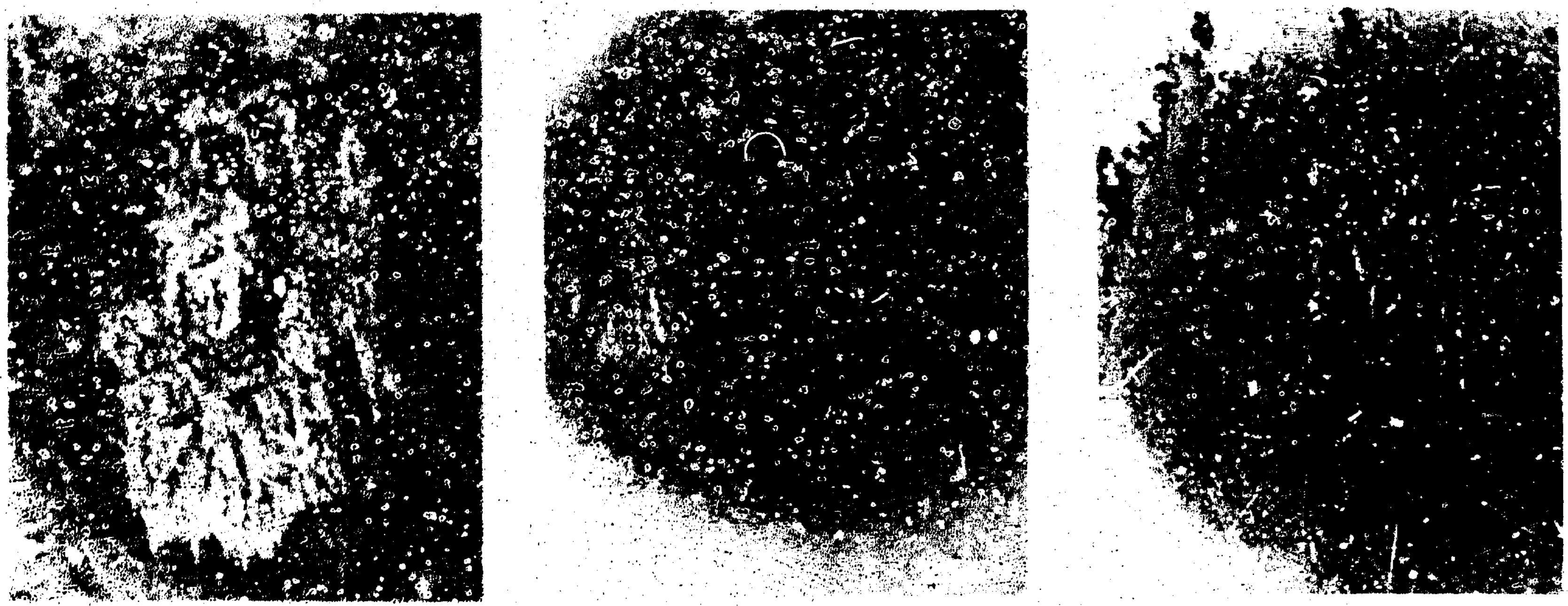
3. Vane Pump Tests

Vickers vane pump tests on Bayol 35 at 300F are compared in Table XXII with those at 240F previously reported. In these tests, an attempt was made to offset the pro-scuff effect of the lowered viscosity caused by the increase in temperature



FRICTION AT VARIOUS TEMPERATURES
(Ball-on-Cylinder Tests-240 RPM, Dry Argon, Bayol 35)

FIGURE 17 - EFFECT OF TEMPERATURE AND LOAD ON FRICTION AND SCUFFING



WEAR SCAR AT FAILURE
(290F)

WEAR SCAR AT HIGH FRICTION
(275F)

FOR 50PPM ER-3
(4KG LOAD, 33CF)

FIGURE 18 - MICROGRAPH (88X) OF WEAR SCAR ON BALLS FROM SCUFFING TEMPERATURE TESTS
(BALL-ON-CYLINDER TESTS, 1000G, 240RPM, ARGON, BAYOL 35

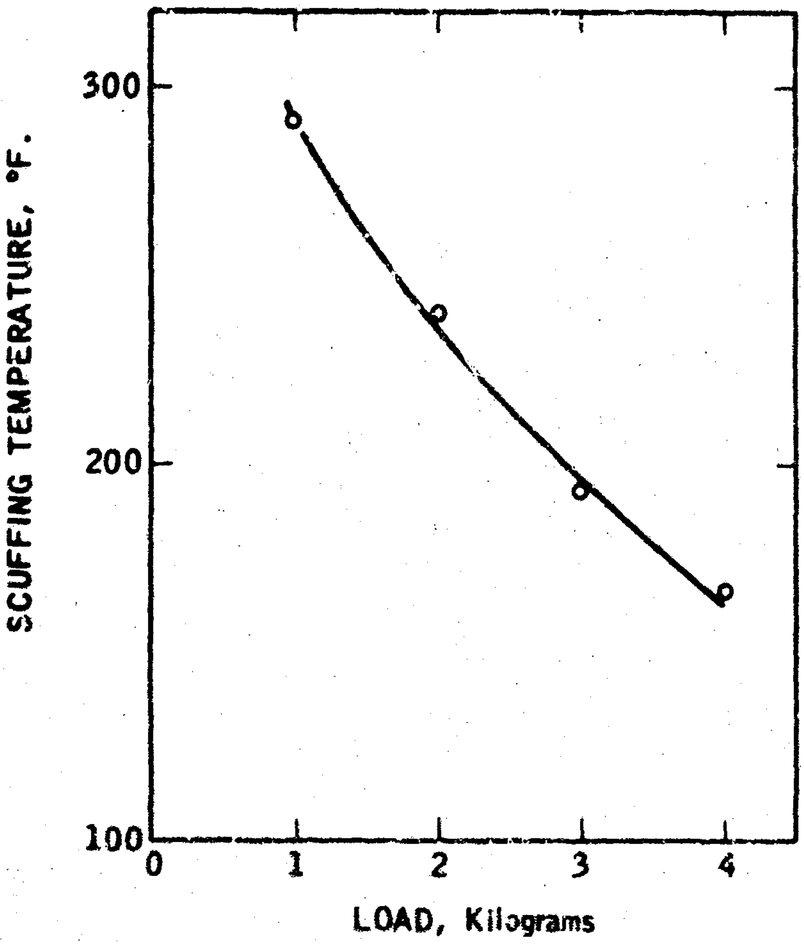


FIGURE 19 - SCUFFING TEMPERATURE VERSUS LOAD
(BALL-ON-CYLINDER TESTS - 240RPM, APCOS, BAYOL 35)

TABLE XXI

ADDITIVE EFFECT ON SEIZURE TEMPERATURE

(Ball-on-Cylinder Tests--4000g, 240RPM,
Argon, Steel-on-Steel)

Base Fuel: Bayol 35

Cylinder No.	Additive	Seizure Temperature °F.	Run Time Min.
136	None	177	5
	50ppm ZnDDP	280 (285)	14 (15)
	50ppm Oleic Acid	328	19
	50ppm ER-1	265	11
	50ppm ER-3	>350	27
137	None	160	3
	5% Dodecene	185	5
	5% 1-Methylnaphthalene	360	25
	5% Indene	310	22
140	None	195	5
	50ppm S as Thiophenol	252	13
	200ppm S as Butyldisulfide	330	18

TABLE XXII

VICKERS VANE PUMP PERFORMANCE OF BAYOL 35 AT HIGH TEMPERATURES

	Dry Nitrogen (24 Hr. Runs)		Wet Air (4 Hr. Runs)	
Sump Temperature, °F	240	300	240	300
Pressure, psig	150	125	150	125
Viscosity, cp at sump temperature	0.60	0.43	0.60	0.43
Pumping Rate, gpm	0.49	0.37	0.27	0.38
Volume Efficiency, %	27	21	15	21
Wear, mg				
Wt. Loss of Vanes	1	11	22	2
Wt. Loss of Ring	23	144	473	19
Surface Roughness, μ inch				
Vanes, Initial	20	5	11	11
Vanes, Final	31	77	>200	12
Rings, Initial	12	11	27	11
Rings, Final	7	41	>200	7

(0.60cp/240F vs. 0.43cp/300F). This was done by reducing the load (outlet pressure) from 150psi to 125psi. In dry nitrogen, the higher temperature gave higher wear. However, in wet air, wear was much more severe at the lower temperature. This is probably because the higher temperature caused oxidation, and the resulting oxidation products were antiwear compounds.

In none of these tests was true scuffing observed. The vane pump is wear-limited, not scuff-limited.

IV. OTHER METALLURGIES

The conclusions for hard steel systems have been strengthened by studying other metallurgies such as stainless steel, K-Monel and silver. Although these systems scuff more easily and give higher wear than 52100 steel, the effect of such parameters as oxygen/water content, fuel composition, additives and temperature are remarkably the same in all metallurgies. Some differences were noted, but these were exceptions rather than commonplace.

A. Corrosive Wear Occurs with Corrosion-Resistant Metals

Corrosive wear is not limited to easily-rusted metals. To the contrary, it is found with nearly all metallurgies. Table XXIII presents data from four-ball tests on eight different metallurgies, ranging from tungsten carbide to silver. The tests were carried out at very low speed, 20rpm, in order to avoid scuffing. In every case, with the exception of silver, wear was higher in wet argon than in dry argon, and still higher in wet air. That is, with all metallurgies, water and oxygen accelerate wear. It is interesting to note that the stainless steels (SS-440C and SS-302) are actually somewhat more prone to corrosive wear than the chrome-alloy 52100 steel.

The explanation of this lies in the nature of corrosion mechanism of stainless steels. They owe their corrosion resistance to the formation of a layer of the alloying element (e.g. chromium) at the surface. This layer prevents the diffusion of iron atoms to the surface. However, the formation of the protective layer also proceeds by a diffusion process and this process takes time. In a rubbing system, this layer is rubbed off even before it has a chance to form. Hence, corrosive wear can take place just as easily with stainless metals as with ordinary steels.

Note in Table XXIII that even tungsten carbide exhibits corrosive wear, although this may be because of attack on the cobalt "cement" used to bind the tungsten carbide granules together. Stainless 302 shows corrosive wear at 1 kg load, but appears to be at incipient scuffing in dry argon at 5kg as evidenced by the large wear scar (0.87mm). Silver gives large wear scars in all three atmospheres. The wear was no greater in wet air (0.53mm) than in dry argon (0.57mm). This could be because silver is very resistant to oxidation (the formation of silver oxide has a slight positive free-energy at room temperature), and therefore does not undergo corrosive wear, or it could be that incipient scuffing is occurring here, too.

A cylinder of K-Monel was fabricated in order to run wear tests on this metal in the ball-on-cylinder machine where scuffing is not such a problem. Table XXIV gives data for loads of 60 and 240g. As in the four-ball test, K-Monel shows increased wear with oxygen and moisture in the order: dry argon, dry air, wet air. Friction is also considerably higher in wet air--about 0.25 vs. 0.10 in the other two atmospheres. This confirms the pro-wear effect of humid air on corrosion resistant metals.

TABLE XXIII

CORROSIVE WEAR IS OBSERVED WITH NEARLY ALL METALS

(Four-Ball Tests: 28rpm, 15min, 77F, Bayol 35)

	Wear Scar Diameter, mm					
	1 kg load			5kg load		
Metallurgy	Dry Argon	Wet Argon	Wet Air	Dry Argon	Wet Argon	Wet Air
Tungsten Carbide	--	--	--	0.20**	--	0.33**
52100 steel, R_c60	0.20	0.20	0.37	0.20	--	0.53
52100 steel, R_c44	--	--	--	0.23	0.25	0.50
52100 steel, R_c25	0.21	0.27	0.37	0.43	--	0.53
SS-440C	0.17	0.20	0.42	--	--	--
SS-302	0.23	0.23	0.50	0.87	--	0.62
K-Monel	0.33*	0.36*	0.49*	--	--	--
Silver	0.57	0.77	0.53	--	--	--

* 960 minutes.

** 960 minutes, 20kg.

TABLE XXIV

EFFECT OF ATMOSPHERE ON LUBRICATION OF K-MONEL-ON-K-MONEL

(Ball-on-Cylinder: 240rpm, 32min, 77F, Bayol 35)

Load, g	Dry Argon	Dry Air	Wet Air
	WSD, mm		
60	0.16	0.21	0.30
240	0.23	0.33	0.52
	CoFr		
60	0.08	0.10	0.26
240	0.10	0.15	0.24

B. Scuffing Occurs Readily with the Softer, More Corrosion-Resistant Metals

Four-ball tests with these light jet fuels on the softer, corrosion-resistant metals frequently give scuffing, even at the lowest loads obtainable on the machine. Stainless 302, for example, scuffs at lower loads at 77F than 52100 steel does at 240F:

Scuff Loads of Two Steels

Steel	Temp. °F	Scuff Load, kg, for Bayol 35 Dry Argon	Wet Argon	Dry Air	Wet Air
Chrome-alloy 52100	240	2	3	20	1
Stainless 302	77	<1	3	5	<1

More complete data on SS-302 are given in Table XXV.

