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PART II

LUBRICITY PROPERTIES
OF
HIGH-TEMPERATURE JET FUELS

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FOREWORD

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ABSTRACT

The study of the lubricity of jet fuels has been expanded to examine several new variables: hydrocarbon type, dissolved oxygen, dissolved water, higher temperatures, and metallurgy. Several important interactions have been found among these variables.

The compounds most responsible for good lubricity are heavy aromatics. Removal of these materials during refining is the major cause of poor lubricity fuels. The heavy aromatics by themselves show unusual friction and wear behavior, giving low wear in air and scuffing in dry, inert atmospheres.

Dissolved oxygen and water increase wear and friction by a corrosion process. Corrosive wear appears to be the most serious cause of friction and wear problems of jet fuels. Nitrogen blanketing can eliminate wear completely in vane pump tests. Certain additives are effective only when water and air are present. A literature survey has been made of the effect of oxygen and water on lubrication. A mathematical model of corrosive wear has been constructed and shows good agreement with experimental data.

Higher temperatures give more wear and friction especially in air. However, oxidation of the fuel will form polar compounds that act as lubricity agents. This reaction tends to mask the effect of temperature. Certain lubricity additives become much less effective at higher temperatures.

Metals that resist corrosive wear, such as stainless steel, are better than chrome steel at low loads, but scuff more easily at higher loads.

Future work will concentrate on higher temperatures and different metallurgies and the interaction of these variables with atmosphere and additive action.

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I

INTRODUCTION

This research program was started when certain jet-engine manufacturers reported friction and wear problems in their engine development programs. These problems appeared to be associated with the very high purity fuels being used. Such fuels had been specially prepared to give superior thermal stability, but in the refining process it was feared that most of the polar materials were being removed, these polar materials being the compounds that impart good lubricity to jet fuels. As initially conceived, the program was to investigate how fuel composition affected lubricity, to identify the good lubricity components and to determine how these fuel variables might interact with other variables such as temperature, metallurgy, and atmosphere.

Before the first six months of the program had been completed, a problem developed in operational aircraft. With certain JP-4 fuels, sticking sometimes occurred in the afterburner fuel-control mechanism. This mechanism consists of a close-fitting plunger in a sleeve, the position of the plunger being controlled by the throttle and returned by a spring. When sticking between plunger and sleeve occurred, the force of the spring was not enough to return the valve to the closed position.

This problem also appeared to be related to fuel quality. A recent change had been made in the JP-4 specifications, calling for more rigid control of water haze, and eliminating the corrosion-inhibitor requirement. This combination of purer fuel and no polar additive was suspected of causing the sticking problem. Accordingly, the research program was widened to investigate this point particularly.

The work during the first year, therefore, was divided into the following parts: (1) a literature survey and field survey to learn what was known or suspected about fuel lubricity, (2) selection of a suitable instrument for measuring the lubricity of jet fuels, so that a reasonable correlation could be obtained with field data, (3) evaluation of a number of commercial or experimental fuels of widely different composition, (4) determination of the effect of trace components such as sulfur and acidic compounds, (5) assessment of the effect of various fuel additives, and (6) evaluation of the lubricity of various JP-4's with and without corrosion inhibitors.

Literature and Field Survey

Neither the literature survey nor the field survey could limit the troubles to one specific problem, and both showed there was considerable disagreement as to possible cures for whatever problem existed. The problems appeared to be aggravated by low viscosity, high temperature and fuel purity, as would be expected. Many factors were claimed to be critically important: viscosity, volatility, sulfur compounds, nitrogen compounds, olefins, oxygenated fuel products, and dissolved oxygen. In most cases there were other data disputing the claims of each of these.

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Selection of Test Instruments

In the experimental work, several test instruments were examined, including the four-ball wear tester, Falex machine, Ryder gear tester, a Vickers vane pump, and the ball-on-cylinder tester. Of these, the last two were found to be most useful and the majority of data were obtained on them. The Vickers vane pump test uses a small 1.1 gpm vane pump, designed for operation with a hydraulic oil at 1000 psi. When used to pump jet fuel, it is grossly overloaded. The volumetric efficiency at 350 psi is only about 60% even with a good fuel; when wear occurs, the volumetric efficiency can drop below 20%. The test is therefore a very sensitive one for fuel lubricity. Wear is measured on both the vanes and the ring on which the vanes ride, and volumetric efficiency is determined periodically during the 24-hour test period.

The ball-on-cylinder device is a simple sliding mechanism in which a half-inch steel ball is loaded against a rotating cylinder that dips in a cup containing the test fuel. The wear scar diameter of the ball is determined at the end of the test -- usually 32 minutes. Continuous measurements are made of friction and metallic contact -- "metallic contact" being defined as the per cent of time that the two surfaces are in contact as determined by an electrical resistance measurement. The formation of additive films during rubbing is often seen by the change in "% metallic contact." Unlike other simple laboratory testers, the ball-on-cylinder device appears to be sensitive enough to detect subtle differences in fuel quality.

It has been found that friction, wear, and metallic contact frequently do not go hand-in-hand. Especially with fuels containing additives, wear and friction sometimes go in opposite directions, so that a simple list of data does not tell the whole story. In general, with the exception of certain phosphate additives, the wear values have given the best correlation with field results.

Evaluation of Commercial Fuels

The ten commercial fuels evaluated showed marked differences in friction and wear. These differences were more related to chemical composition than to physical properties. Thus, most highly-refined fuels were consistently worse in lubricity than the commercial fuels, even though the latter included low-viscosity JP-4 and light naphtha. However, the low-viscosity fuels were always more sensitive to fuel purity, thus indicating the importance of viscosity as well.

Effect of Polar Constituents

The commercial (less highly-refined) fuels contained more polar materials of all kinds: sulfur compounds, nitrogen compounds, organic acids, and aromatics. Therefore it was necessary to assess the performance of each class of compounds in a separate manner. Somewhat surprisingly, it was found that sulfur compounds in the C_8 range were all ineffective in concentrations up to 1% sulfur. The same was true for nitrogen compounds going up to C_{12}. It was left for the present report to establish whether acids or aromatics were the most important.

Fuel Additives

Several different types of fuel additives were examined. Neither oxidation inhibitors nor metal deactivators were found to have any lubricity characteristics in the concentrations used in jet fuels. However, most of the corrosion inhibitors showed a pronounced effect, even at concentrations as low as 15 ppm.

It was concluded that the presence of corrosion inhibitors would help alleviate problems associated with poor fuel lubricity. (In March, 1966, a change order was made in specification MIL-T-5624G reinstating corrosion inhibitor in JP-4.)

Additives especially designed to improve lubricity were also evaluated. In general these were superior to the corrosion inhibitors, oleic acid being one of the best.

The present report continues the work on polar fuel components and fuel additives. Additional data are presented on the effect of higher temperatures, different metallurgies, and the presence of dissolved water and oxygen. Water and oxygen were found to have such a profound effect that frequently some of the earlier tests were repeated in controlled atmospheres. To complicate matters further, a marked interaction was found between the atmosphere and the fuel composition, certain fuels being better in air and others better in an inert atmosphere. The effectiveness of additives also depends on the atmosphere, as does the effect of metallurgy.

II

EFFECT OF POLAR CONSTITUENTS ON LUBRICITY

In the previous Annual Report (AFAPL-TR-66-89 Part 1), it was noted that the best fuels in lubricity were those having the most aromatics, the most sulfur and nitrogen compounds, and the highest acidity. These data are summarized in Table I. All of these polar compounds are suspected as being good lubricity additives; additives have been reported as better than paraffins in wear tests; sulfur compounds are often used as EP additives; oleic acid was shown to be an excellent lubricity agent.

Each of these has been studied in greater detail. It has been concluded that high molecular weight aromatics are the most likely lubricity agents in the better jet fuels.

A. Sulfur Compounds

The previous work had shown a good correlation between lubricity and sulfur content, but this did not appear to be a cause-and-effect relationship. Rather, both lubricity and sulfur content seemed to be a result of the degree of refining. Addition of various sulfur compounds to cetane at the 1% S level did not show a great improvement in lubricity. However, to confirm this point, more sulfur compounds were run, covering a wider spread in molecular weight, at more typical concentrations, and in an actual jet fuel, the highly-refined PW-523.

Tests were carried out on the ball-on-cylinder machine at 240 rpm, under 240 g load, and for 32 minutes. The base fluid PW-523 was tested on the same cylinder just before each sulfur compound was evaluated, thus providing a better basis for comparison.

1. Mercaptans

Four alkyl mercaptans were tested with the alkyl chain length varying from C_8 to C_{18}. One aromatic mercaptan, thiophenol, was also included. Results are tabulated in Table II. None of them showed any improvement in performance at the 30 ppm level. Above 30 ppm, their effectiveness in reducing wear and friction increases with increasing chain length. For example, n-octyl mercaptan has no effect at concentrations lower than 2000 ppm, whereas n-octadecyl mercaptan begins to show effect at 100 ppm and becomes very effective at high concentration levels.

However, jet fuel specifications set the maximum allowable mercaptan level at 0.001% S (10 ppm). Since none of the mercaptans tested were lubricity agents even at 30 ppm, they do not appear to be a factor in the lubricity of jet fuels.

2. Dialkyl Sulfides

Low molecular weight sulfides were found to give no improvement in lubricity, agreeing with earlier data. Thus, n-butyl, i-butyl, t-butyl and n-hexyl sulfides were all ineffective. In fact, at low concentrations they actually increased wear somewhat. However, higher molecular weight sulfides, octyl and dodecyl, showed pronounced antiwear activity at concentrations of 500 and 2000 ppm

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TABLE I

Description of Test Fuels

Code	Description	Viscosity/ 77°F, cp	Hydrocarbon Type			Carbon No.	Boiling Range °F
			% Paraffinic	% Naphthenic	% Aromatic		
Highly Refined							
HR-1	"SST Fuel"	1.15	54.0	44.6	1.4	C_9-C_{12}	325-425
HR-2	75 Lum. No.	1.25	64.3	25.6	10.1	C_{10}-C_{13}	350-425
HR-3	PW-523	1.51	87.6	10.8	1.6	C_{10}-C_{14}	400-475
HR-4	Naphthenic	2.15	17.9	79.7	2.4	C_9-C_{16}	375-500
HR-5	White Oil	2.42	———100———		0	C_{11}-C_{14}	400-500
Conv. Refined							
CR-6	Naphtha	0.28	82.8	15.3	1.9	C_4-C_7	100-200
CR-7	JP-4	0.56	41.2	34.3	24.5	C_5-C_{15}	175-425
CR-8	Jet A	1.31	44.9	39.8	15.3	C_9-C_{16}	325-475
CR-9	JP-5	1.47	46.1	38.3	15.6	C_9-C_{15}	375-475
CR-10	Diesel Fuel	2.85	42.7	30.3	27.0	C_{10}-C_{17}	400-575

TABLE II

LUBRICITY OF VARIOUS SULFUR COMPOUNDS

Ball-on-Cylinder Tests (240rpm, 240g, 77F, 32min, Steel-on-Steel)

Cyl. No	Sulfur Compound	S, ppm	WSD, mm	CoFr
246	None	0	0.51	0.19
	Dodecyl Mercaptan	30	0.53	0.19
	"	100	0.55	0.20
	"	500	0.47	0.20
	"	2000	0.43	0.18
	None	0	0.54	0.20
	Hexadecyl Mercaptan	30	0.55	0.19
	"	100	0.51	0.19
	"	500	0.43	0.17
	"	2000	0.41	0.18
271	None	0	0.48	0.18
	n-Dodecyl Mercaptan	30	0.49	0.19
	n-Hexadecyl Mercaptan	30	0.45	0.19
	None	0	0.52	0.18
	n-Octyl Mercaptan	30	0.56	0.19
	"	100	0.58	0.20
	"	200	0.55	0.20
	"	500	0.50	0.19
	"	2000	0.41	0.19
	None	0	0.50	0.18
	n-Octadecyl Mercaptan	30	0.50	0.19
	"	100	0.44	0.18
	"	500	0.37	0.17
	"	2000	0.34	0.15
	"	10,000	0.31	0.13
315	None	0	0.60	0.18
	Thiophenol	10	0.75	0.17
	"	30	0.84	0.20
	"	100	0.87	0.18
	None	0	0.62	0.18
267	None	0	0.46	0.19
	Thiacyclopentane	30	0.45	0.19
	"	100	0.44	0.19
	"	500	0.45	0.19
	"	2000	0.51	0.19
	1,4 Dithiacyclohexane	30	0.58	0.20
		100	0.58	0.20
		500	0.58	0.20
		2000	0.97	0.24

TABLE II (Cont'd)

Cyl. No	Sulfur Compound	S, ppm	WSD, mm	CoFr
267	None	0	0.56	0.20
	Thiacyclohexane	30	0.51	0.20
	"	500	0.54	0.20
	"	2000	0.42	0.19
	None	0	0.55	0.20
288	None	0	0.58	0.20
	Thiacyclohexane	10	0.64	0.22
	"	20	0.57	0.20
	"	30	0.48	0.20
294	None	0	0.52	0.19
	Thiacyclohexene	30	1.00	0.21
	"	100	0.67	0.18
	"	500	0.54	0.19
	"	2000	0.52	0.21
	None	0	0.49	0.20
	Dodecyl Sulfide	30	0.55	0.20
	"	100	0.46	0.19
	"	500	0.40	0.18
	"	2000	0.35	0.18
	None	0	0.55	0.20
279	None	0	0.52	0.19
	Iso-butyl Sulfide	30	0.53	0.20
	"	100	0.56	0.20
	"	500	0.54	0.19
	"	2000	0.53	0.19
	None	0	0.54	0.19
	Tert-butyl Sulfide	30	0.58	0.20
	"	100	0.57	0.20
	"	500	0.57	0.20
	"	2000	0.52	0.19
	n-Butyl Sulfide	100	0.48	0.18
	"	200	0.49	0.19
254	None	0	0.49	0.19
	n-Butyl Sulfide	30	0.48	0.19
	"	100	0.47	0.19
	"	500	0.47	0.18
	None	0	0.47	0.19
	n-Hexyl Sulfide	30	0.49	0.19
	"	100	0.48	0.19
	"	500	0.46	0.19
	"	2000	0.45	0.18
	None	0	0.48	0.19
	n-Octyl Sulfide	30	0.51	0.19
	"	100	0.47	0.19
	"	500	0.44	0.19
	"	2000	0.37	0.19

TABLE II (Cont'd.)

Cyl. No	Sulfur Compound	S, ppm	WSD, mm	CoFr
321	None	0	0.44	0.19
	Benzothiophene	30	0.48	0.19
	"	100	0.47	0.18
	"	500	0.48	0.18
	"	2000	0.48	0.18
	None	0	0.42	0.18
	Dibenzothiophene	30	0.49	0.19
	"	100	0.52	0.20
	"	500	0.46	0.19
	"	2000	0.43	0.18

as S (0.4 to 2.0% as S-compounds). It is barely possible that these sulfides could be in the highest boiling fraction of the fuels. Octyl sulfide has a molecular weight of 258, corresponding to a C_{18} hydrocarbon; dodecyl sulfide is 370 MW, corresponding to a C_{26}. Gas chromatography has shown that the highest-boiling jet fuel, RAF-176-64, has nothing higher than C_{16}, and diesel fuel, nothing higher than C_{18} (0.2%). It seems unlikely that these high molecular weight sulfides could be present in high enough concentrations to be significant factors in lubricity.

3. Cyclic Sulfides

Three cyclic sulfides were tested:

Thiacyclohexane

Thiacyclopentane

1,4-dithiacyclohexane (dithiane)

Thiacyclohexane seems to show some improvement at 30 ppm S-concentration, but not at concentrations lower than 30 ppm.

The other cyclic sulfides were ineffective.

4. Thiophene Compounds

Both benzothiophene and dibenzothiophene were tested at four concentration levels. No improvement in performance could be detected.

5. Tests at Higher Temperature

Two sulfur compounds, thiophenol and dodecyl sulfide, were tested at 240F to see if they developed any lubricity effects at higher temperatures. To the contrary, thiophenol was still prowear and dodecyl sulfide still had no appreciable effect except at 500 ppm S. Data are in Table III.

Summarizing, some activity has been found for certain sulfur compounds but, with one exception, only at concentrations far above that in the jet fuels. The exception is thiacyclohexane which seems to be an exception even in the class of cyclic sulfides. Unless there are some unusual interactions, it seems doubtful that the differences in lubricity noted among the jet fuels can be ascribed to sulfur compounds.

B. Acidity

Acidity in most of the fuels is exceedingly low, with a neutralization number of less than 0.002 ($<$2 ppm KOH/g). Only two fuels were higher: RAF-176-64, the second best fuel, has a value of 0.01; diesel fuel, the best in lubricity, was 0.120. However, even values of 0.003 could be important. If the acid were present as oleic acid, 15 ppm would give a neutralization number of only 0.003. And 15 ppm oleic acid has a profound effect on lubricity.

To discover if the acids present in diesel fuel might similarly affect lubricity, a sample of the fuel was stirred over NaOH pellets for 15 minutes. The fuel turned hazy, presumably from the formation of sodium soaps, and was filtered through filter paper. The resulting clear solution had a neutralization

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number of 10 ppm KOH/g, a 90% reduction. A second sample of diesel fuel was per-colated several times through a glass column packed with NaOH pellets, and then filtered. This removed all acidity, and left a fuel having an alkaline neutraliza-tion number of 0.024. Both fuels were tested in the ball-on-cylinder machine.

No substantial difference was found in the three tests. Wear scars were about equal. The friction traces were somewhat more erratic with the treated fuels but the differences were minor compared, say, to the difference between diesel fuel and PW-523.

It appears that the acids present in diesel fuel (probably naph-thenic acids) are not lubricity agents. They do not act like oleic acid, and they are not responsible for the good performance of diesel fuel.

C. Aromatics

The fuel property correlating best with friction and wear appears to be aromatic content. The highly-refined fuels and the light naphtha had less than 2.5% aromatics. In contrast, the four commercial fuels -- JP-4, JP-5, RAF-176-64 (Jet A), and diesel fuel -- had 15-27% aromatics. Friction and wear tests also made the same distinction. In particular, the good performance of JP-4 in spite of its low viscosity and relatively low sulfur, is best explained by its high aromatic content of 24%.

To determine the effect of aromatics on wear performance, several aromatic compounds were added to poor-lubricity fuels, and evaluated in ball-on-cylinder and four-ball tests. Results confirm that high-molecular weight aromatics reduce friction and wear of the highly-refined fuels.

In the first series of tests, PW-523 was used as the base fuel. In a ball-on-cylinder test it gave moderately high friction and a wear scar of 0.45 mm. The addition of n-butyl benzene caused a noticeable increase in friction, both in average level and in erraticness. The wear scar, however, decreased to 0.37. This anomalous behavior is unexplained but is nevertheless real, having been confirmed in subsequent runs. Solvesso 150, a commercial aromatic solvent boiling between 185 and 210C (C_5 and C_6 alkyl benzenes) at 20% was only slightly better. However, methylnaphthalene (redistilled) was effective even at 5%, reducing both wear and friction. Even better was 20% of a heavy aromatic naphtha, a mixed solvent of 190-280C boiling range. These data are summarized in Table IV.

The unusual behavior of polynuclear aromatics is particularly noted in Table V. Mixtures of methyl-naphthalene and the paraffinic Bayol 35 gave less wear than either component alone. As little as 5% methyl-naphthalene reduced the wear scar from 0.45 to 0.32. Friction was also reduced, the lowest being for 100% methyl-naphthalene. In contrast, adding a single-ring aromatic -- n-butyl benzene -- resulted in very erratic friction, so much so that at 40% the friction became excessive.

The unique performance of polynuclear aromatics is discussed more com-pletely in a later section. It appears that the differences in lubricity noted in commercial non-additive jet fuels is most probably their polynuclear-aromatic content. Compounds containing hetero atoms (sulfur nitrogen or oxygen) normally found in jet fuels do not seem to be responsible for good lubricity.