1. Stainless Steels Scuff Easily in Wet Air

Note from the above table that the effect of atmosphere is the same with both steels. The presence of either moisture (wet argon) or oxygen (dry air) reduces scuffing Oxygen is particularly effective. However, the combination of the two (wet air) causes scuffing to occur even more easily than does dry argon. As already discussed, the scuffing in wet air of 52100 steel is believed to be caused by the abrasive action of iron oxides cutting through the surface films. That is, this scuffing is induced by heavy corrosive wear and stainless steels are apparently just as subject to it. This is another indication that steels which can prevent static corrosion cannot prevent corrosive wear.

2. Soft Steel and Other Metallurgies are Resistant to Scuffing in Wet Air

Not all metallurgies show high scuffing in wet air. K-Monel, for example, scuffs less in wet air than in either dry air or wet argon (Table XXVI). The anti-scuff properties of oxygen and water appear to be additive in this case. The same is true for softened 52100 steel. Data are summarized below:

Atmosphere	Four-Ball Scuff Load, kg, for Bayol 35 K-Monel	Soft 52100 Steel
Dry Argon	<1	7
Wet Argon	4	10
Dry Air	2	20
Wet Air	>10	25

TABLE XXV

EFFECT OF ATMOSPHERE ON SS-302

(Four-Ball Tests: 1200rpm, 15min, 77F, Bayol 35)

	Wear Scar Diameter, mm			
Load, kg	Dry Argon	Wet Argon	Dry Air	Wet Air
1	*	0.27	0.30	*
2	*	0.28	0.30	*
3	*	*	0.28	*
4		*	0.33	
5			*	

* Scuffed--high erratic friction trace.

TABLE XXVI

4-BALL TESTS: K-MONEL

(1200rpm, 15min, 77F, Bayol 35)

	Wear Scar Diameter, mm							
Load, kg:	1	1.5	2	3	4	5	7	10
Dry Argon	*	-	*	*	-	-	-	-
Wet Argon	0.48	-	0.53	0.54	*	*	-	-
Dry Air	0.40	0.43	0.45, *	*	-	-	-	-
Wet Air	0.51	-	-	0.58	0.54	0.57	0.61	0.61

	Coefficient Of Friction							
Load, kg:	1	1.5	2	3	4	5	7	10
Dry Argon	0.77**	-	0.51**	0.57**	-	-	-	-
Wet Argon	0.08	-	0.11	0.10	**	Off Scale	-	-
Dry Air	0.10	0.14	0.13, **	**	-	-	-	-
Wet Air	0.16	-	-	0.12	0.14	0.13	0.13	0.09

* Scuffed
** Friction erratic

Apparently with these metals the oxide products formed in wet air do not cause sufficient abrasion to bring on scuffing. Hence, the formation of the oxide layer simply protects against scuffing. Fig. 20 is a photomicrograph of the wear scars obtained in dry argon (scuffing) and in wet air (non-scuffing).

3. Polar Impurities Give <u>Ambiguous Scuffing Behavior</u>

It was already noted in Section III that the presence of polar impurities (as found in commercial fuels) could suppress the corrosive effect of oxygen and moisture. In those cases where corrosive wear causes scuffing, its suppression by polar impurities is beneficial. Thus, RAF-176-64 was much better than Bayol 35 in its scuffing behavior on 52100 steel in wet air. However, in the case of K-Monel and soft 52100 steel, the reaction of oxygen and moisture at the surface is helpful in reducing scuffing. Hence, if polar impurities interfere with this reaction, they could be harmful. That is, polar impurities can have two opposing effects: they can adsorb on the surface to prevent wear; they can interfere with the adsorption of oxygen and moisture.

Table XXVII shows data for RAF-176-64 on K-Monel. These data, along with those for Bayol 35, are presented graphically in Fig. 21. In wet argon, RAF-176-64 is better than Bayol 35, whereas in wet air the reverse is true. Apparently, the impurities in RAF-176-64 are more effective in preventing scuffing than is moisture alone, but the combination of moisture and oxygen is even more effective, and the impurities in RAF-176-64 prevent them from their maximum effectiveness.

This ambiguous effect is even more striking with soft 52100 steel. Figs. 22-25 compare Bayol 35 with RAF-176-64 in the four atmospheres, and the scuff loads are summarized below.

	Four-Ball Scuff Load, kg	
Atmosphere	Bayol 35	RAF-176-64
Dry Argon	7	25
Wet Argon	10	15
Dry Air	20	20
Wet Air	25	7

The two fuels show almost diametrically opposite effects. In this case, the polar impurities apparently so conflict with the oxygen and moisture that neither one can function effectively. Hence, scuffing occurs at low loads in wet air. That is, the polar impurities appear to be pro-scuff agents. This same effect will be noted later with lubricity additives.

From the point of view of field experience, this phenomenon does not seem to be pertinent. Apparently, scuffing of this kind is not a problem in the field. At least, there are no reported cases where less-highly-refined fuels have shown poorer lubricity, as they did in these scuffing tests.

(a) DRY ARGON (3.5 Min.)

(b) WET AIR (15 Min.)

FIGURE 20 - PHOTOMICROGRAPHS OF WEAR SCAR
(FOUR-BALL TESTS - 1200RPM, K-MONEL,
BAYOL 3[illegible], ROOM TEMP., 3KG)

TABLE XXVII

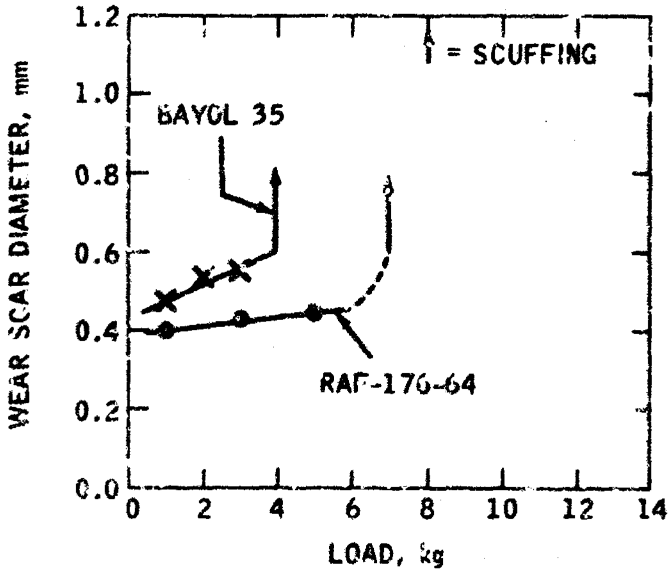
4-BALL TESTS: K-MONEL

(1200rpm, 15min, 74F, RAF-176-64)

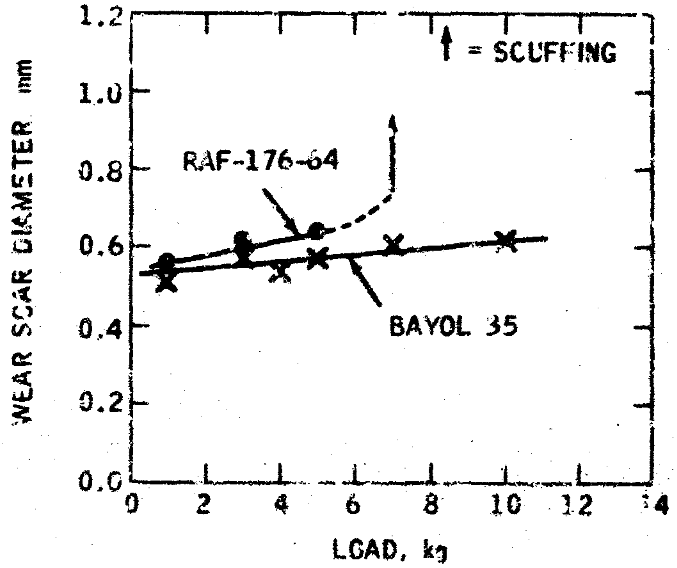
Load, kg:	1	3	5	7
	-------Wear Scar	Diameter	------------	
Dry Argon	*	*	-	-
Wet Argon	0.40	0.42	0.43	*
Dry Air	0.48	*	-	-
Wet Air	0.55	0.61	0.63	*

Load, kg:	1	3	5	7
	--------Coefficient	Of Friction	------	
Dry Argon	0.85**	0.93**	-	-
Wet Argon	0.25	0.08	0.07	0.60**
Dry Air	0.12	0.91**	-	-
Wet Air	0.12	0.12	0.11	Off Scale

* Scuffed
** Friction erratic



(a) WET ARGON



(b) WET AIR

FIGURE 21 - COMPARISON OF BAYOL 35 WITH RAF-176-64 ON K-MONEL (FOUR BALL TESTS - 1200RPM, 15MIN, 77F)

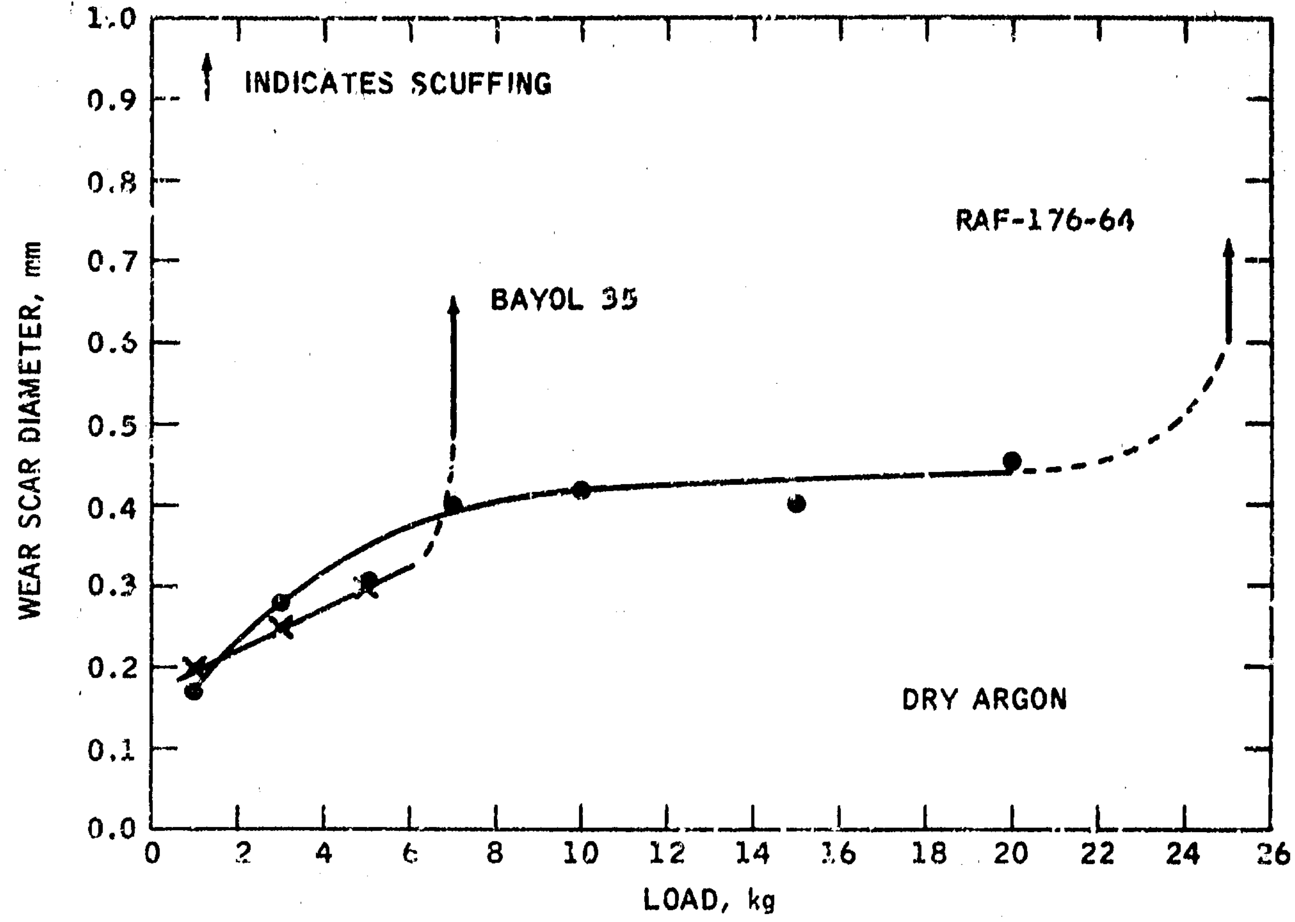


FIGURE 22 - FUEL TYPE AFFECTS WEAR AND SCUFFING (FOUR BALL TESTS - 1200RPM, 15MIN, 74F, R_c 25 STEEL)