TABLE III

LUBRICITY OF TWO SULFUR COMPOUNDS AT HIGHER TEMPERATURE

(Ball-On-Cylinder Tests, 240F, 240 g, 240 rpm, 32 Minutes)
Base Fuel: PW-523

Cylinder No.	Sulfur Compound	PPM S	Atmosphere	Coefficient of Friction	Wear Scar Diameter, mm
315	None	0	Room Air	0.20	0.50
"	Thiophenol	10	Room Air	0.20	0.60
"	Thiophenol	30	Room Air	0.17	0.62
333	None	0	Room Air	0.24	0.72
"	Dodecyl Sulfide	30	Room Air	0.24	0.70
"	Dodecyl Sulfide	100	Room Air	0.24	0.72
"	Dodecyl Sulfide	500	Room Air	0.17	0.58

TABLE IV

LUBRICITY OF AROMATICS IN HIGHLY-REFINED FUEL

(Ball-On-Cylinder Tests, 240rpm, 240g, 32min)

Cyl.	% Aromatic in PW-523	WSD, mm	Friction
249	None	0.45	Moderate
	20% n-Bu Benzene	0.37	Erratic
	20% Hvy. Arom. Naphtha	0.32	Smooth
248	None	0.51	Erratic
	20% Solvesso 150	0.41	Erratic
	5% Me-naphthalene	0.37	Smooth
	12% Me-naphthalene	0.36	Smooth

TABLE V

AROMATICS EFFECT ON LUBRICITY

Ball-on-Cylinder Tests: Steel-on-steel, 32 minutes,
240g, 240rpm, 77F

Composition			
% Bayol 35	% Me-Naphthalene	WSD, mm	CoFr
100	0	0.45	0.19
95	5	0.32	0.15
80	20	0.31	0.15
50	50	0.32	0.14
20	80	0.34	0.13
5	95	0.39	0.13
0	100	0.33	0.12
% Bayol 35	% n-Butyl Benzene		
100	0	0.45	0.19
95	5	0.42	0.17*
80	20	0.41	0.17*
60	40	0.37	**

 * Frequent bursts of very high friction.
** Very erratic friction throughout run. Level higher than
    with Bayol 35 alone.

III

CHARACTERISTICS OF PURE HYDROCARBONS

Several pure hydrocarbons in the jet-fuel boiling range have been obtained and examined in some detail. Viscosities and densities are reported here along with friction and wear data in the ball-on-cylinder test. Later sections of this report will contain data on the performance of mixtures of many of these compounds.

Table VI presents the viscosity and density data. As in the previous report, kinematic viscosities were obtained with a Ubbelohde capillary viscometer, densities with a precision hydrometer. Calculated absolute viscosities are plotted in Figure 1, using the modified ASTM viscosity-temperature chart.

Comparing the viscosity of these pure compounds with that of jet fuels presented in the previous report, it can be seen that the pure compounds cover a viscosity range wider than the jet fuels. They range from 0.5 cp/77F for n-octane to 12 cp/77F for dimethano-decalin. Also, like the jet fuels, the viscosity-temperature slopes of all compounds is about the same, regardless of the molecular structure. The pressure-viscosity relationships would be expected to be similarly parallel. Therefore, there would not be any "crossover" effect: the viscosity of these compounds in the rubbing contact region would be predictable from the viscosities reported in Table VI. This situation is quite different from that of the higher-viscosity lubricants, which can have quite different viscosity-temperature slopes.

Purity of the hydrocarbons was checked by gas chromatography. Analyses are given in Table VII. Most of the compounds were 99+% pure. One of the exceptions (important because of the amount of data obtained with this compound) was the 1-methyl-naphthalene. As originally obtained, it was a dark amber liquid. Redistillation gave a heart-cut of yellow-blue fluorescence, analyzing as 58% 1-methyl and 40% 2-methyl-naphthalene. However, it had a sulfur content of 0.85%. A second sample from a different source (supposedly of higher purity) showed 0.3% sulfur. A third sample from a third source gave only 0.03% sulfur. All recent tests have been run with this third material, although much of the data in this report are with the first material. However, no substantial differences in lubricity have been observed among the three samples.

Wear performance of these hydrocarbons is given in Table VIII. The hydrocarbons are listed in increasing order of viscosity. It will be seen that with few exceptions wear decreases with viscosity, irrespective of molecular type. It was noted that hexadecene, a C_{16} olefin, gave somewhat lower wear than the corresponding saturated C_{16}'s, hexadecane and heptamethyl-nonane. Overall, however, the effect of hydrocarbon structure is much less important than the effect of additives or other polar materials already reported. Only the condensed-ring aromatics show differences from other hydrocarbons. As already mentioned, they act as an anti-wear additive in a fuel. In a later section, friction and wear data are presented on many hydrocarbons and hydrocarbon mixtures under conditions of controlled atmosphere. In an inert atmosphere condensed-ring aromatics tend to scuff very easily.

TABLE VI

VISCOSITY AND DENSITY OF HYDROCARBONS

Temp. °F.	Kinematic Viscosity, cs					Density, g/ml					Absolute Viscosity, cp				
	77	100	140	210	300	77	100	140*	210	300	77	100	140	210	300
n-Octane	0.733	0.642	0.524	0.387	---	0.698	0.688	0.670	0.638	---	0.512	0.442	0.351	0.247	---
n-Nonane	0.932	0.804	0.641	0.464	---	0.713	0.703	0.686	0.655	---	0.665	0.565	0.440	0.304	---
n-Dodecane	1.828	1.496	1.117	0.740	0.503	0.746	0.736	0.720	0.691	0.656	1.364	1.101	0.804	0.511	0.330
n-Cetane	3.987	3.053	2.083	1.250	0.789	0.770	0.761	0.746	0.719	0.686	3.070	2.323	1.554	0.899	0.541
1-Hexadecene	3.528	2.736	1.911	1.163	0.745	0.778	0.770	0.754	0.727	0.693	2.745	2.107	1.441	0.845	0.516
Heptamethyl-nonane	4.262	3.240	2.187	1.300	0.782	0.781	0.773	0.758	0.732	0.699	3.329	2.504	1.658	0.952	0.547
n-Butyl-benzene	1.126	0.965	0.746	0.533	---	0.857	0.847	0.830	0.799	---	0.965	0.817	0.619	0.426	---
Decalin (cis-trans)	2.772	2.271	1.577	0.975	0.627	0.883	0.874	0.856	0.825	0.789	2.448	1.985	1.350	0.804	0.495
Tetralin	2.074	1.680	1.185	0.780	0.517	0.962	0.952	0.934	0.904	0.866	1.995	1.599	1.107	0.705	0.448
Diethylcyclohexane	1.275	1.080	0.820	0.570	0.396	0.799	0.790	0.773	0.744	0.706	1.019	0.853	0.634	0.424	0.280
Isopropyl-bicyclohexyl	9.42	6.22	3.558	1.809	1.003	0.882	0.873	0.859	0.833	0.801	8.31	5.430	3.056	1.507	0.803
Dimethano-decalin	11.49	8.06	4.687	2.284	1.223	1.003	0.993	0.976	0.946	0.911	11.52	8.00	4.575	2.160	1.114
Methylnaphthalene	2.655	2.045	1.414	0.869	0.561	1.013	1.004	0.981	0.958	0.921	2.690	2.053	1.387	0.832	0.517

* Interpolated
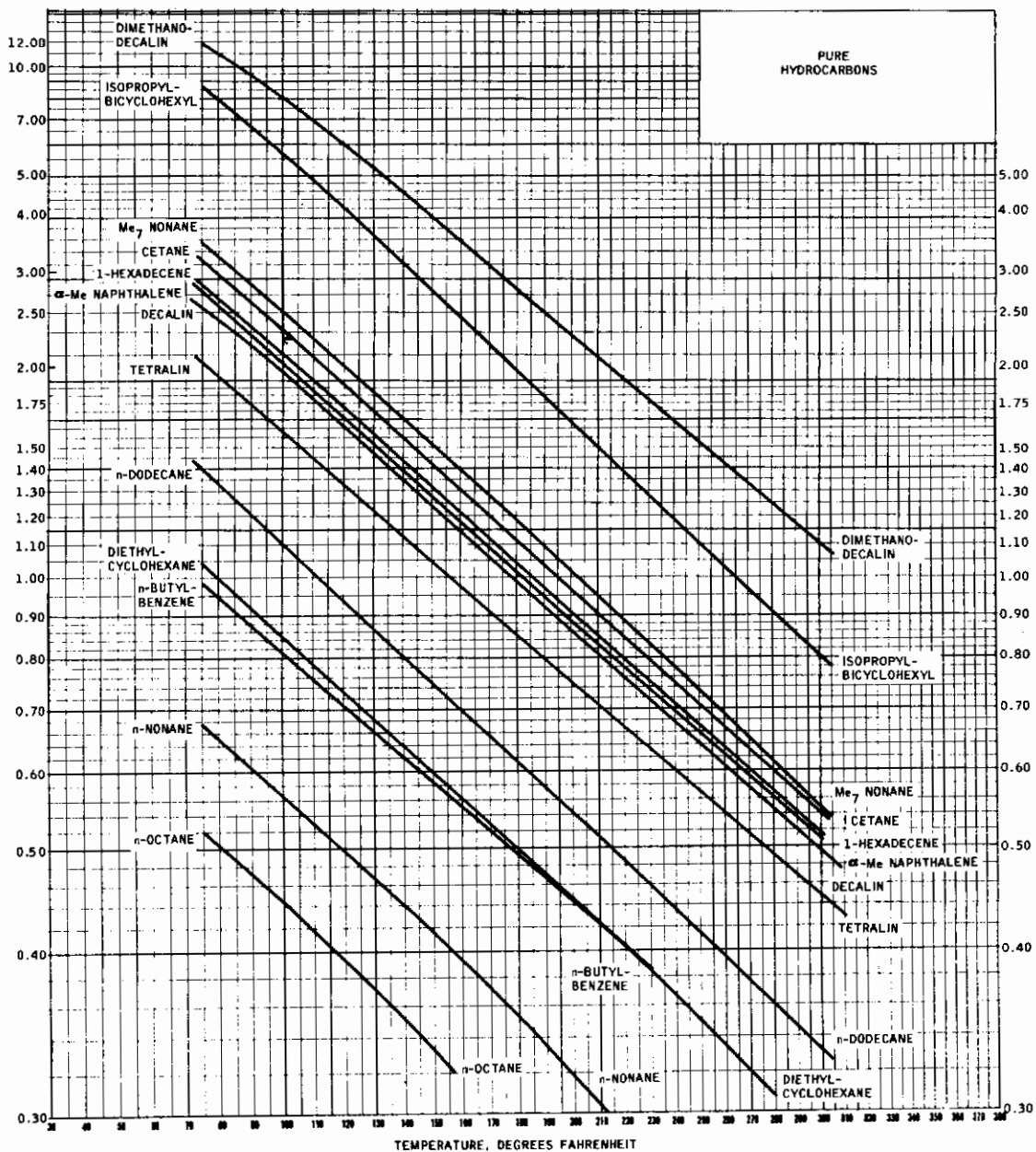
FIGURE 1 - VISCOSITY-TEMPERATURE PROPERTIES OF HYDROCARBONS