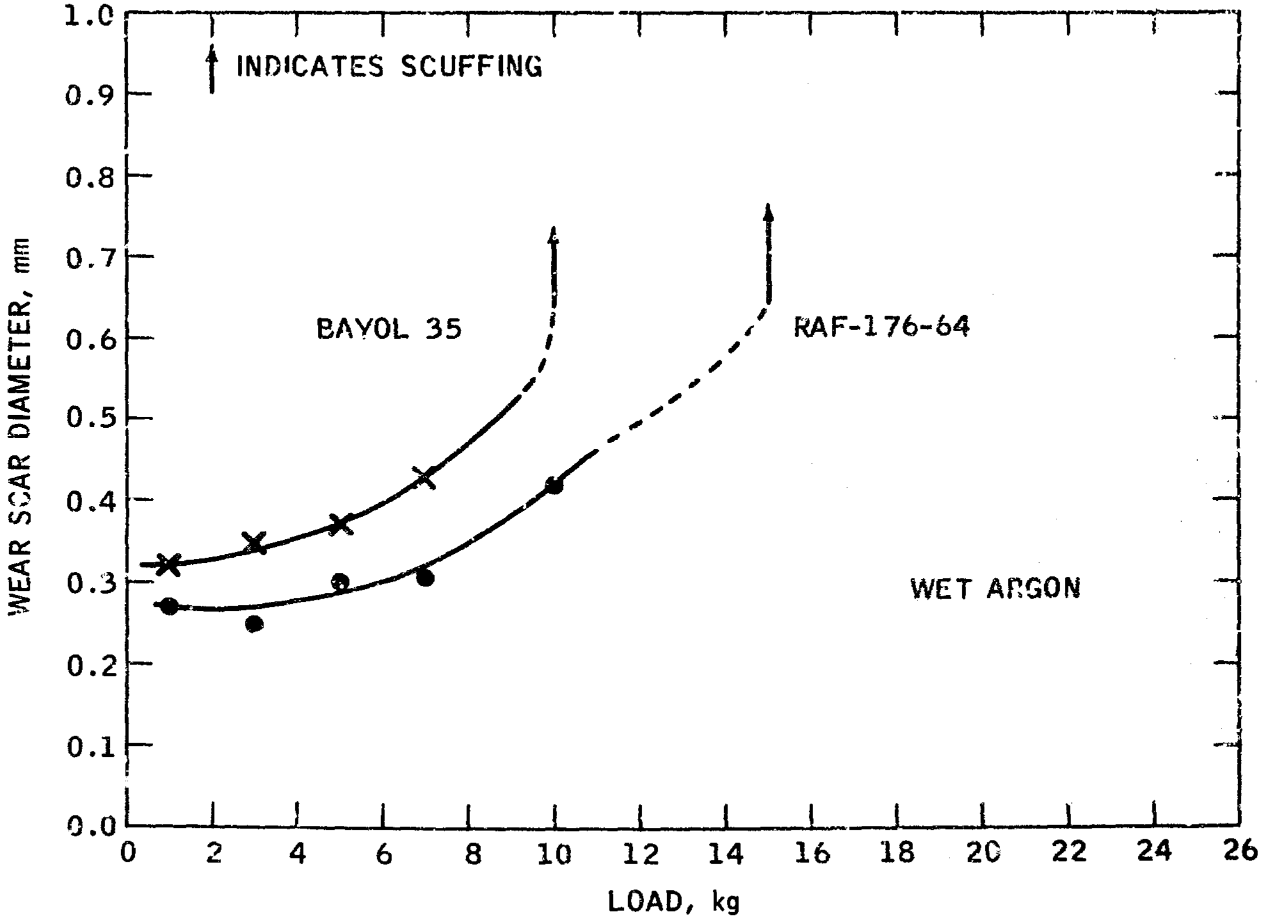


FIGURE 23 - FUEL TYPE AFFECTS WEAR AND SCUFFING (FOUR BALL TESTS - 1200RPM, 15MIN, 74F, R_c 25 STEEL

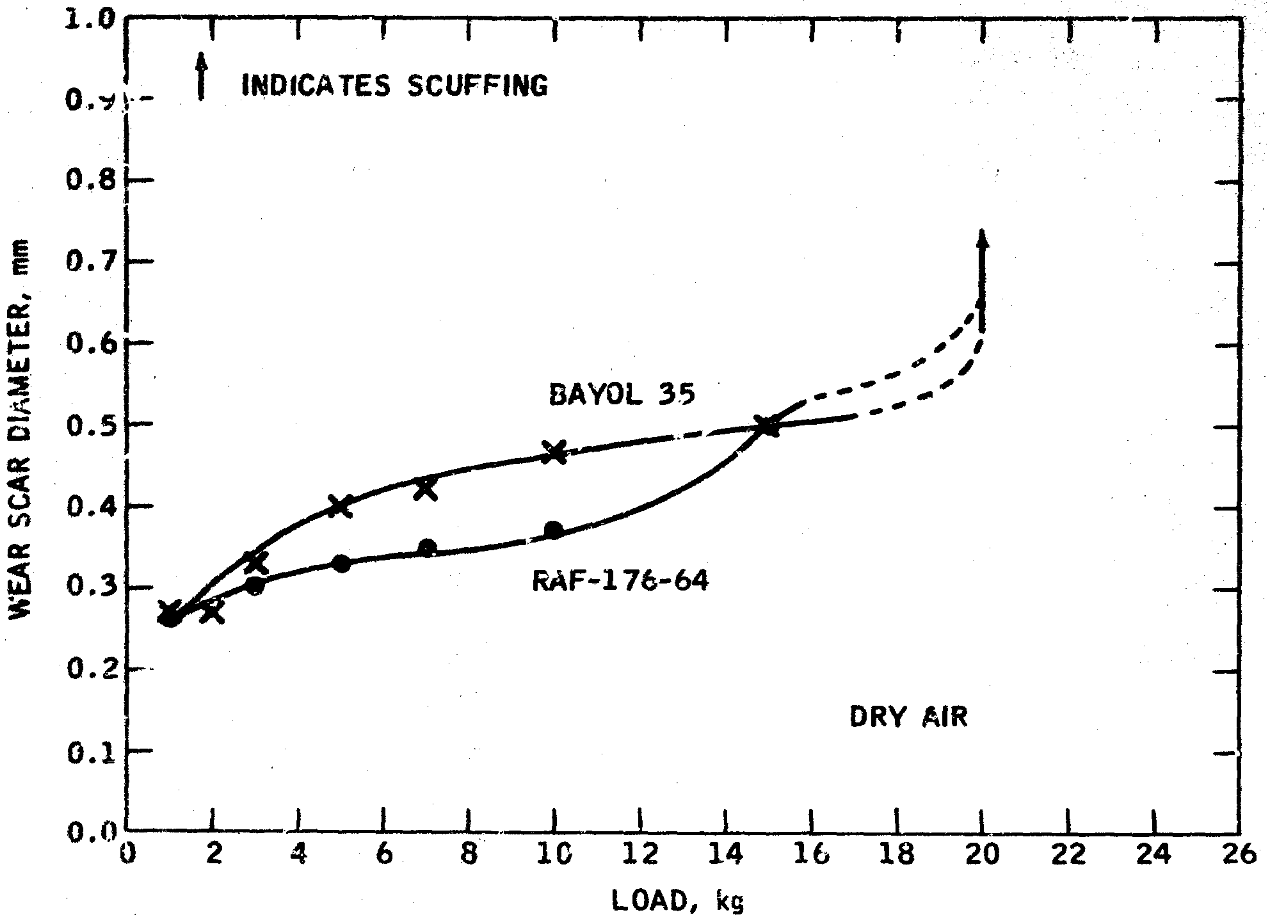


FIGURE 24 - FUEL TYPE AFFECTS WEAR AND SCUFFING (FOUR BALL TESTS - 1200RPM, 15MIN, 74F, R_c 25 STEEL)

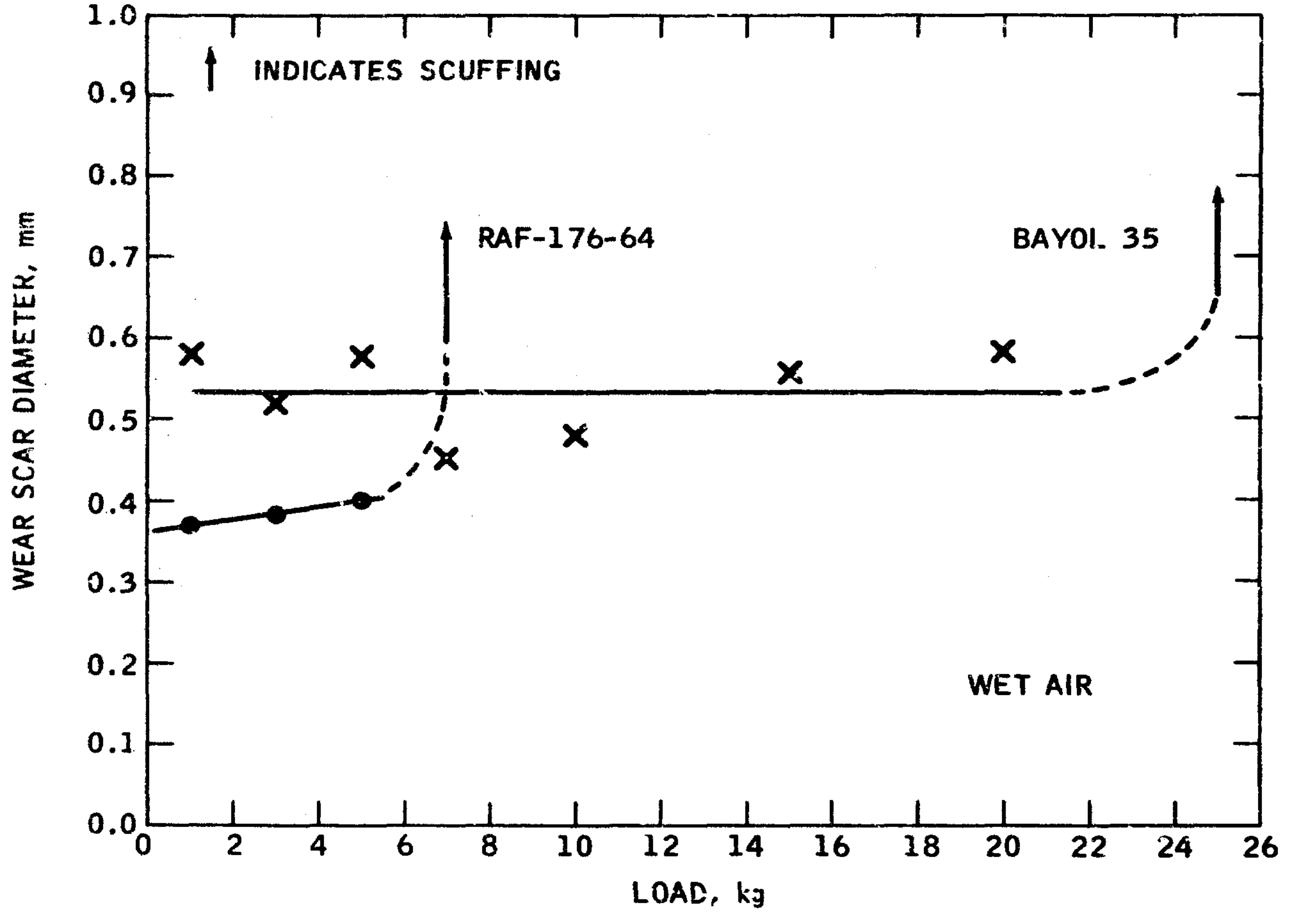


FIGURE 25 - FUEL TYPE AFFECTS WEAR AND SCUFFING (FOUR BALL TESTS - 1200RPM, 15MIN, 74F, R_c 25 STEEL)

C. Condensed-Ring Aromatics are Good Antiscuff, Antiwear Agents in Other Metallurgies

It had been previously reported that 1-methylnaphthalene scuffed easily in dry argon, and further that mixtures of 1-methylnaphthalene and paraffins had exceptionally good lubricity in all atmospheres. Data were presented for both 52100 steel and 440-C stainless steel. These findings have now been extended to other metallurgies, with substantially the same results (Table XXVIII).

In the table below are summarized data on SS-302, K-Monel and silver in dry argon.

Scuffing Behavior of Condensed-Ring Aromatics in Dry Argon

(Four-Ball Tests: 1200rpm, 15min, 77F)

	SS-302 (1 kg)	K-Monel (3kg)	Silver (1 kg)
Bayol 35	Scuff	Scuff	Scuff
30% 1-Methylnaphthalene in Bayol 35	0.25	0.48	0.78
1-Methylnaphthalene	0.82	Scuff	Scuff

In each metallurgy, the performance of the paraffin/aromatic blend was superior to either component alone. Although the reason for this superiority has still not been discovered, it appears to be a property of the liquid and not a specific reaction between the hydrocarbon and a single metal type. The effect is particularly striking in the case of silver, for silver scuffs in all atmospheres, as seen in Table XVIII. The runs with the paraffin/aromatic blend, although giving somewhat high wear, were quiet and the friction traces were smooth.

Some differences among metallurgies were found in their behavior with aromatics and paraffins as can also be seen in Table XXVIII. In wet air, K-Monel scuffs with methylnaphthalene, but not with Bayol 35. The reverse is true for 302 stainless, which scuffs with Bayol 35 but not with methylnaphthalene. Other anomalies can also be found. However, the most important observation is that in every case the 30% blend of methylnaphthalene in Bayol 35 gives no scuffing.

Some higher temperature tests on K-Monel were carried out with aromatic/paraffinic hydrocarbon blends. These results are shown in Table XXIX. In argon (wet and dry) both base fuels scuffed even at a low load of 1 kg. Apparently, the higher temperature offsets the effect of water in preventing scuffing in wet argon. In air, scuffing did not occur and the wear was not too great. Oxidation of the fuel probably accounts for the reduced wear at the higher temperature. Both 1-methylnaphthalene and indene are very effective as antiscuff agents. This is in agreement with data at 77F. Table XXIX also shows that indene exhibits high antiwear activity in dry air.

TABLE XXVIII

SCUFFING OF VARIOUS METALLURGIES WITH PARAFFIN/AROMATIC BLENDS

(Four-Ball Tests: 1200rpm, 15min, 77F)

% 1-Methyl Naphthalene in Bayol 35	Wear Scar Diameter, mm													
	Dry Argon				Wet Argon			Dry Air			Wet Air			
	K-Monel (3kg)	Soft 52100 Steel (1 kg)	SS-302 (1 kg)	Silver (1 kg)	Soft 52100 Steel (1 kg)	SS-302 (1 kg)	Silver (1 kg)	Soft 52100 Steel (1 kg)	SS-302 (1 kg)	Silver (1 kg)	K-Monel (3kg)	Soft 52100 Steel (1 kg)	SS-302 (1 kg)	Silver (1 kg)
0	Scuff	0.20	Scuff	Scuff	0.32	0.27	Scuff	0.27	0.30	Scuff	0.58	0.58	Scuff	Scuff
5	Scuff	--	--	--	--	--	--	--	--	--	0.51	--	--	--
15	Scuff	--	--	--	--	--	--	--	--	--	0.63	--	--	--
30	0.44	0.30	0.25	0.78	0.35	0.26	0.87	0.26	0.27	0.65	0.53	0.37	0.30	0.70
100	Scuff	0.25	0.82	Scuff	0.27	--	Scuff	0.24	--	Scuff	Scuff	0.40	0.24	Scuff

TABLE XXIX

EFFECT OF BASE FUEL AND CONDENSED RING AROMATICS AT 160F ON K-MONEL

(4-Ball Tests, 1200rpm, 15min, 1 kg)

Fuel	Wear Scar Diameter, mm			
	Dry Argon	Wet Argon	Dry Air	Wet Air
Bayol 35	*	*	0.38	0.34
RAF-176-64	*	*	0.39	-
5% 1-methylnaphthalene in Bayol 35	*	0.33	0.42	-
30% 1-methylnaphthalene in Bayol 35	0.31	0.35	0.32	-
30% Indene in Bayol 35	0.48	0.40	0.29	-

* Scuffed

D. Additives are Not as Effective, and Sometimes are Pro-Scuff Agents

In general, it was found that lubricity additives, which were very effective for steel-on-steel, varied in their effectiveness with other metallurgies such as K-Monel and silver.

1. K-Monel

The effect of several lubricity additives on K-Monel are shown in Table XXX. The most striking feature is that oleic acid is not an antiscuff additive, but in fact increases scuffing. This is summarized below:

	Scuff Load, kg	
Additive in Bayol 35:	None	0.1% Oleic Acid
Dry Argon	<1	<1
Wet Argon	5	<1
Dry Air	3	3
Wet Air	>5	1

This effect is similar to the comparison of Bayol 35 and RAF-176-64. The presence of polar additives apparently interferes with the antiscuff action of oxygen and moisture. Other acids, such as stearic and elaidic, show the same effect, as noted in Table XXX.

The phosphate additives, tricresyl phosphate and n-butyl acid phosphate, show a similar effect. Although TCP shows some antiscuff behavior in dry argon, and both additives show some antiwear activity in wet air, they cause scuffing in wet argon and wet air.

The lubricity additives ER-1 and ER-3 are somewhat better. They do not show any pro-scuff tendency, and they have some antiscuff properties in certain cases. At a higher temperature, 160F, ER-3 is clearly superior to ER-1 as shown in Table XXXI. It prevents scuffing in all atmospheres even at 50ppm, whereas ER-1 allows scuffing in dry argon and wet argon at 1000ppm. Again, note from the table that oleic acid is a pro-scuff agent in wet air.

The ability of several additives to reduce corrosive wear with K-Monel is shown in the table below. For this, the ball-on-cylinder apparatus was used.

(See table following page)

TABLE XXX

EFFECT OF LUBRICITY ADDITIVES ON K-MONEL

(4-Ball Test, 1200rpm, 15min, 77F)

	-----	-----	-----	-----	-----Wear Scar Diameter, mm-----	-----	-----	-----	-----	-----	-----
	Dry Argon		Wet Argon			Dry Air			Wet Air		
Load, kg:	1	3	1	3	5	1	3	5	1	3	5
Wt.% Additive In Bayol 35											
None	*	*	0.48	0.54	*	0.40	*	-	0.51	0.58	0.57
0.1 Oleic Acid	*	*	*	-	-	0.60	*	-	0.55	*	-
0.1 Stearic Acid	*	-	*	-	-	-	-	-	0.52,*	-	-
0.1 Elaidic Acid	*	-	*	-	-	-	-	-	*	-	-
0.1 n-Butyl Acid phosphate	-	-	-	-	-	0.30	*	-	0.30	*,*	-
0.1 TCP	0.35	*	0.45	*	-	0.62	*	-	0.43	0.55	*
0.1 ER-1	-	*	0.36	0.37	*	0.35	0.41	*	-	0.54	-
0.1 ER-3	0.36	0.43	0.42	0.48	*	0.45	0.50	*	0.50	0.60	-
0.1 ER-4	-	*	-	-	-	-	-	-	-	0.53	-

* Scuffing - high friction and noise.

TABLE XXXI

EFFECT OF LUBRICITY ADDITIVES AT 160F ON K-MONEL

(4-Ball Tests, 1200rpm, 15min, 1 kg)

Wt.% Additive In Bayol 35 (ppm)	Wear Scar Diameter, mm			
	Dry Argon	Wet Argon	Dry Air	Wet Air
None	*	*	0.38	0.34
0.1 ER-3 (1000)	0.53	0.43	0.43	0.38
0.005 ER-3 (50)	0.30	0.46	0.34	-
0.1 ER-1 (1000)	*	*	0.36	0.33
0.1 Oleic Acid (1000)	*	*	0.67	*

* Scuffing

Effect of Additives on K-Monel

(Ball-on-Cylinder: 240rpm, 32min,
77F, 240g, wet air)

% Additive in Bayol 35	WSD, mm	CoFr
None	0.52	0.24
0.1 ER-3	0.18	0.08
0.1 Oleic Acid	0.38	0.12
0.1 TCP	0.28	0.13
0.1 ZnDDP	0.31	0.12
0.1 n-Butyl Acid Phosphate	0.37	0.10
30% 1-Methylnaphthalene	0.25	0.12

As found in the four-ball tester, ER-3 is the most effective additive, but the other additives also show antiwear activity.

2. Silver

Several additives were tested to determine their effectiveness as anti-scuff agents on silver. Table XXXII shows the results obtained with the four-ball tester. ER-3 was the best of the four tested -- it eliminated scuffing in all four atmospheres. Oleic acid was an antiscuff additive in both wet and dry air. This is just the opposite to its behavior with K-Monel, where it was a pro-scuff additive. Apparently, silver is so inert that it does not react significantly with oxygen or moisture, and so the oleic acid does not have a competing reaction. Under these conditions, it is quite effective.

Referring again to Table XXXII, ZnDDP was effective as an antiscuff agent in three out of the four atmospheres -- it was ineffective in dry argon. Its effectiveness probably lies in the fact that it contains sulfur which can form silver sulfide as the antiscuff agent.

Three of these additives were also tested on the ball-on-cylinder machine using silver-on-silver. Table XXXIII shows that all were effective in preventing high friction, chatter, and excessive wear. Oleic acid was the most effective as indicated by the size of the wear scar and friction coefficient. This is also shown in a plot of friction vs. time (Fig. 26). Oleic acid immediately reduces friction and maintains it at a low level. On the other hand, TCP and ZnDDP show a gradual rise in friction with time. These results agree with previous steel data: in wet air oleic acid is more effective than ZnDDP or TCP. More importantly, these data show that organic acids are rather effective additives even on an unreactive metal like silver.

The work on metallurgy effects has added to the idea that corrosive wear is a major wear process. Unlike static corrosion, it cannot be prevented by using so-called corrosion resistant metals, but it can be controlled by using surface active agents in the lubricant.

TABLE XXXII

EFFECT OF ADDITIVES AS ANTISCUFF AGENTS ON SILVER

(4-Ball Test, 1200rpm, 15min, 77F, 1 kg)

% Additive In Beycl 35	Wear Scar Diameter, mm			
	Dry Argon	Wet Argon	Dry Air	Wet Air
None	*	*	*	*
0.1 ER-3	0.73	0.70	0.93	0.95
0.1 Oleic Acid	*	*	1.17	0.93
0.1 ZnDDP	*	1.30	0.80	0.73
0.1 TCP	*	*	0.85	0.67

* Scuffing

TABLE XXXIII

EFFECT OF ADDITIVES WITH SILVER-ON-SILVER

(Ball-on-Cylinder: 240rpm, 32min, 77F, 60g, wet air)

% Additive in Bayol 35	WSD (mm)	CoFr
None	1.32*	*
0.1% Oleic Acid	0.28	0.097
0.1% ZnDDP	0.65	0.46
0.1% TCP	0.75	0.46

* Test discontinued at 20min due to high friction and chatter.

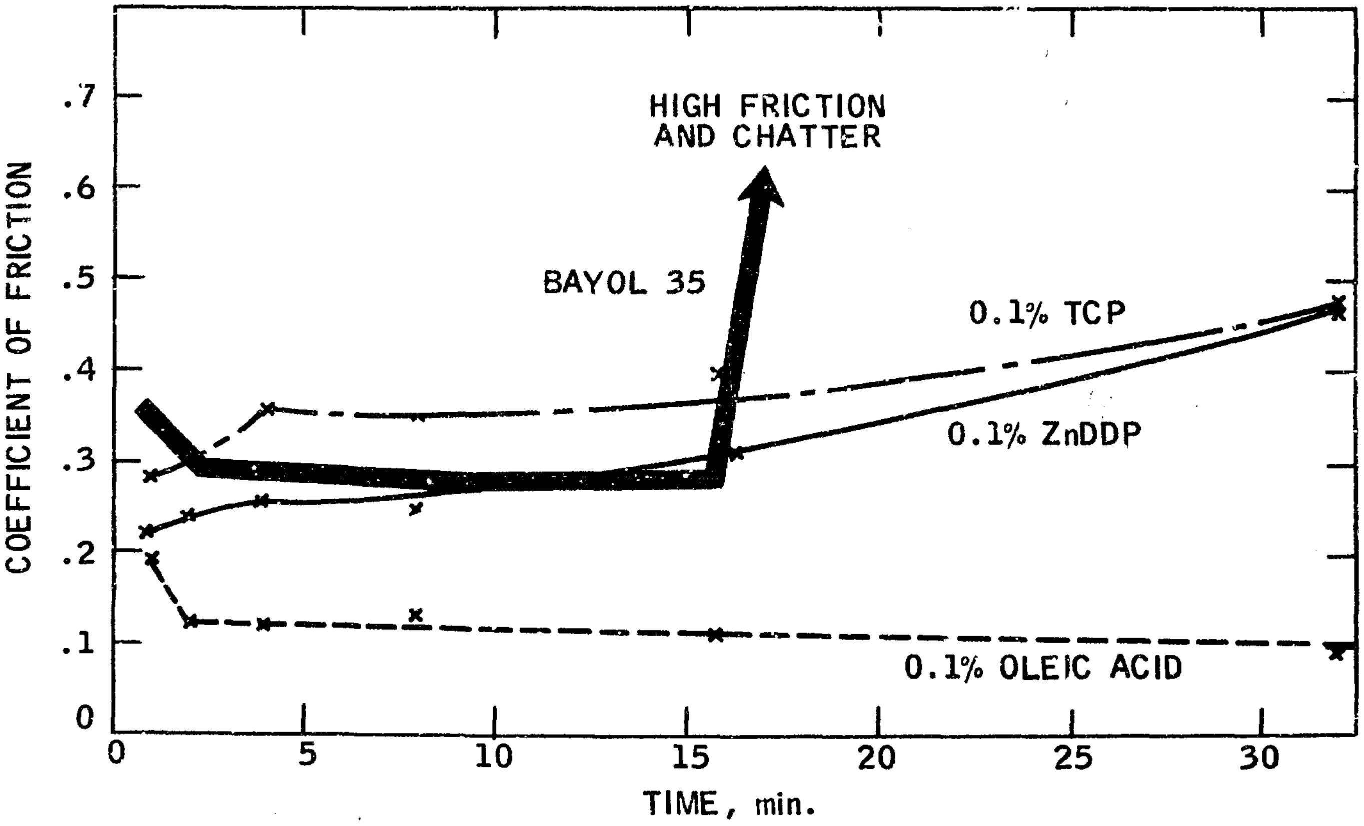


FIGURE 26 - EFFECT OF ADDITIVES ON FRICTION OF SILVER-ON-SILVER (BALL-ON-CYLINDER: 240RPM, 60G, WET AIR, 77F)

V. ABRASIVE WEAR

A third important mode of wear is by abrasion. This can be of two kinds: (1) If the surfaces are rough, the asperities of one surface can plow or scratch the other surface, (2) If hard particles (dirt or wear debris) are suspended in the liquid, they can become entrapped between the rubbing surfaces and cause scratching. This latter kind is of most interest here. It is particularly critical if the surfaces are case-hardened, for then the initial wear will result in very hard wear particles.