TABLE VII

GAS CHROMATOGRAPHIC ANALYSIS OF HYDROCARBONS[1]

n-Octane		
C_8(sats)		0.19
n-C_8		99.42
C_9(sats)		0.39

n-Nonane	
n-Nonane	99.7
(imp)	0.3

n-Dodecane		
C_{12}(sats)		0.43
n-C_{12}		99.55
C_{13}(sats)		0.02

n-Hexadecane		
C_{13}	=	0.26
C_{14}	=	0.54
C_{15}	=	0.33
C_{16}	=	97.49
C_{17}	=	1.10
C_{18}	=	0.22
C_{19}	=	0.06

n-Butyl Benzene	
n-Propyl Benzene	0.02
sec-Butyl Benzene	0.03
iso-Butyl Benzene	0.03
n-Butyl Benzene	99.83

Diethyl Cyclohexane[3]		
C_9	=	0.09
C_{10}	=	99.88
C_{11}	=	0.03

1-Hexadecene		
C_{15}	=	0.60
C_{16}	≈	99.40

Heptamethyl Nonane	
C_{16}-Major	96.92
C_{16}-Minors	3.08

Decalin	
trans	34.89
cis	65.06
(imp)	0.05

Tetralin	
trans-Decalin	0.27
cis-Decalin	0.97
Tetralin	97.64
(imp)	1.12

Isopropyl Bicyclohexyl[2]		
C_{14}	=	0.8
C_{15}	=	99.2

Dimethano Decalin		
C_{11}	=	2.5
C_{12}(trans)	=	74.6
C_{12}(cis)	=	14.6
C_{12}(other)	=	8.3

α-Methyl Naphthalene		
C_{11}	39.4	Two
	57.6	Major
(imp)	3.0	Peaks

(1) G. C. Analysis via Perkin-Elmer 226; 300' DC 550 Column

(2) Four major components at C_{15}.

(3) Six major components at C_{10}.

TABLE VIII

WEAR CHARACTERISTICS OF PURE HYDROCARBONS
(Ball on Cylinder Test, 240 rpm, 77 F, Room Air, 32 min.)

	Wear Scar Diameter, mm							
Load, g:	15	30	60	120	240	480	1000	2000
n-Octane	0.24	0.27	0.29	0.33	0.31	0.31	Fail	--
n-Nonane	--	0.28	0.38	0.58	0.70	Fail	--	--
n-Butylbenzene	0.29	0.32	0.41	0.51	0.55	0.51	0.63	Fail
Diethylcyclohexane	--	0.24	0.28	0.36	0.39	0.45	--	--
n-Dodecane	0.21	0.25	0.26	0.28	0.32	0.37	0.42	Fail
Tetralin	0.18	0.21	0.25	0.27	0.35	0.44	0.48	0.54
Decalin	0.17	0.19	0.23	0.28	0.33	0.43	0.54	Fail
1-Methylnaphthalene	--	0.17	0.18	0.20	0.25	0.29	0.43	--
1-Hexadecene	0.18	0.20	0.21	0.24	0.26	0.28	0.32	0.40
n-Hexadecane (Cetane)	0.17	0.19	0.21	0.23	0.26	0.33	0.39	Fail
Heptamethylnonane	0.20	0.21	0.24	0.25	0.29	0.37	0.42	Fail
Isopropylbicyclohexyl	--	0.17	0.18	0.23	0.25	0.27	--	--
Dimethano-decalin	--	0.16	0.18	0.20	0.24	0.28	--	--

IV

EFFECT OF DISSOLVED OXYGEN
AND WATER -- LITERATURE SURVEY

The data reported so far have all been obtained in ordinary room air;
that is, with an oxygen concentration of 21% and varying degrees of humidity.
The test fuels therefore contain appreciable amounts of dissolved oxygen and
water. It has been found experimentally that the friction and wear character-
istics of jet fuels are very dependent on both oxygen and water content -- much
more so than for lubricants.

It is therefore worthwhile to consider the solubility properties of
oxygen and water in hydrocarbons and review the literature on the effect of dis-
solved oxygen and water on lubrication.

A. Basic Processes

From data to be presented later, it will be seen that the effect of
oxygen and water is at the rubbing surface. Oxidation of the hydrocarbons, or
similar chemical changes in the liquid, are not the phenomenon involved. There-
fore, the pertinent question is how much oxygen or water is actually available
at the rubbing surface.

For permanent gases such as oxygen, the availability will depend on
several factors: the solubility of oxygen in the hydrocarbon (the Bunsen co-
efficient), the partial pressure of oxygen in the surrounding atmosphere, the
diffusion rate of oxygen through the hydrocarbon, and the rate of oxygen deple-
tion by reaction with the surface or (particularly at higher temperatures) with
the hydrocarbon. Thus, oxygen availability is a dynamic equilibrium between a
driving force (partial pressure times the Bunsen coefficient) and a depletion
factor (reaction with metal or hydrocarbon). If the depletion factor is large,
the diffusion rate can then be important. Each of these factors will be con-
sidered in turn.

Oxygen Solubility

The solubility of oxygen in various hydrocarbons differs considerably.
Oxygen is most soluble in paraffins and least soluble in aromatics, the differ-
ence being 3-4:1. This difference among hydrocarbons is a function of the solu-
bility parameter, which is the square root of the cohesive energy density:

$$\delta = \left(\frac{\Delta H - RT}{V} \right)^{\frac{1}{2}}$$

where
δ = solubility parameter
ΔH = heat of vaporization of the solvent
V = molar volume of the solvent
R = gas constant
T = absolute temperature

The relationship between solubility parameter and gas solubility is given in Figure 2, taken from Reference 1. However, for precise purposes it is best to measure the gas solubility directly, using for example, gas chromatography. (For a review of older methods, see Reference 2.) In all the n-paraffins, the solubility of oxygen is essentially the same, even more so than the solubility parameter would indicate. Isoparaffins have greater solubility for oxygen than do n-paraffins; olefins and aromatics have less. This is in accordance with Hildebrand's solubility theory: oxygen has a very low solubility parameter and thus resembles isoparaffins most and aromatics least.

The solubility of any single gas is usually expressed as the Ostwald coefficient or the Bunsen coefficient, which are based on Henry's Law. Henry's Law states that the solubility of a gas is directly proportional to the partial pressure of that gas in the atmosphere above the liquid:

$$C = kP.$$

For atmospheric pressures and below, this law is quantitatively exact. If P is 760 mm and C is expressed as volume of gas at STP per volume of liquid, then k is Bunsen's coefficient. Ostwald's coefficient is similar except that the volume of gas is at the actual temperature. Ostwald's coefficient is therefore independent of partial pressure. For our purposes, the Bunsen coefficient is more meaningful, for we are interested in the number of molecules available at the rubbing surface and not the volume they would occupy in the gas phase.

The solubility of most gases changes with temperature. For petroleum oils this has been reduced to a single chart (3), reproduced as Figure 3. This is a plot of the Ostwald coefficient vs. temperature. (Had the Bunsen coefficient been plotted, the lines would have a somewhat greater negative slope.)

Very soluble gases, such as CO_2, show decreasing solubility, whereas less soluble gases, such as helium, show increasing solubility with temperature. Argon and oxygen have very similar solubility characteristics and neither shows much change with temperature. This is a happy coincidence, for we can observe the effect of temperature on wear directly, without having to make corrections for the amount of oxygen dissolved.

Water Solubility

Unlike oxygen, water has a large solubility parameter and therefore is most soluble in aromatics and least soluble in paraffins and isoparaffins. In all cases, the water molecules are widely separated from each other and do not exhibit hydrogen bonding. Hence, water behaves more like a gas of molecular weight 18 than like a liquid. However, at temperatures below 100C, water can also be emulsified and it is very difficult to distinguish between a microemulsion and a true solution. Small amounts of polar materials can greatly increase the amount of dissolved or emulsified water. Therefore, measurements of water solubility in highly-purified liquids may not have much pertinence in practical fuels.

Total water content is best measured by the Karl Fischer method, but care must be taken to insure that the water content does not change between the time of the lubricity test and the time of analysis. Diffusion of water in hydrocarbons is quite rapid.
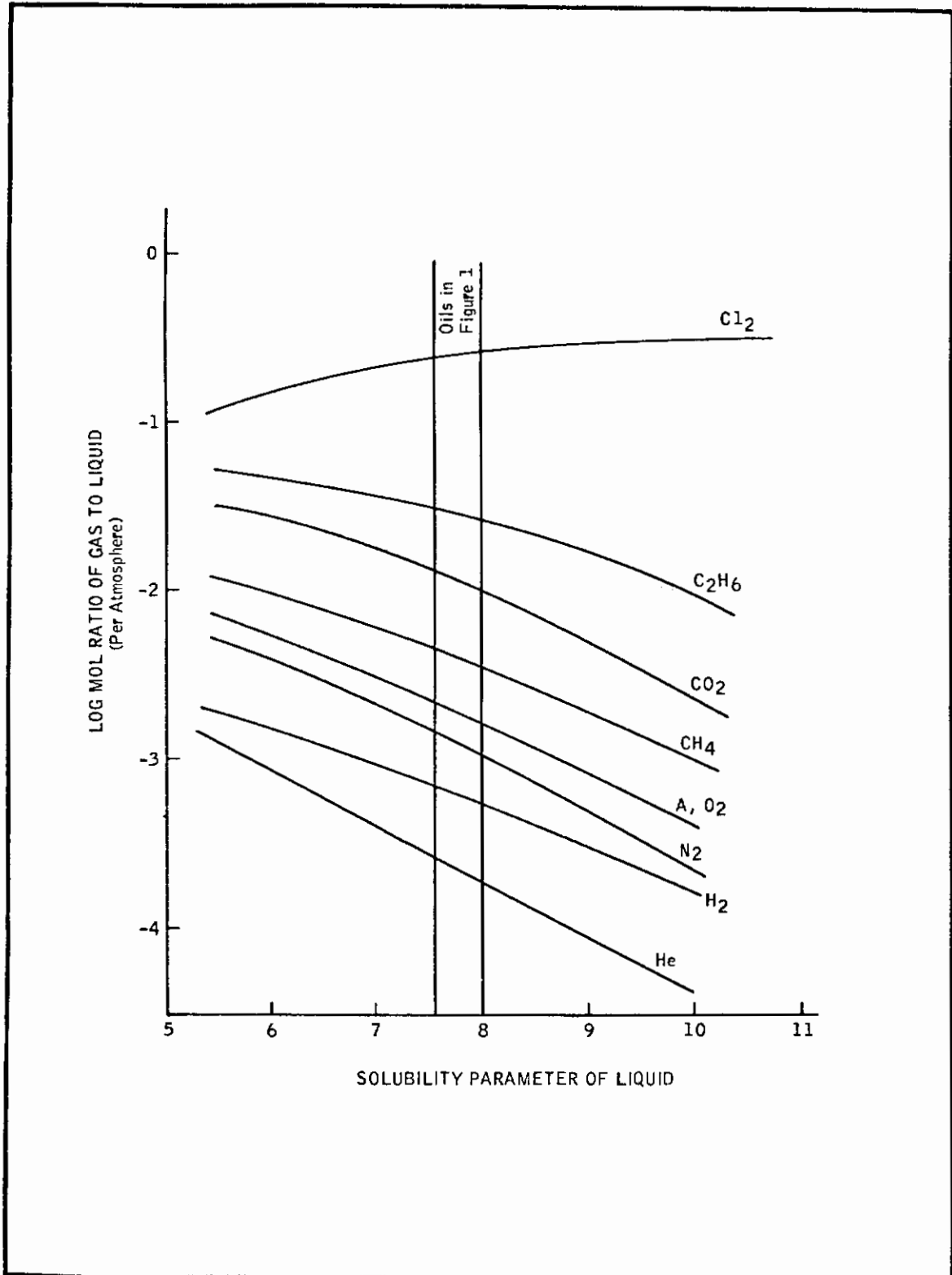
FIGURE 2 - SOLUBILITY OF GASES IN VARIOUS LIQUIDS AT 25°C.
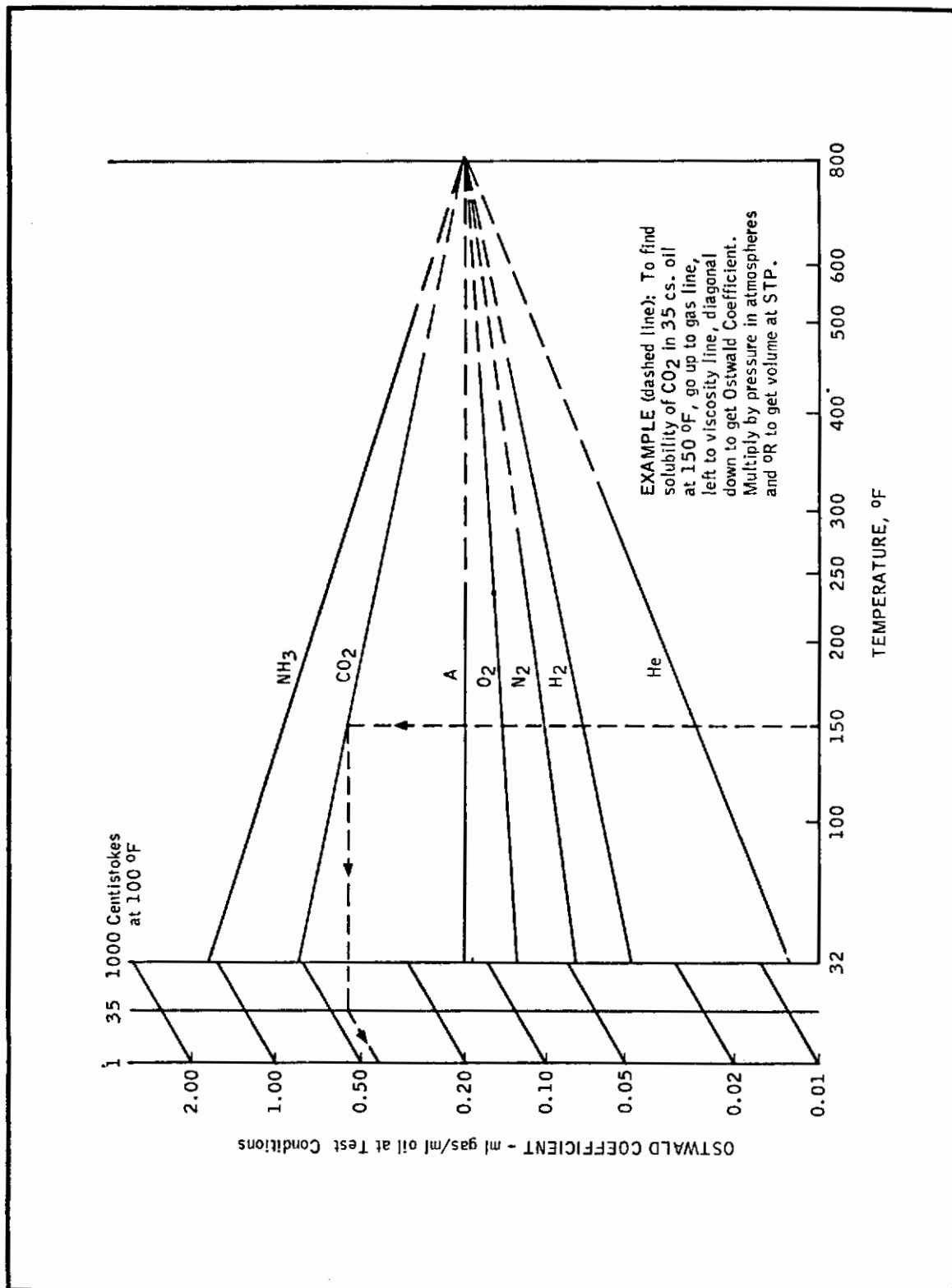
FIGURE 3 - SOLUBILITY OF GASES IN PETROLEUM OILS

EXAMPLE (dashed line): To find solubility of CO_2 in 35 cs. oil at 150 °F, go up to gas line, left to viscosity line, diagonal down to get Ostwald Coefficient. Multiply by pressure in atmospheres and °R to get volume at STP.

It is obvious that the relative humidity of the surrounding atmosphere is the factor controlling dissolved water content. Normally humidity is not controlled during wear tests and so it remains a major cause of irreproducibility. In our work it is controlled either at 0% or 100% RH. The gas from compressed gas cylinders, having been made by liquefaction, is extremely dry -- so much so that passing it through a conventional desiccant will actually increase its moisture content. Saturated gas is conveniently obtained by bubbling through water.

Reaction of Oxygen with Metal Surfaces

The kind of wear encountered here is believed to be corrosive wear. That is, the primary cause of wear is the reaction of the metal surface to form iron oxide. The oxide wears away, exposing fresh metal surface which can then oxidize further. This kind of wear is an entirely different mechanism from abrasive wear or scuffing wear. It is akin to fretting corrosion except that the reactions are in reverse order. In fretting corrosion, the first process is a "molecular plucking" or adhesive wear, in which a metal particle is removed from the surface by vibration; it quickly oxidizes to form wear debris. In corrosive wear, the first process is the oxidation to form a loosely-bound oxide which is then worn away.

Corrosive wear is a common form of wear in engine cylinders. The cylinder walls are cooled by the water jacket on one side, and exposed to combustion products on the other. These combustion products, consisting in part of water and corrosive acids, can condense on the walls and cause corrosion. It has been shown (4) that when the wall temperature drops below the dew point of the combustion products, wear increases suddenly and severely.

Corrosive wear is therefore dependent on the amount of oxygen and water vapor available, the ability of the oil additives to protect the surface, the temperature of the surface, and the degree of corrosion resistance of the metal.

As will be shown later, there is some disagreement as to the exact mechanism of corrosive wear. An alternate explanation is that the oxide particles formed by corrosion are themselves abrasive. Being harder than the steel surface, they give excessive abrasive wear. In either explanation, however, the primary cause is the initial attack of the iron by oxygen.

Diffusion

Preliminary calculations have shown that diffusion could easily be the controlling factor in corrosive wear. The amount of corrosive wear would deplete the oxygen supply at the metal surface, and the rate of diffusion would not be enough to replenish the supply.

However, the actual situation is quite complicated, involving a changing area of corrosion, a very thin layer of liquid, and an oxygen concentration that changes with both direction of travel and film thickness. Hence, a complete mathematical analysis is being made to determine if the reaction is diffusion-limited, and what effect the diffusivity of the liquid may play. This will be in a subsequent section.

B. Literature Articles Pertaining to Corrosive Wear

Baber et al. (5) studied the effect of oxygen in a Ryder gear machine. They took exceptional pains to remove all the oxygen from the system. (They also removed all the moisture, and therefore, did not study the effect of humidity.) The standard Ryder gear procedure was used, which consists of a series of ten-minute steps, each step at a higher load than the preceding step, until 22.5% of the tooth area is scuffed.

With petroleum oils, both with and without antiwear additives, they found a pronounced effect for oxygen. Better performance was always obtained when oxygen was absent. In fact, running in an inert gas gave about the same improvement in scuff load as adding 5% TCP.

They also noted a significant difference in the nature of the surface failure. With air, the failure was predominately scoring or light welding, while with argon there was excessive scuffing and plowing. It appeared that failure in an inert atmosphere required a higher load before it occurred, but once it did occur (as might be expected at the higher load), it was abrupt and severe.

Interestingly, the effect of inert-gas blanketing did not show up with two MIL-L-7808 (ester) oils, nor with two out of three silicone oils.

In a more recent paper (6), the same authors carried out a similar investigation using nitrided gears. These gears are relatively non-corrodible and the results were quite different. Better load-carrying was invariably attained in air than in nitrogen. At higher temperatures, the tests in air showed an additional improved load-carrying capacity -- probably due to oxidation of the oil. In nitrogen, however, higher temperatures gave worse performance -- probably because of the lower viscosity.