A short program was carried out in the Vickers vane pump to learn more about abrasive wear with jet fuels. From this work, the following conclusions can be drawn:

- There is considerable evidence that corrosive wear triggers abrasive wear.
- The increase in wear with increasing load appears to be largely due to an increase in abrasive wear.
- The amount of abrasive wear is not linearly dependent on the amount of wear particles present, but requires a certain minimum amount before wear becomes serious.
- Abrasive wear is not correlated with Moh hardness, crystal structure or particle size of several metal oxides.
- Abrasive wear can be controlled by additives.

A. Abrasive Wear Is Caused By Corrosive Wear

Abrasive wear and corrosive wear occur by two entirely different mechanisms. In corrosive wear, the iron is first oxidized and then rubbed off; the resulting debris is either an iron oxide or iron hydroxide. In abrasive wear, the steel surfaces are mechanically attrited, and the resulting debris is largely iron. If it is postulated that the ratio of abrasive wear to corrosive wear is the ratio of unoxidized iron to oxidized iron, then a chemical analysis of the wear debris is an exact indication of the kind of wear occurring.

Accordingly, two Vickers vane pump tests were run under identical conditions (90F and 150psig), one in dry air and one in wet air. The wear particles were so fine that they could pass through the 20 μ filter in the circulating system. The fuel after tests was filtered through a 5 μ Millipore filter, washed with hexane, and dried. Microscopic examinations were made on these samples before and after filtration.

The results with optical microscopic examination is briefly summarized as follows: Some particles are black and do not transmit light. Others are semi-transparent and of an orange to brownish color, indicating the presence of Fe_2O_3 and/or $Fe(OH)_3$. These appear to be aggregates of small particles. Some agglomerates are combinations of black and brown particles. The opaqueness of the particles makes it difficult to determine, with any certainty, if crystallinity exists. A sample was examined by X-ray diffraction. Only α-Fe could be definitely identified. The particles vary in size from an occasional large one, about 30 μ in its longest dimension, to ones as small as 2 μ. Even the smallest appear to be agglomerates. The particle size that accounts for the bulk of the material is estimated in the 10-15 μ range.

Electron microscopic examinations were also made on both the Bayol 35 before and after pump tests and the filtrate from the Millipore filter. The micrographs are shown in Figs. 27-29. The filtrate, although appearing clean by visual observation, still contained a considerable amount of very fine particles of <2 μ size.

Chemical analyses were made on these wear debris. The iron of various valence states was analyzed by an unpublished procedure developed at Esso Research. The oxygen was analyzed by neutron activation. The carbon and hydrogen analyses were by the IKA Microcombustion method. The results are shown in Table XXXIV. The composition of oxides, as shown in Table XXXV was estimated by solving three simultaneous equations which were formulated by the Fe^{+3}, Fe^{+2} and O_2 balances and assuming the iron hydroxide to be either $Fe(OH)3$ or $Fe(OH)_2$. The computed % H agrees well with the analytical results. The Fe-distribution in wear debris, assuming it contains $Fe(OH)_3$, is summarized below:

	In Wet Air		In Dry Air	
	% By Weight	% Distribution	% By Weight	% Distribution
Fe	59.1	65.0	71.1	77.1
FeO	11.6	12.7	10.0	10.9
Fe_2O_3	7.6	8.4	6.9	7.5
$Fe(OH)_3$	12.6	13.9	4.1	4.5
	90.9	100.0	92.1	100.0

It will be seen that oxidation is greater in wet air than in dry air. About 30% of the wear debris was in oxides in wet air, and only 20% in dry air. In particular, the amount of iron hydroxide is greater. It is also noteworthy that the majority of the wear is an unoxidized iron, the ratio of iron to iron oxides being 2-3 to 1, indicating the importance of abrasive wear when iron oxide particles are present. This abrasive wear is clearly triggered by corrosive wear, since it does not occur under an inert blanket.

The effect of temperature is also unequivocal. When tests were run at 240F or 300F in dry nitrogen, very little wear occurred, as already seen in Table XXII. The absence of oxygen and water precluded corrosive wear and this precluded abrasive