Unfortunately, none of the oils run in the first set of experiments were also run in the second, so that an exact comparison cannot be made. Also, none of the oils resemble the relatively high-purity of hydrocarbon fuels so that is is difficult to apply the results to jet fuel problems. However, the importance of metallurgy is clearly shown. In one case, an inert atmosphere is favored; in the other, better results are obtained in air.

Fein and Kreuz (7) used a modified four-ball machine where speeds could be as low as 0.35 rpm and the atmosphere could be controlled by an elaborate seal system. Humidity was not controlled. Runs in air were at ambient humidity, but it may be assumed that in an inert gas the atmosphere was moisture-free. It is not clear whether the runs at intermediate oxygen levels were similarly moisture-free, but the humidity was probably very low. Lubricants were generally highly pure hydrocarbons ranging in viscosity from 0.5 to 1350 cs/100F.

Runs in air showed that paraffinic hydrocarbons gave the highest wear, and aromatics the lowest. For the low viscosity hydrocarbons of all kinds and for the intermediate-viscosity paraffins, the friction increased rapidly shortly after the start of the test, and the wear rate was high for the remainder of the test. The wear product was α-Fe_2O_3. This behavior was termed "seizure" by the authors. Higher-viscosity oils, including squalane (a paraffin), did not behave in this manner. The authors believed this was because the heavier hydrocarbons dissolve less oxygen. There was also a difference in the wear products, paraffins giving iron oxide, and aromatics giving an amorphous solid.

The effect of oxygen content was quite different with squalane than with cyclohexane vapor. With squalane, the wear rate decreased with decreasing oxygen content for loads of 5 and 20 Kg. At 50 Kg load, however, wear jumped 10-fold when the oxygen content in the air was decreased from 21% to 0.5%. This was atributed to seizure resulting from insufficient oxygen.

With cyclohexane vapor, seizure occurred at high oxygen concentrations and disappeared at low. The authors apparently distinguish between two kinds of

"seizure," one occurring at high oxygen concentrations, the other at low. They believe a "friction polymer" forms on the rubbing surface and that this acts as a heavy viscous liquid, separating the two surfaces. This "friction polymer" forms only at intermediate oxygen levels and is dependent of the hydrocarbon type.

Klaus and coworkers (8 , 9) measured wear rates in the four-ball wear tester for a large number of lubricants of different chemical types. Their tests were mostly at three different temperatures (167 to 310F) and were run in both air and nitrogen. Humidity was not controlled.

A clear effect of temperature was found: in a great majority of cases, wear was higher at higher temperatures. The major exception to this rule was the behavior in air of several of the hydrocarbon lubricants, which gave less wear at higher temperatures. The authors noted that oxidation of the hydrocarbon occurred under these conditions and it seems probable that the oxidized hydrocarbon was acting as an anti-wear agent.

The effect of oxygen was generally to increase wear, although in about one-third of the cases the difference was negligible. Wear was lower in oxygen only for the hydrocarbons at the highest temperature. It is not clear whether this was because of the anti-wear action of the oxidized hydrocarbons, or whether there was an abnormal increase in wear in nitrogen at the highest temperature. If the second, it is not clear whether this is a viscosity effect or whether it is due to the absence of oxygen. The authors favor the latter explanation, partly because they had plotted wear rate against dissolved oxygen, rather than against temperature. The amount of dissolved oxygen was found to decrease with increasing temperature, whereas from Henry's Law it should have been about constant. It appears that the small amount of oxygen dissolved under the nitrogen atmosphere reacted with the hydrocarbon before the analysis could be made. The authors concluded that oxygen is an anti-wear agent in very low concentrations, but their proof is somewhat tenuous.

In the absence of any liquid lubricant, the effect of oxygen is also confusing. Bowden and Tabor (10) stress that an oxide film greatly reduces the "galling tendency" of the surfaces. Tabor (11) points out that "oxygen reduces junction growth and thus is generally beneficial. However, if abrasive wear by hard oxides is serious, rapid oxidation may be accompanied by greatly increased wear." Note that this explanation for the increase of wear in oxygen is different than that of corrosive wear.

Cocks (12) studied high-speed sliding in an unlubricated system and similarly concluded that the presence of oxygen decreased both wear and friction. This was true for steel-on-steel. copper-on-steel, and nickel-on-nickel. Glaeser (13) investigated AISI 52100 steel ball bearings both lubricated and dry. When dry, the bearings failed rapidly in an inert atmosphere. When flooded with oil, they were about equivalent in air and inert atmospheres. This makes cooling appear to be the important contribution of the lubricant.

However, Begelinger and deGee (14), studying silver-on-steel, found that oxygen increased both wear and friction. They concluded that the wear mechanism changed from mild abrasive to severe adhesive and that this was due to a reaction between the oxygen and the iron surface. The iron oxide so formed is postulated to increase the adhesion between the iron and silver. This latter behavior appears to be very similar to lubricated results with steel-on-steel.

This review of the literature on the effect of inerting a lubrication system shows the extent of the disagreement in both the data and the interpretation of the data. Whether oxygen and water vapor are helpful or harmful depends on the specific metallurgy, the lubricant, and the operating conditions.

V

EFFECT OF DISSOLVED OXYGEN AND WATER
ON FRICTION AND WEAR: EXPERIMENTAL DATA

The experimental data clearly show that friction and wear of steel sur-
faces are critically dependent on the presence of oxygen and water. The wear
mechanism is believed to be as follows: oxygen dissolves in the fuel; it reacts
with the fresh rubbing surface to form iron oxide; this reaction is accelerated
by water; the oxide is loosely bound and is worn away immediately, exposing a
fresh surface that again oxidizes. In Section XI, a mathematical model of cor-
rosive wear is developed. It shows that the wear can be quantitatively accounted
for by corrosion alone, with no additional wear from abrasion by iron oxide
particles.

Obviously the data obtained with hard steel (AISI 52100), which con-
stitutes most of this report, cannot be applied to all other metallurgies.
Stainless steel, for example, will resist oxygen atack and therefore will not be
so sensitive to corrosion by oxygen and water. Also iron oxide is hard and
abrasive, which is not true of some other metal oxides. The data presented here
should therefore be restricted to steels similar in corrosion resistance to the
steels used in the various tests. However, since hard steels are the most com-
mon material for gears, cams and pumps, the data reported herein are widely ap-
plicable.

A. Modification of Test Instruments

In order to study the effect of dissolved oxygen and water on friction
and wear, each of the test instruments was modified. In all cases, the procedure
was the same: 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%. It was not
dried further for these experiments. For tests at 100% RH, the gas was 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.

1. Ball-On-Cylinder Apparatus

The first modification to the ball-on-cylinder apparatus consisted of
adding a fuel-circulating system, which also allowed the use of higher tempera-
tures. The schematic flow diagram is shown in Figure 4. 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 (Beckman Model No. 777). The test is started when the
oxygen in the fuel, as indicated in the oxygen analyzer, and the temperature reach
a steady state.

- 29 -
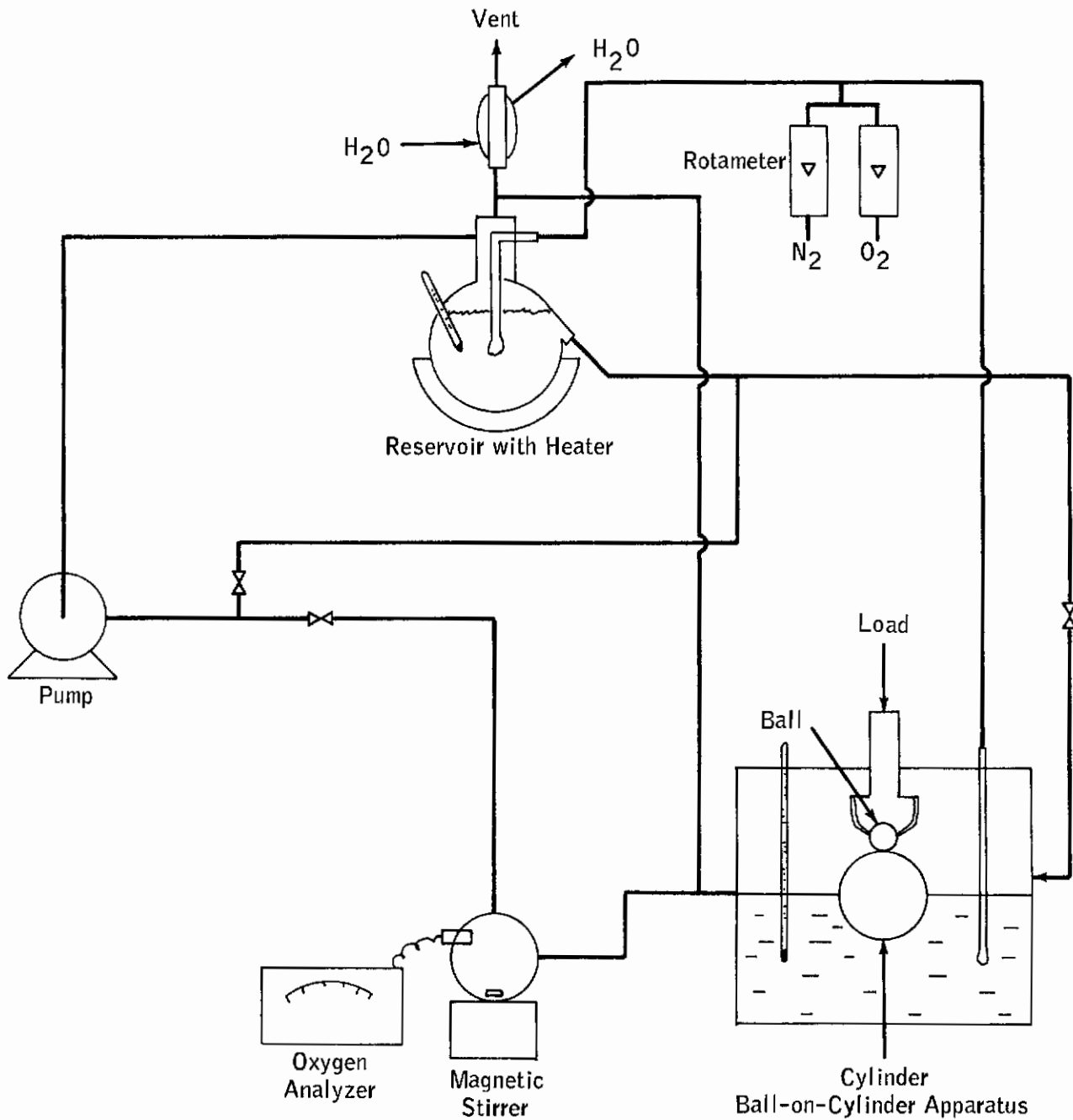
FIGURE 4 - SCHEMATIC DIAGRAM FOR FUEL CIRCULATING SYSTEM OF
BALL-ON-CYLINDER APPARATUS

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:

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

$$4 Ag + 4Cl^- \longrightarrow 4AgCl + 4e^- \text{(at anode)}$$
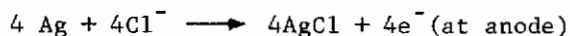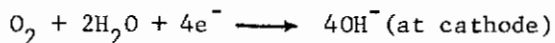
The current in the cell is proportional to the partial pressure of the oxygen present. To calibrate the analyzer, air or nitrogen is bubbled through the fuel at the same temperature at which tests were made. When the analyzer reading stabilizes, actual oxygen content in ppm is determined by gas chromatography. The oxygen content in ppm of any subsequent reading is interpolated from these two determinations.