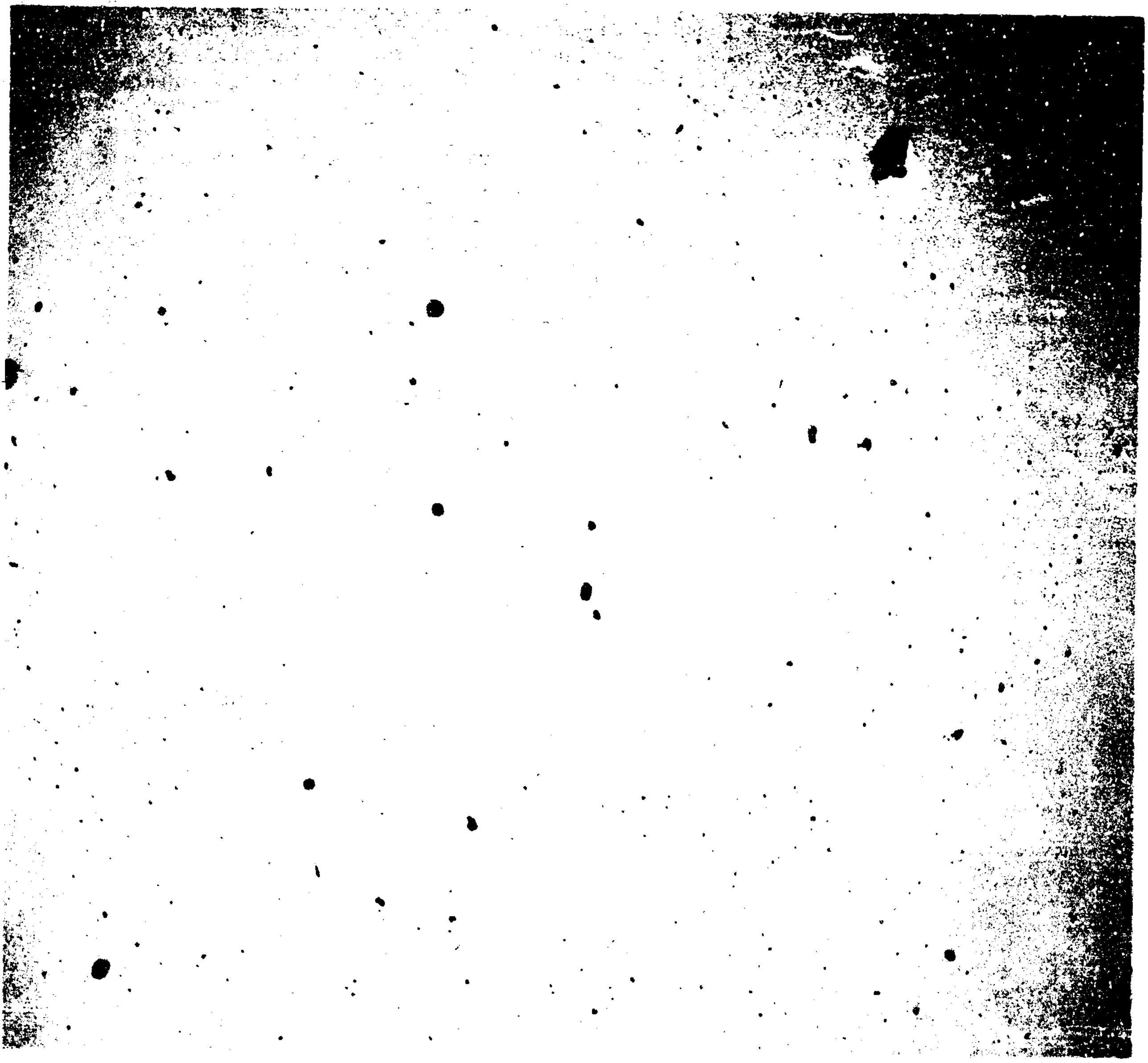


FIGURE 27 - ELECTRON MICROGRAPH OF BAYOL 35--7000X

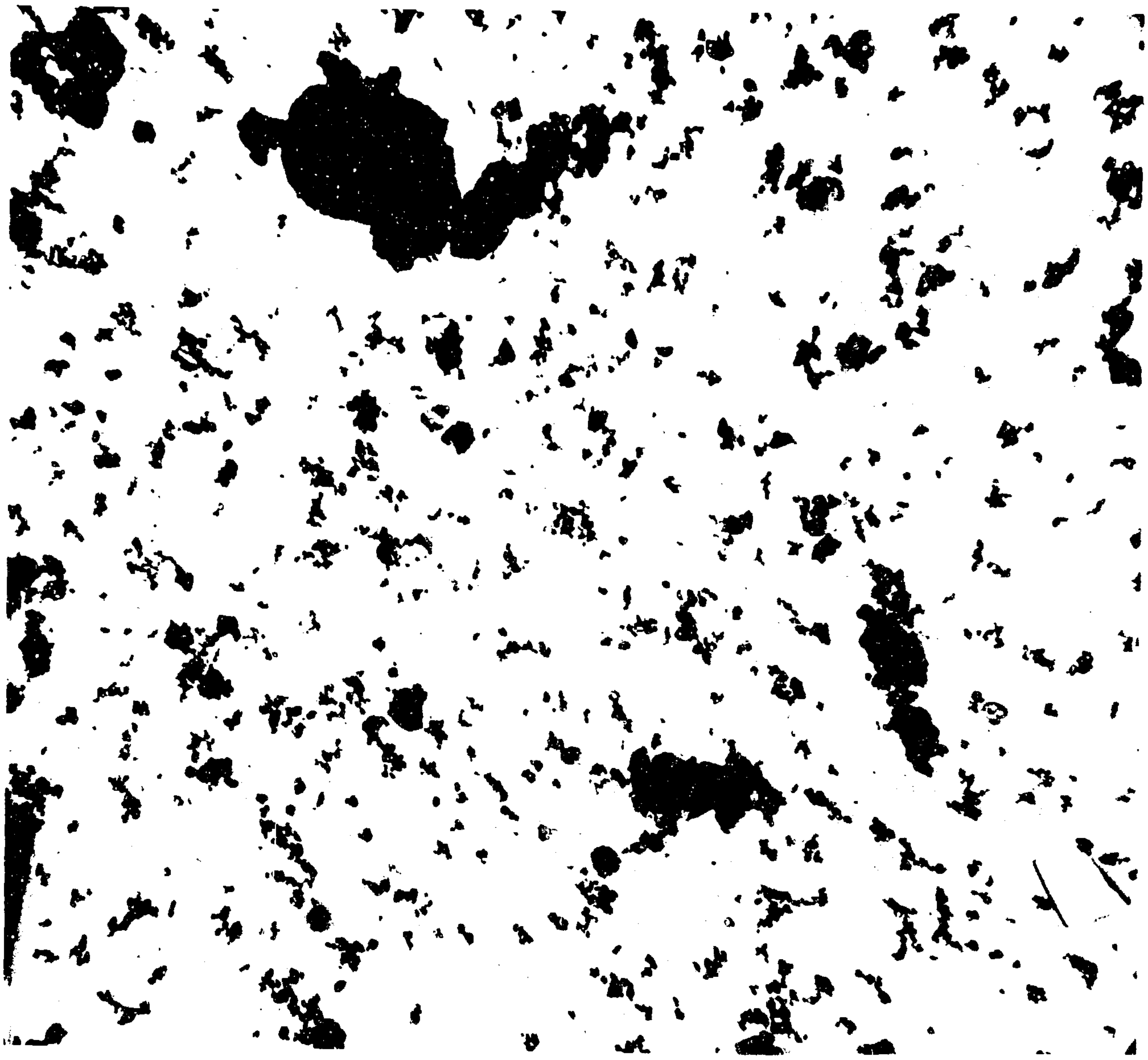


FIGURE 28 - ELECTRON MICROGRAPH OF BAYOL 35 AFTER A PUMP TEST AT 350 PSIG IN WET AIR--7000X

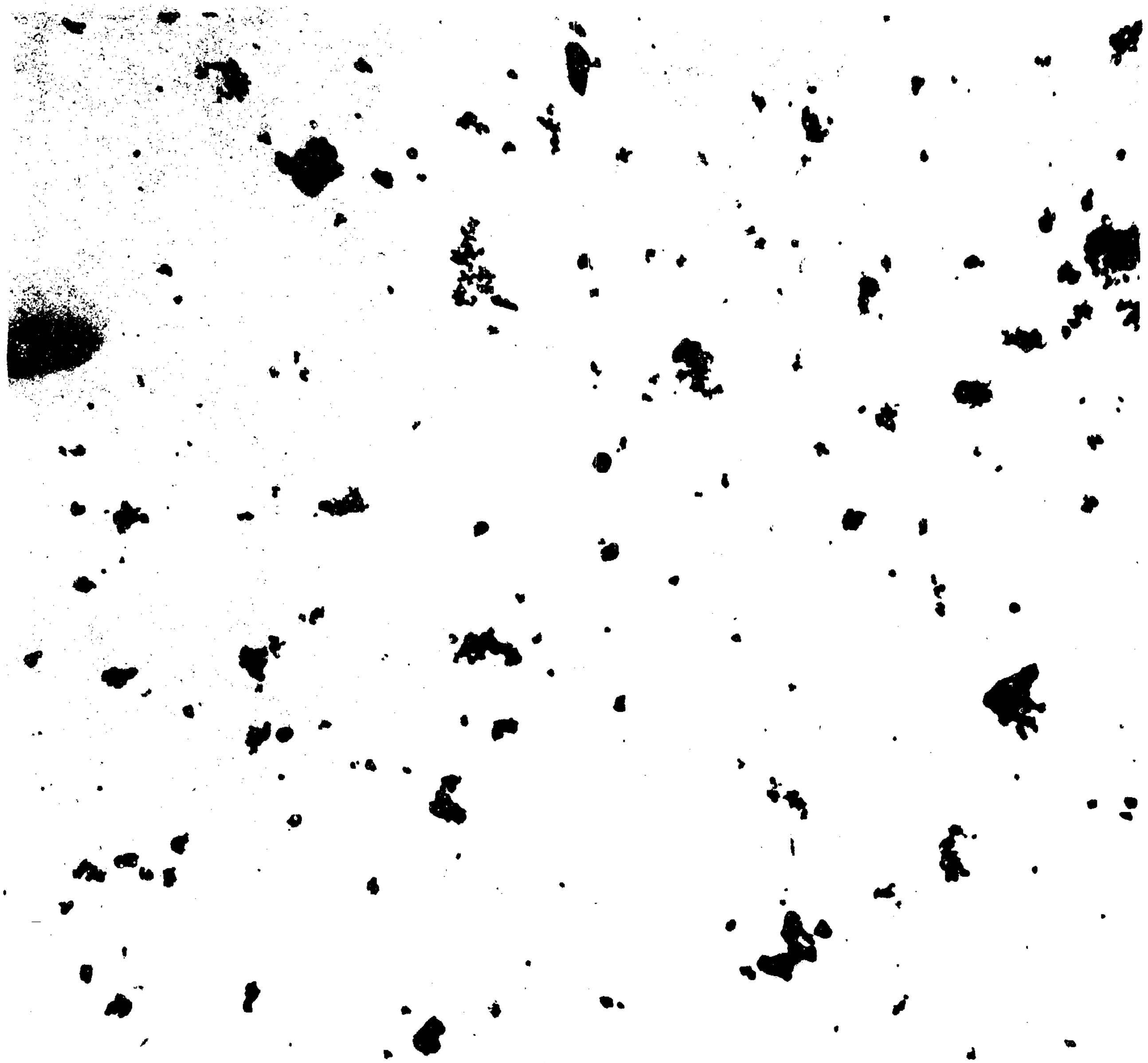


FIGURE 29 - MICROGRAPH OF FILTRATE FROM 5 μ MILLIPORE FILTER FOR BAYOL 35 AFTER PUMP TEST--7000X

TABLE XXXIV

ANALYSES OF WEAR DEBRIS FROM PUMP TESTS

Analyzed Items	Sample From a Pump Test at 350 psig, 90F in Wet Air		Sample From a Pump Test at 350 psig, 90F in Dry Air	
Fe^0	59.1	80.0	71.0	85.9
Fe^{+2}	9.0		7.8	
Fe^{+3}	11.9		7.1	
Total Fe (By Analysis)	80.4		84.8	
Oxygen	10.5		6.1	
C	7.0		7.0	
H	0.2		0.1	

TABLE XXXV

ESTIMATED COMPOSITION OF IRON OXIDE IN WEAR DEBRIS

		Percent			
In Wet Air	Percent	Fe^{+2}	Fe^{+3}	O	H
1. Assumed to Contain $Fe(OH)_3$:					
FeO	11.6	9.0	--	2.6	--
Fe_2O_3	7.6	--	5.3	2.3	--
$Fe(OH)_3$	12.6	--	6.6	5.7	0.3
	32.0	9.0	11.9	10.6	0.3
2. Assumed to Contain $Fe(OH)_2$:					
FeO	0	--	--	--	--
Fe_2O_3	17	--	11.9	5.1	--
$Fe(OH)_2$	15.2	9.4	--	4.6	0.3
	32.2	9.4	11.9	9.7	0.3
In Dry Air					
1. Assumed to Contain $Fe(OH)_3$:					
FeO	10	7.8	--	2.2	--
Fe_2O_3	6.9	--	4.9	2.0	--
$Fe(OH)_3$	4.1	--	2.1	1.9	0.1
	21.0	7.8	7.0	6.1	0.1
2. Assumed to Contain $Fe(OH)_2$:					
FeO	6.5	5.0	--	1.5	--
Fe_2O_3	10.1	--	7.0	3.1	--
$Fe(OH)_2$	4.6	2.9	--	1.6	0.1
	21.2	7.9	7.0	6.1	0.1

wear. When run in wet air at 240F, there was such noise and obvious distress in the pump that the test was stopped after four hours. The higher temperature had accelerated the corrosive wear. At a still higher temperature, 300F, serious oxidation of the fuel occurred. The oxidation products acted to inhibit corrosive wear and thus prevented abrasive wear as well.

B. Abrasive Wear Increases With Load

To assess the effect of load, two pump tests were run at two different outlet pressures, 250 and 350psig. The wear debris was analyzed for Fe°, Fe^{++}, and Fe^{+++}, as well as for O, C, and H. From this and the total weight loss, the amount of abrasive wear can be calculated. Table XXXVI presents the data. Raising the load from 250psig to 350psig increased wear from 3.2g to 6.1g. All of this increase was due to abrasive wear, the corresponding values being 2.2 and 4.9g. The amount of corrosive wear was almost exactly the same in the two cases: 1.47 and 1.43g as iron oxides.

This conclusion is entirely logical. It means that corrosion occurs irrespective of load, but that abrasion is load-dependent.

C. Abrasive Wear Does Not Occur Until the Amount of Wear Debris Passes A Threshold Value

It is obvious that abrasive wear will not occur unless corrosive wear precedes it, for in the absence of oxygen no pump wear occurs at all. This makes it possible to test the abrasiveness of wear particles, uncomplicated by corrosive wear. Accordingly, the effect of particle concentration was evaluated in a series of tests on Bayol 35 in a nitrogen atmosphere. New Bayol 35 was mixed with varying amounts of Bayol 35 from an earlier test run in air at 250psig. The amount of wear debris was 0, 25%, 50% and 100% (100% equals 1.6mg debris per gram of fuel). The 100% test (no dilution with fresh fuel) was run by first running in air at 200psig and then in nitrogen using a new pump cartridge.

The data are given in Table XXXVII. As expected, the fuels containing large amounts of wear debris gave very severe wear: 13.3g for the fuel containing all the wear debris from the preceding test, 11.7g for the fuel containing 50% of the debris. Surprisingly, however, the fuel with 25% of the debris showed almost no wear at all. Thus, abrasive wear is not a linear function of the amount of wear particles, but is in the form of Fig. 30.

Analysis of the wear debris from the high wear tests shows that very little of it is iron oxide, thereby confirming that this is pure abrasive wear. Table XXXVIII shows that the run containing 50% added wear debris started with 736mg iron oxide in the fuel and finished with 553mg. The entire 11,775mg wear was thus unoxidized iron.

D. Abrasive Characteristics of Iron Oxides Are Not Correlated with Hardness, Crystal Structure or Particle Size

Several different iron oxides and other metal oxides were obtained and tested for abrasive wear in the Vickers pump. They were added to Bayol 35 at 100ppm, which should be enough to cause abrasive wear, based on earlier tests. The results are given in Table XXXIX. Both of the ferric oxides, α-Fe_2O_3 and γ-Fe_2O_3, gave severe wear, the weight loss being about 8 grams. Alundum (α-Al_2O_3) gave about 0.25g. The other three oxides--Fe_3O_4, FeO(OH) and Cu_2O--gave less than 50mg wear. FeO(OH) did give severe wear when the amount was increased to 320ppm, as

TABLE XXXVI

EFFECT OF LOAD ON ABRASIVE WEAR

(Vickers Vane Pump Tests - 90F, Room Air)

Pump Pressure, psig	250		350	
Ring Wear, mg	3122		5951	
Vane Wear, mg	125		171	
Total Wear, mg	3247		6122	
Analyses of Wear Debris, wt%				
Fe°	53.9		71.8	
Fe^{+2}	11.7	36.3	7.5	21.0
Fe^{+3}	11.3		6.8	
Oxygen	13.3		6.7	
C	5.4		7.6	
H	0.4		0.6	
Estimated Wear Debris*, mg	4055		6810	
Fe° in Wear Debris, mg	2190		4890	
Fe - Oxides in Wear Debris	1473		1430	

$$* = \frac{\text{(Total pump wear) (\% Fe in steel)}}{\text{\% Total Fe in Wear Debris}}$$

TABLE XXXVII

EFFECT OF WEAR DEBRIS ON ABRASIVE WEAR

(Vickers Vane Pump Tests, 350psig, 90F, in nitrogen)

Base Fuel: Bayol 35

% of Wear Debris*	None	25%	50%	100%
Wear, mg				
Vane	3	11**	1681	1551
Ring	0	61**	10094	11768
Surface Finish, μ-inch				
Vane, Initial	20	6	6	8
Final	38	7	137	85
Ring, Initial	13	10	33	7
Final	8	33	128	70
Chemical Analyses of Wear Debris, %				
Fe°	--	59.2	87.0	86.4
Fe+2	--	6.6	0.7	0.4
Fe+3	--	13.8	1.1	1.3
Oxygen	--	6.4	6.1	6.2
C	--	0.6	0.3	0.2
H	--	12.2	2.2	1.9

* Wear debris obtained from previous test at 350psig in air. 100% equals 0.16% by weight in the fuel.

** Averages of two runs.

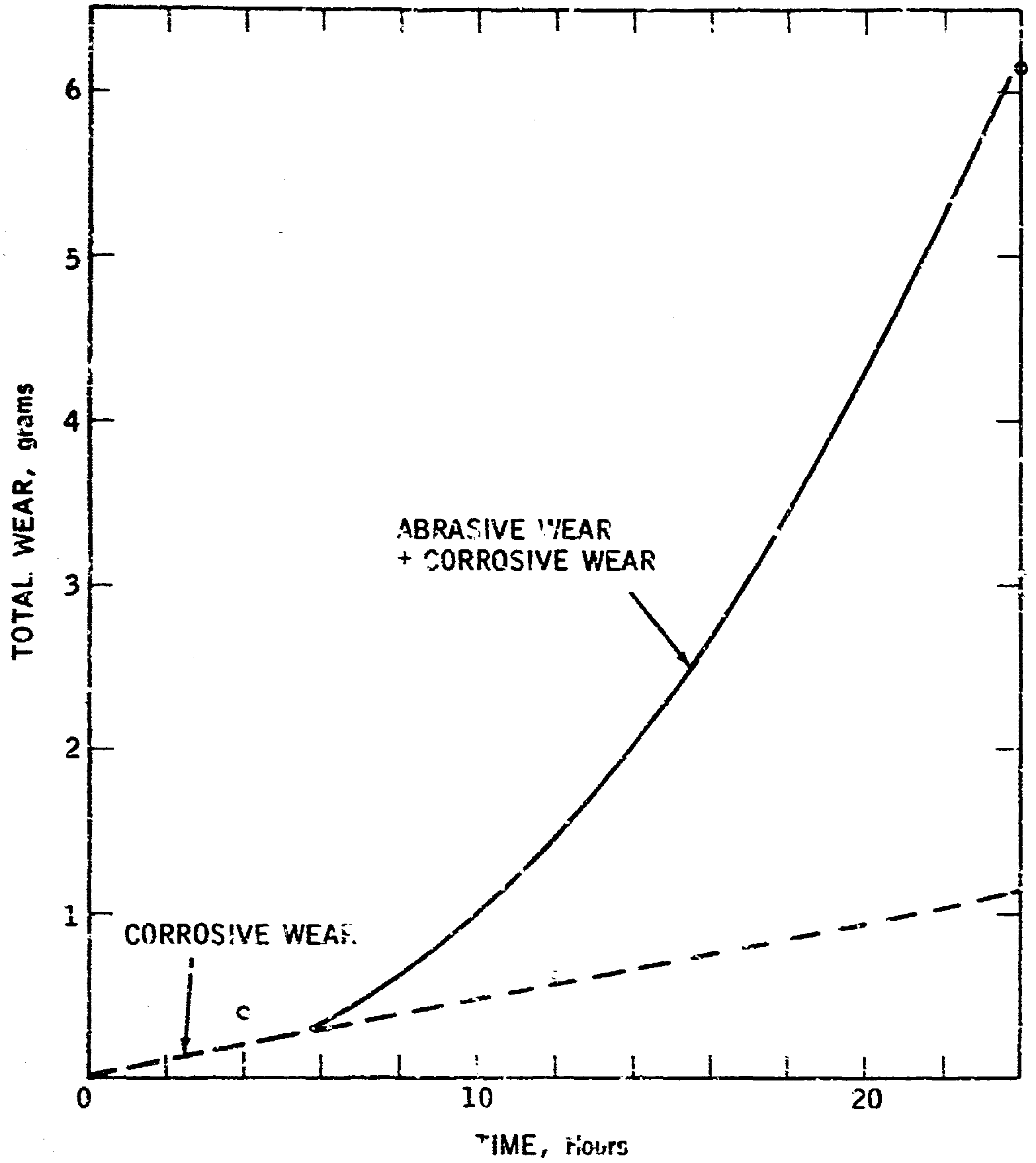

TOTAL WEAR, grams
6
5
4
3
2
1
0
10
20
TIME, Hours
ABRASIVE WEAR
+ CORROSIVE WEAR
CORROSIVE WEAR

TABLE XXXVIII

MATERIAL BALANCES OF ABRASIVE WEAR DUE TO WEAR DEBRIS

	25% Wear Debris	50% Wear Debris
Wear Debris		
Weight, mg	974	13803
% Fe°	59.2	87.0
% Fe Oxides*	32.6	4.0
Fe°, mg	577	12000
Fe Oxides, mg	317	553
Fe° Balance, mg		
From Added Wear Debris	546	1090
From Pump Wear**	72	11775
Total Fe°	628	12865
Fe Oxides Balance, mg		
From Added Wear Debris	368	736

* Summation of % Fe^{+2}, % Fe^{+3} and oxygen.

** If assumed all wear is abrasive; i.e. all Fe°.

TABLE XXXIX

ABRASIVE WEAR BY VARIOUS METALLIC OXIDES*

(Vickers Vane Pump Tests, 350psig, 90F, Nitrogen)

Base Fuel: Baycl 3%
Concentration: 100ppm

	None	α-Fe_2O_3	γ-Fe_2O_3	$FeO(OH)$	α-Al_2O_3	Cu_2O	Fe_3O_4**
Wear, mg							
Vanes	3	942	759	5	114	7	19
Ring	0	7027	7102	27	136	44	6
Surface Finish, μ-inch							
Vanes, Initial	20	6	8	8	13	10	--
	38	139	84	10	74	7	--
Ring, Final	13	8	12	31	11	8	--
	8	59	31	23	76	20	--
Moh Hardness	--	5.6	5.6	--	9	3.5-4	5-6
Crystal Structure	--	Rhombohedral	Cubic	Orhomb	Rhombohedral	Cubic	Spinel
Particle Size, micron (microscopic examination)	--	0.5-1.5	0.5-1	0.5-1	0.3-1	1-5	0.3-0.7

* Iron oxides supplied by courtesy of Columbia Carbon Company.

** 500ppm.

shown in Table XL, another indication that abrasive wear is concentration-dependent. However, Fe_3O_4 gave no wear, even at 1000ppm.

It was rather surprising that no correlation could be found between abrasiveness and other properties such as hardness, particle size or crystal structure. Aluminum oxide is easily the hardest, yet it was not as abrasive as ferric oxide. Its particle size, by microscopic examination, was only slightly smaller. These data are also given in Table XXXIX.

E. Oleic Acid Reduces Abrasive Wear

It has generally been assumed that additives such as oleic acid function as antiwear agents by chemisorbing on the surface, thus inhibiting corrosive wear and also decreasing adhesion. It was therefore quite unexpected to find that oleic acid could eliminate abrasive wear. A Vickers pump test was run on Bayol 35 containing 200ppm α-Fe_2O_3 and 500ppm oleic acid. Without oleic acid, only 100ppm α-Fe_2O_3 would cause severe abrasive wear, 7079mg. Adding oleic acid reduced the wear to 5mg (Table XLI).

To try to get some explanation for the effect of oleic acid the solids were filtered out of the fuels and examined under the electron microscope and by IR. No difference could be noted in the IR spectra. The electron micrographs of the oxide particles are shown in Figs. 31 and 32. Some differences can be seen. The fuel containing oleic acid showed more clumping of the solid particles and the individual oxide crystals seem less sharp. One can only speculate whether this has any significance.

To summarize the work on abrasive wear, it appears that not enough is known about why particles are abrasive, why there should be a threshold concentration, or why or how additives act to prevent abrasive wear. However, it was not within the scope of this contract to investigate abrasive wear more thoroughly.

TABLE XL

CONCENTRATION EFFECT ON ABRASIVE WEAR

(Vickers Vane Pump Tests, 350psig, 90F, Nitrogen)

Base Fuel: Bayol 35

	FeO(OH)		Fe_3O_4	
	100ppm	320ppm	500ppm	1000ppm
Wear, mg				
Vanes	5	1169	19	0
Ring	27	9378	6	0
Surface Finish, μ-inch				
Vanes, before test	8	6	--	--
after test	10	151	--	--
Ring, before test	31	12	--	--
after test	23	39	--	--

TABLE XLI

EFFECT OF ADDITIVE ON ABRASIVE WEAR

(Vickers Vane Pump Tests, 350psi, 90F, Nitrogen)

	Bayol 35	100ppm α-Fe_2O_3 in Bayol 35	200ppm α-Fe_2O_3 +500ppm Oleic Acid in Bayol 35
Wear, mg			
Vanes	3	942	1
Ring	0	7027	4
Surface Finish, μ-inch			
Vanes, before test	20	6	13
after test	38	139	16
Ring, before test	13	8	18
after test	8	59	14

FIGURE 31 - ELECTRONMICROGRAPH OF α-Fe_2O_3

FIGURE 32 - ELECTRONMICROGRAPH OF α-Fe_2O_3 AFTER A PUMP TEST WITH OLEIC ACID

VI. CONCLUSIONS

From this three-year study the following general facts have been learned:

Marked differences in the lubricity of jet fuels do indeed exist. Fuels available commercially can vary from good lubricity to lubricity as bad as that of a pure hydrocarbon. These differences are largely due to the chemical composition of the fuels and not to their physical characteristics such as viscosity or volatility. Although as a class the low-viscosity JP-4's are worse than the higher-viscosity JP-5's, it is entirely possible for one sample of JP-4 to have considerably better lubricity than that of a high-purity JP-5.

The two most important constituents in jet fuels leading to good lubricity are aromatic hydrocarbons and surface-active additives. The importance of aromatics (particularly condensed-ring aromatics) had not been appreciated before. Their removal in the refining process--to get low luminometer number and high thermal stability--appears to be the chief reason for lubricity problems in the field.

Surface-active additives are excellent lubricity agents. Organic acids are particularly effective, imparting lower friction and wear at concentrations as low as 5ppm. Corrosion inhibitors of the type normally used in jet fuels are good lubricity agents, but special lubricity additives are even better.

The other components of jet fuels are relatively unimportant. No differences were noted between paraffinic and naphthenic components (alicyclic and cyclic aliphatics). Olefins have some mild lubricity, but they are generally present in only minor amounts. Somewhat surprisingly, neither sulfur compounds nor nitrogen compounds have any effect, at least not in the concentrations normally found in jet fuels. Additives other than corrosion inhibitors were also relatively ineffective. These include the anti-icing agents, metal deactivators and antioxidants.

To study the lubricity of jet fuels in the laboratory, the apparatus must be capable of operating at very low loads. Higher loads causes scuffing, an entirely different kind of wear phenomenon, and one apparently not related to jet fuel problems in the field. The ball-on-cylinder device was the best all-around apparatus for this purpose. A good correlation was obtained between wear in this device and friction problems in the field.

The atmosphere surrounding the rubbing surfaces was found to be extremely important. Very low wear and friction could be obtained by blanketing the system with a dry inert gas. A vane pump, for example, could operate without wear and with good volumetric efficiency in dry nitrogen, under conditions where it would wear out in a few hours in ordinary air. It appears that inerting fuel tanks would be beneficial, not only for reducing thermal degradation of the fuel, but for better lubrication as well.

Scuffing is aggravated by an inert atmosphere. The presence of either oxygen or water greatly reduces this effect as do condensed-ring aromatics, but the effect of additives is frequently poor. The importance of water has usually been overlooked. It may be possible to exclude oxygen from a fuel system and still avoid any possibility of scuffing, by maintaining a certain amount of dissolved water in the fuel.

Wear and scuffing increase with temperature and certain additives may become less effective. This effect is often obscured by the oxidation of the fuel which results in the formation of good-lubricity oxidation products.

This research has also resulted in several findings that are important in the better understanding of the wear process. In particular, this work has shown the importance of corrosive (oxidative) wear as a major wear mechanism. The nature of scuffing and abrasion has also been clarified. The importance of condensed-ring aromatics in imparting lubricity not only applies to fuels, but is apparently the major difference between good-lubricity petroleum lubricants and poor-lubricity white oils. These findings have resulted in several papers submitted for publication.

VII. APPENDIX

EQUIPMENT AND TECHNIQUES

A. Test Equipment And Procedures

In this program three test devices were mainly 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. The Micro-Ryder test was also evaluated a possible lubricity tester for jet fuels. This device has been described in Section II above.

1. Ball-On-Cylinder Machine

This apparatus measures metallic content and friction and has been previously described (5, 6). The apparatus is shown in Figure 33. The system, consisting basically of a fixed metal ball loaded against a rotating cylinder, is 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."

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. In the case of scuffing, the wear on the cylinder is large and may easily be measured by means of a surface profile taken axially across the wear track.

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 misleading 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.

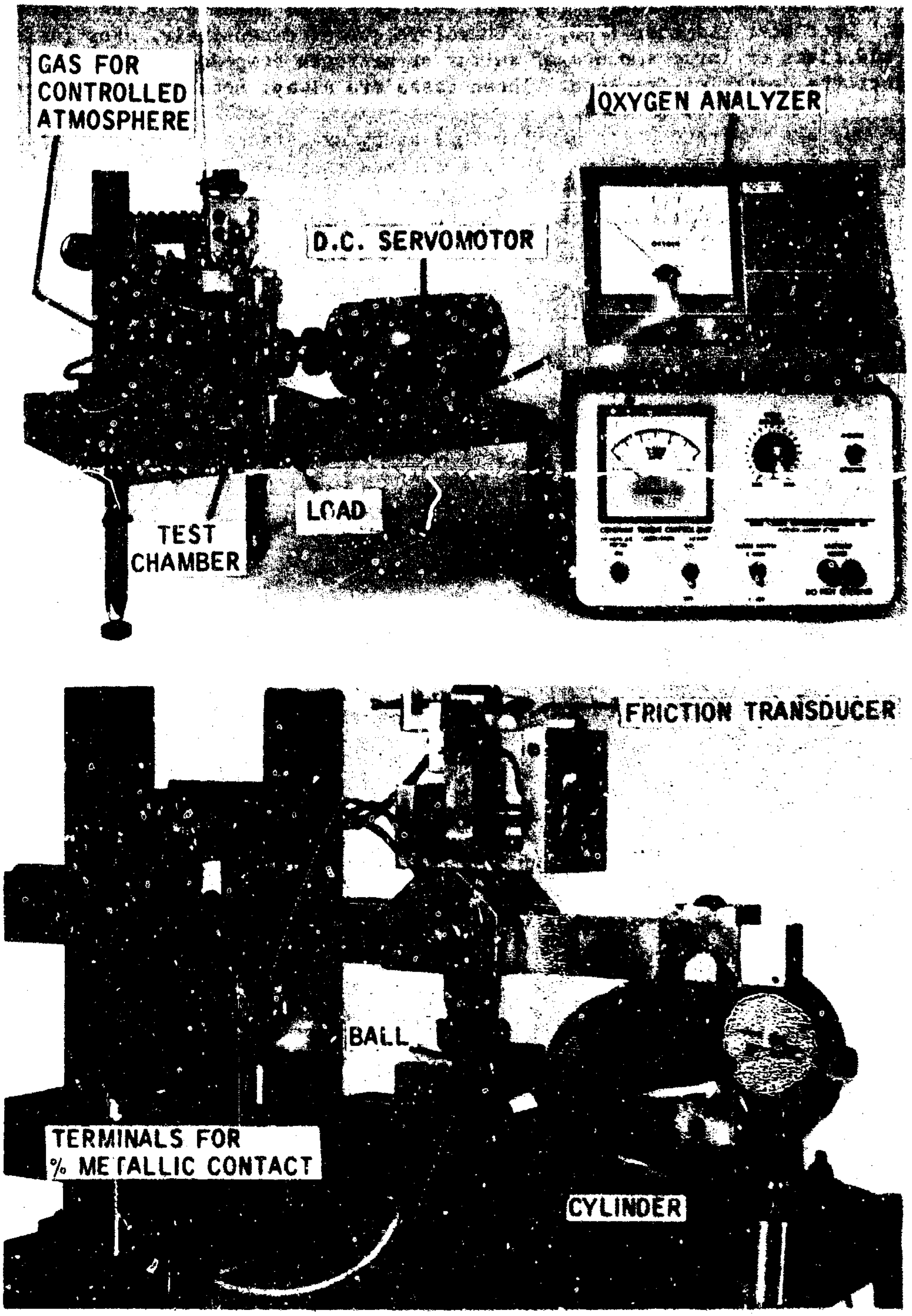


FIGURE 33 - PHOTOGRAPH OF BALL-ON-CYLINDER DEVICE

TOP - GENERAL VIEW
BOTTOM - CLOSEUP OF BALL-ON-CYLINDER

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.