Later it became obvious that the test fuel was equilibrating very rapidly with the gas environment. A 15-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.

2. Four-Ball Wear Machine

The standard 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.

Later, a G.E.-Brown modification of the four-ball wear tester was obtained. 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 reduce the error to less than 50 g.

3. Vickers Vane Pump Apparatus

To investigate jet fuel lubricity at higher temperatures and under controlled atmospheres, a new pump test stand (Mark II) was built. A schematic flow diagram is shown in Figure 5. 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:

- 31 -
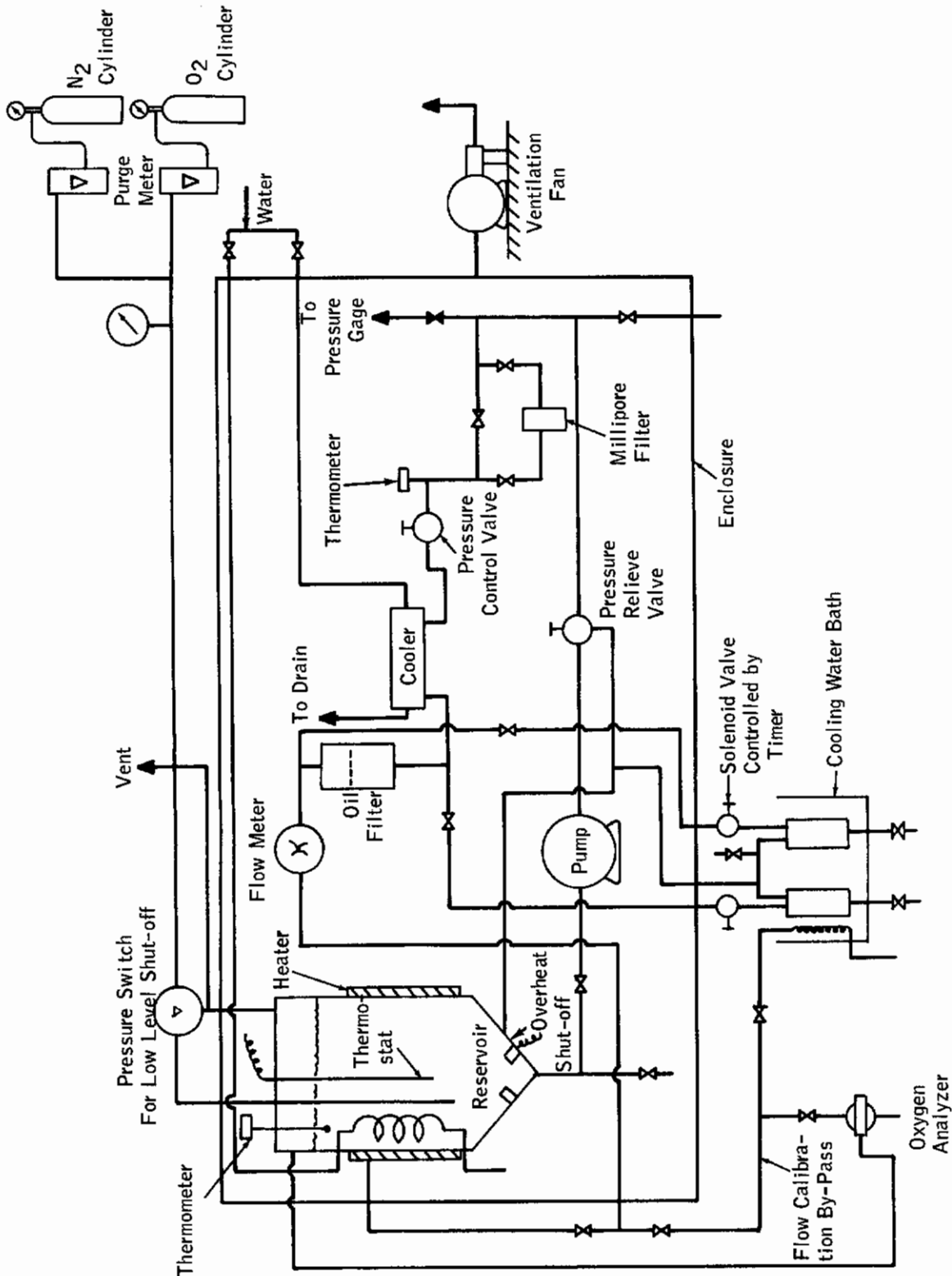
FIGURE 5 - SCHEMATIC DIAGRAM OF JET FUEL PUMP TEST RIG

(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.

B. Effect of Oyxgen Concentration

1. Ball-On-Cylinder Tests

Tests were made on Bayol 35 in an atmosphere containing various concentrations of oxygen at a temperature of 160F. These test results are shown in Table IX and Figure 6. It will be seen that the more oxygen present, the higher the friction and wear. Thus, atmospheric environment is quite critical to the friction and wear properties of fuels.

The friction and the wear in the nitrogen atmosphere (0.7 ppm O_2 in Bayol 35) are not only lower than in air, but are also less dependent on load, as shown in Figure 7. The difference of wear in air and in nitrogen is thus more evident at higher load. The ratio of wear scar diameter in air to that in nitrogen range from 1.4:1 at 120 g load to 2.7:1 at 1000 g load. This may be explained in two ways: (1) at the higher loads, the temperature at the rubbing surface is higher and the oxygen attack is more rapid, and (2) the abrasiveness of the iron oxide particles is greater at the higher pressures and smaller clearances.

2. Vickers Vane Pump Tests

Vickers vane pump tests were made on Bayol 35 in air, nitrogen, and a controlled atmosphere of 7% oxygen. Test results are shown in Table X. During the run with air, an operating difficulty was encountered: pressure control valve (throttle valve) could not hold the pressure at 350 psig. The test was therefore run at 300 psig. for 22 hours. The wear (about 3000 mg) was again severe, confirming the previous results which showed a high severity of wear with Bayol 35 in air. In nitrogen atmosphere, although a small trace of oxygen (about 1 ppm) could not completely be driven off from the fuel, the wear was strikingly low, only 3 mg. Under a controlled atmosphere of 7% oxygen, the wear was only 270 mg. These results agree with the ball-on-cylinder test that wear becomes more severe at higher oxygen concentration, but the increase of wear in a Vickers vane pump was more abrupt when the oxygen concentration was increased from 17 ppm (exposed to 7% oxygen) to 52 ppm (exposed to air).

These tests confirm the findings of the ball-on-cylinder tests and suggest that inerting the gas over the fuel might be a practical way of reducing friction and wear problems in the field.

C. Effect of Water

1. Four-Ball Tests

Since oxygen increases wear by a corrosion process, it would be likely that this corrosion would be accelerated by the presence of dissolved water. This was first confirmed by a series of four-ball wear tests run in air using heptane as the test liquid. In these tests, a layer of liquid water was put in the bottom of the test cup. This insured that the heptane was saturated

TABLE IX

EFFECT OF OXYGEN ON WEAR OF BAYOL 35

Ball-on-Cylinder Tests (240rpm, 32min, 160F)

O_2 in Bayol 35, ppm	Load, g:	Wear Scar Diameter, mm				Coefficient of Friction			
		1000	480	240	120	1000	480	240	120
52 (in air)		0.57	0.34	0.30	0.25	0.27*	0.16*	0.15*	0.18*
17		0.41	0.30	0.28	0.24	0.16*	0.17*	0.17*	0.18*
5.0		0.30	0.23	0.20	0.18	0.16*	0.18*	0.19*	0.18*
2.5		0.26	0.23	0.20	0.17	0.17*	0.13	0.11	0.11
0.7 (in N_2)		0.21	0.19	0.18	0.18	0.14	0.12	0.11	0.12