Most of 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 20 Rockwell C.

For a portion of this work, several different metallurgies were employed. Half-inch balls were used and special cylinders were fabricated of the desired metallurgy. The balls were very smooth (CLA about 2 μ in) and the cylinders were polished to similar smoothness. Hardness values are shown below:

Metal	Rockwell Hardness, R_C Ball	Rockwell Hardness, R_C Cylinder
Stainless Steel 440C	60	-
K-Monel	30	32
Tungsten Carbide	70	-
Stainless Steel 302	31	-
Silver	98(R_B)	98(R_B)

In the case of silver, steel specimens were electrolytically plated to a thickness of 1/20 inch. After all tests, microscopic examination showed that the silver coating had not been broken-through.

In order to study the effect of dissolved oxygen and water on friction and wear, each of the test instruments was modified. The first modification to the ball-on-cylinder apparatus consisted of adding a fuel-circulating system, which also allowed the use of higher temperatures. The test fuel is heated in a reservoir while bubbling in a gas containing a certain percentage of oxygen. It flows by gravity into the fuel container which is enclosed and kept at the same atmosphere as that of the fuel reservoir. The temperature of fuels in the container is controlled by varying the heating of the reservoir with a Variac. The test fuel is pumped back to the reservoir through a glass bulb containing a sensor for oxygen analysis. The test is started when the oxygen in the fuel, as indicated in the oxygen analyzer, and the temperature reach a steady state.

Later it became [illegible] that the test fuel was equilibrating very rapidly with the gas environment. [illegible]5-minute soak period was found to be ample. Therefore the apparatus was simplified by designing a new test cup having a smaller fuel capacity, a built-in electrical heating element and thermocouple, and a gas inlet line to the bottom of the fuel sample. A cover fits over the cup and around the chuck holding the ball. A gas flow rate of 0.5 cu.ft./min effectively prevents any back diffusion.

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 4000 g, corresponding to mean Hertz pressures of 21,800 to 128,000 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.

For controlled atmospheres, the apparatus was fed with a continuous stream of gas of known oxygen content and humidity. Oxygen content was controlled by mixing metered amounts of air and an inert gas from compressed gas cylinders. The inert gas was either nitrogen or argon, generally argon because of a specified 99.995% purity. In a few cases, pure oxygen was also used.

For all compressed gas cylinders, the water content is exceedingly low -- 15-20 ppm, corresponding to a relative humidity of 0.1%. Some tests were conducted under bone-dry conditions. The method used to obtain bone-dry conditions is discussed in the text under "Bone-Dry Atmospheres" (Section III). For tests at 100% RH, the gas bubbled through water. In a few cases, a layer of water was inserted at the bottom of the cup containing the test fuel. Only the extremes of humidity were examined--0 or 100% RH. Intermediate humidities were examined only in the room-air runs.

2. Four-Ball Wear And Scuff Tester

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, time, and atmosphere.

The instruments used early in this investigation were the Normal Four-Ball Wear Tester (Scientific Precision Company, Chicago, Illinois, Catalog #73603) and the Shell Extreme Pressure Four-Ball Tester (Catalog #2008). These are discussed in the annual Technical Report, Part I of this study. The Normal four-ball wear tester was modified to include a plastic collar around the test specimens. Oxygen can be excluded by passing dry argon into the test zone. Dissolved oxygen was not purged but from the results it is apparent that most, if not all, of the oxygen is removed during the soak period preceding the test.

For the results presented in this report, a G.E.-Brown modification of the four-ball wear tester was used. In this unit, the load is applied by a pneumatic piston rather than mechanically. This machine has an enclosed space around the test specimens. In the machine as purchased, the gas is fed above the test liquid. This was modified to feed the gas to a point near the bottom of the test cup, thus getting a better and more rapid purging.

The new machine also needed modification of the loading arrangement. The load is transmitted from the pneumatic piston to the test balls through a shaft sliding in a sleeve. Considerable friction was found between the shaft and sleeve, with the result that the actual load could be as much as 2,000 g in error. The sticking was eliminated by enlarging the sleeve and inserting a rolling-element bushing between the sleeve and shaft. This reduces the error to less than 50 g.

Only the general procedures can be mentioned here as the details of each specific test series are discussed in the text with the results. The general technique was to place the balls in contact and set the desired loading. The system was then purged with the desired atmosphere for about 15 minutes (previously found to be ample time). The test was then started at the pre-set desired speed (for most of the work, 1200 rpm top ball speed). Unless otherwise stated, test time was 15 minutes. Previously it had been shown (see annual Technical Report, Part I, p. 24, of this study) that 15 minutes was well into the so-called normal wear rate region (7), so that meaningful comparisons could be made.

3. Vickers Vane Pump

A photograph of the Vickers Vane Pump system is shown in Figure 34. 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 pgm 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 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 driven 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 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.

To investigate jet fuel lubricity at higher temperatures and under controlled atmospheres, a new pump test stand (Mark II) was built. The entire system has an enclosure which is constantly exhausted during the test. The fuel flow is basically the same as that of the other unit used for previous tests. Major modifications include: (1) reducing the sump to two gallons capacity, (2) automatic recording of the pressure and flow rate, (3) provision for controlling atmospheric environment in the sump, (4) adding a bypass for a high-pressure millipore filter to check the pump wear at any time, (5) adding a fuel-sampling system controlled by a timer, and (6) various safety features, such as overheating shutoff, low-fuel-level shutoff, and automatic extinguishing system in case of fire. The system was designed to be operable at sump temperature of 300F and a pump discharge pressure of 3000 psig.

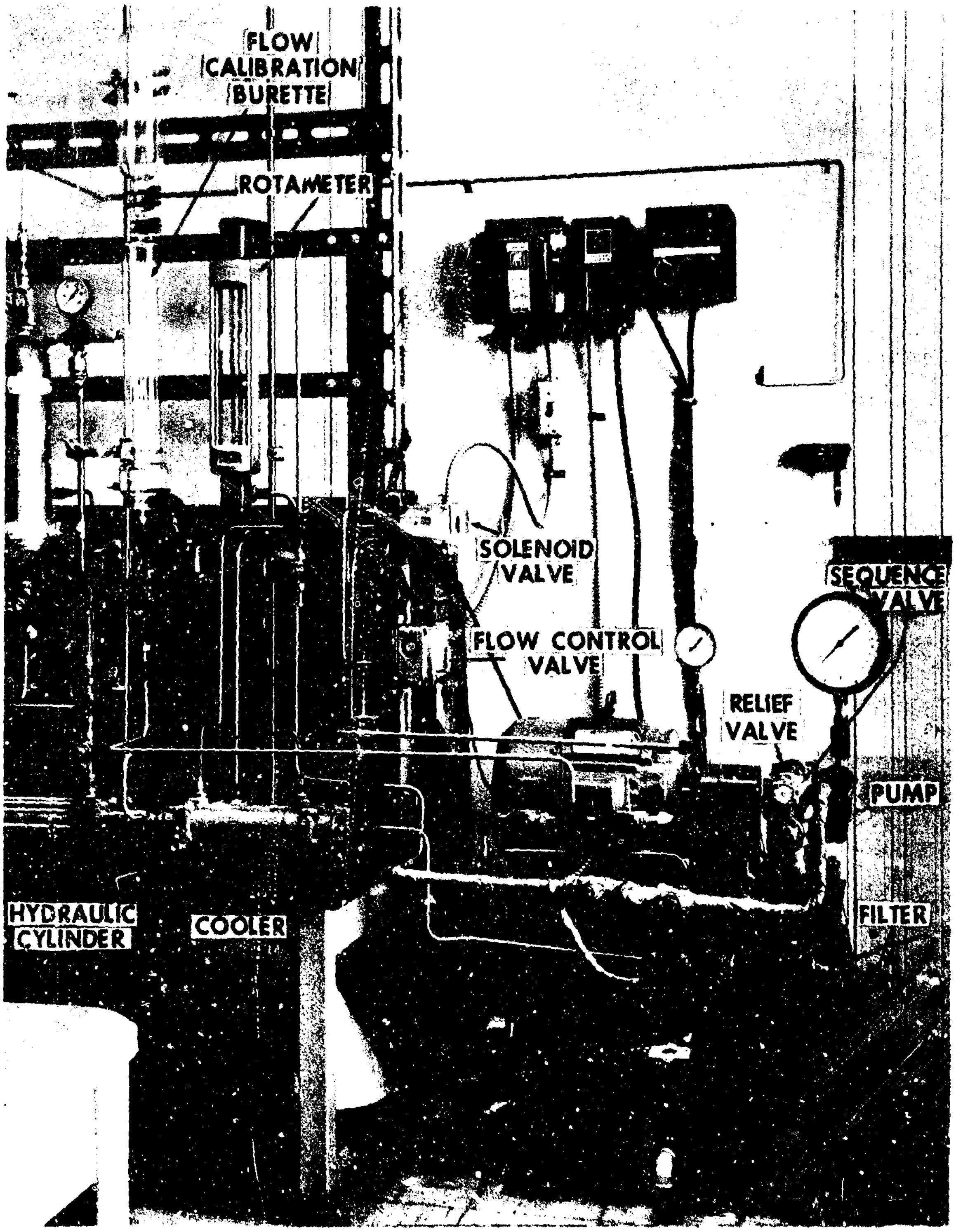


FIGURE 34 - PHOTOGRAPH OF VICKERS VANE PUMP SYSTEM

4. Oxygen Analyzer (Beckman Model No. 777)

The sensor for the oxygen analyzer consists of a gold cathode separated from a tubular silver anode by an epoxy coating. The anode and cathode are electrically separated by a KCl gel. The assembly is separated from the fuel by a gas permeable Teflon membrane. The dissolved oxygen comes in contact with the electrode by diffusing through the membrane and the following reactions occur:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \text{(at cathode)}$$

$$4\,Ag + 4Cl^- \longrightarrow 4AgCl + 4e^- \text{(at anode)}$$

The current in the cell is proportional to the partial pressure of the oxygen present. To calibrate the analyzer, air or nitrogen is bubbled through the fuel at the same temperature at which tests were made. When the analyzer reading stabilizes, actual oxygen content in ppm is determined by gas chromatography. The oxygen content in ppm of any subsequent reading is interpolated from these two determinations.

B. Data Analysis Techniques

No general data analysis techniques were necessary for this study. Data treatment for specific series of tests are discussed at appropriate places in the text. For example, in the evaluation of the scuffing characteristics of the fuels, the method of plotting the wear scar size vs. the load is discussed in the section on "Scuffing of Steel" (III).

REFERENCES

(1) Skarstrom, C. W., U.S. Patent, 2,944,627 (July 1960).

(2) King, W. H., U.S. Patent, 3,164,004 (January 1965).

(3) Boland, J. L., Trans. Faraday Soc. 46, 358 (1950).

(4) Russell, G. A., J. Am. Chem. Soc. 78, 1035 (1956).

(5) Furey, M. J., ASLE Trans. 4, 1 (1961).

(6) Tao, F. F. and Appeldoorn, J. K., Presented at ASLE Annual Meeting, Cleveland (May, 1968). To be published in ASLE Transactions, 11 (1968).

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

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13. ABSTRACT

Previous studies on the friction and wear properties of jet fuels have been extended to metallurgies other than steel and to other kinds of wear, both abrasive and scuffing. Corrosive wear is found with most metals, even those that are nominally corrosion resistant, and can be controlled by using surface-active additives. Abrasive wear is triggered by corrosive wear and can be controlled indirectly by eliminating corrosive wear or indirectly by polar additives. Unlike corrosive wear, scuffing is most severe in dry inert atmospheres. Antiwear additives are usually also antiscuff agents.

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