* Friction trace erratic.
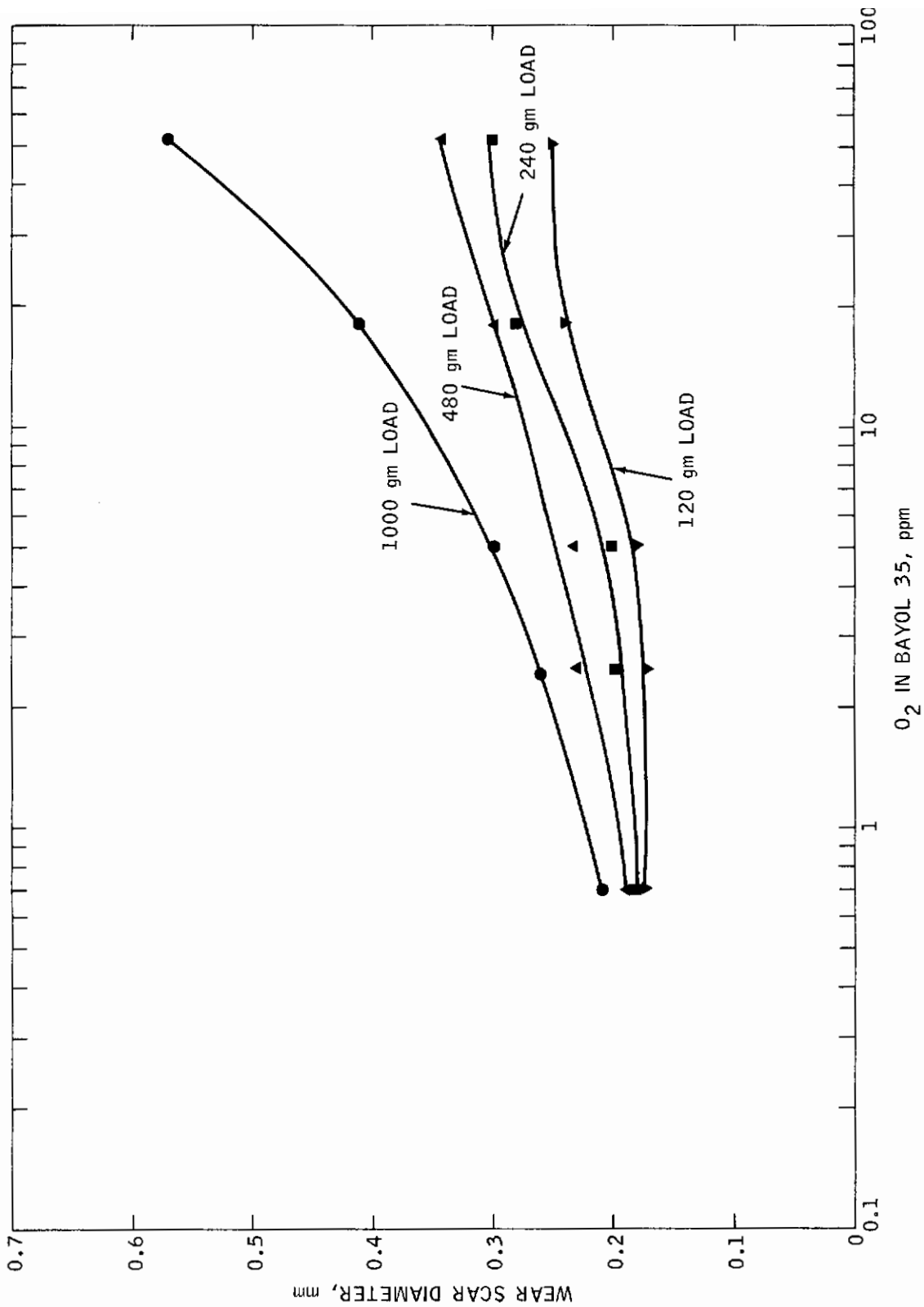
FIGURE 6 - WEAR VS OXYGEN CONCENTRATION FOR BAYOL 35:
BALL-ON-CYLINDER TESTS AT 160F
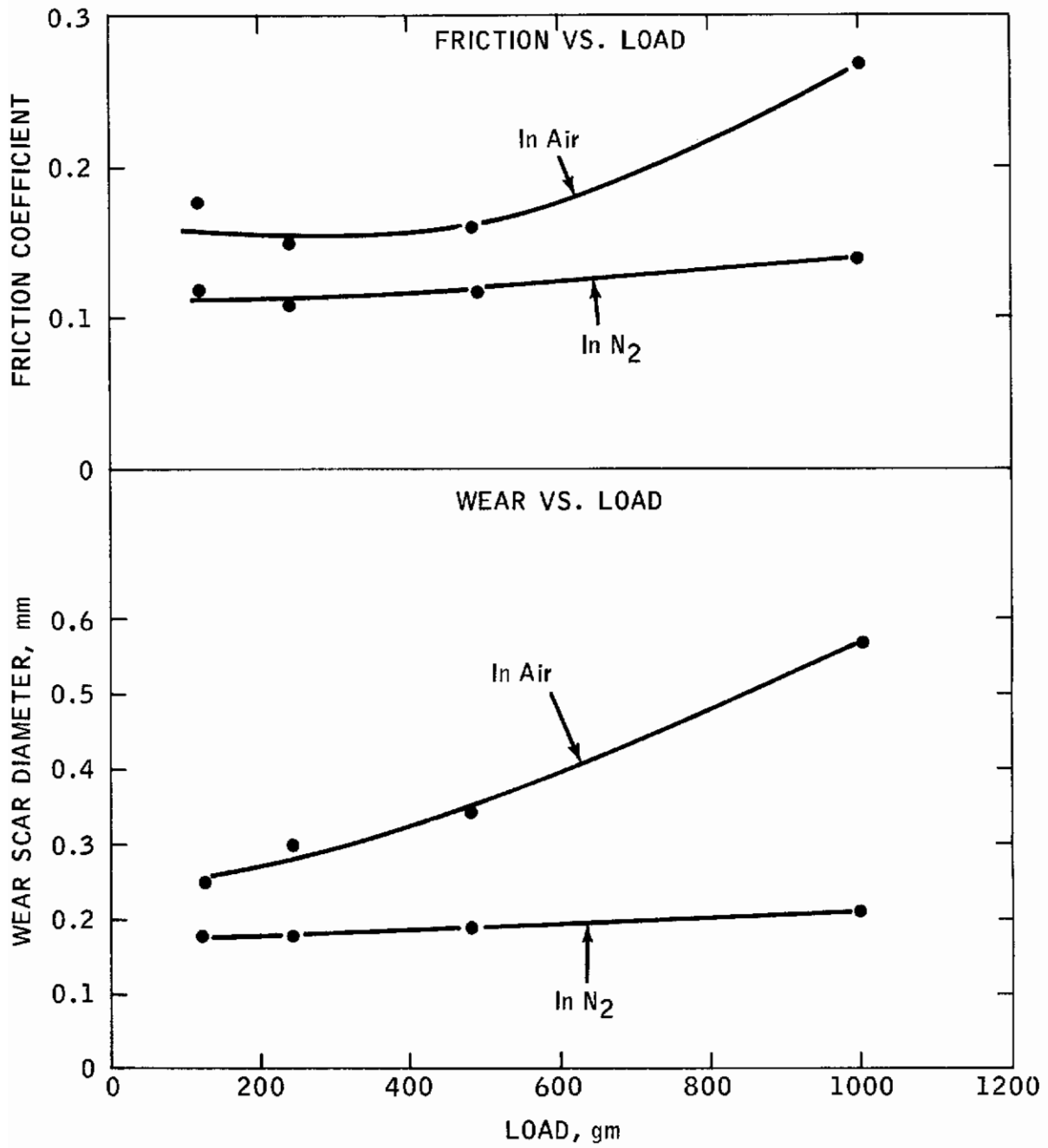
FIGURE 7 - FRICTION AND WEAR VS LOAD FOR BAYOL 35:
BALL-ON-CYLINDER TESTS AT 160F

TABLE X

EFFECT OF OXYGEN CONCENTRATION IN VICKERS VANE PUMP TESTS

Fuel: Bayol 35

Atmosphere	Mark II			Mark I
	N_2	7% O_2	Air	Air
O_2 in Fuel, ppm	1.3	17	52	52
Pressure, psig	350	350	300*	350
Sump Temperature, °F	90	90	90	90
Pumping Rate, gpm	0.72	0.62	00.52	0.43
Vol. Efficiency, %	40	34	29	24
Wear, mg				
Wt. Loss of Vanes	3.3	44	272	204
Wt. Loss of Ring	0	227	2,848	5,150
Total Wt. Loss	3.3	271	3,120	5,354
Surface Roughness, CLA, μ"				
Vanes, Initial	20	18	19	4
Final	38	96	122	96
Ring, Initial	13	8	11	16
Final	8	24	144	96

* Pressure could be held at 300psig due to operating difficulty of
pressure control valve.

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with water throughout the test.

The effect of this dissolved water is shown in Figure 8. The wear
scar diameter increased by 40%, corresponding to an increase in wear rate (grams/
minute) of 4-fold.

This result made it obvious that the relative humidity of the at-
mosphere around the test is a very important variable: The amount of water that
will dissolve can be expected to depend on the partial pressure (i.e., the humidity)
of the surrounding atmosphere.

2. Ball-On-Cylinder Tests

The effect of water in the four-ball test was confirmed in the ball-
on-cylinder apparatus. Bayol 35 was run in air at various humidities: 0, 26, and
100% RH. The friction and wear results are compared in Table XI, along with a
test in dry argon. Both wear and friction increased markedly at the higher humid-
ities. The run in room air (26% RH) resembled that in saturated air (100% RH).

As a result of this preliminary study, all subsequent tests, whether
ball-on-cylinder, four-ball or Vickers vane pump, were run under a controlled
atmosphere. Usually these were one of the four extremes: dry inert, wet inert,
dry air, or wet air. Intermediate humidities and intermediate oxygen concentra-
tions were not studied, with a few exceptions. Often the run in the wet inert
atmosphere was omitted, since this run supplied little additional information in
most cases.

D. Effect of Dissolved Water and Oxygen With Commercial Fuels

Because of the importance of both oxygen and water vapor in the sur-
rounding atmosphere, the commercial jet fuels were evaluated once again, this time
under the four combinations of wet air, dry air, wet argon, and dry argon. Pre-
vious data had been obtained in room air -- 21% oxygen and uncontrolled humidity.

Five commercial fuels were chosen (PW-523, RAF-176-64, JP-4, JP-5,
and Bayol 35) and were run at loads of 240g, 480g, and 1000g at a temperature of
160F.

The test results are shown in Table XII and the wear scar diameters
versus loads are plotted in Figures 9 through 13. Several common friction and
wear phenomena among these fuels are noteworthy: (1) friction and wear are higher
in air than in argon for both dry and wet conditions; (2) friction and wear in
argon are not only lower but also less dependent on load than in air, so that the
differences between air and argon is more evident at higher loads; (3) wear in wet
air is higher than in dry air; and (4) the difference in friction and wear in dry
and wet argon is rather small, indicating that moisture may not be detrimental in
an inert atmosphere.

These results again showed that the highly-refined fuels give higher
wear than other commercial fuels in air: in wet air, PW-523 and Bayol 35 gave
appreciably higher wear than other fuels, both at 480g and 1000g; in dry air,
PW-523 consistently gave higher wear at all loads. In argon, the highly-refined
fuels did not appear to be inferior to other fuels. On the contrary, JP-5 and
RAF-176-64 gave slightly higher wear than the other two fuels in wet argon at

FOUR-BALL WEAR TESTS
1200 rpm, 10 kg, 36°C
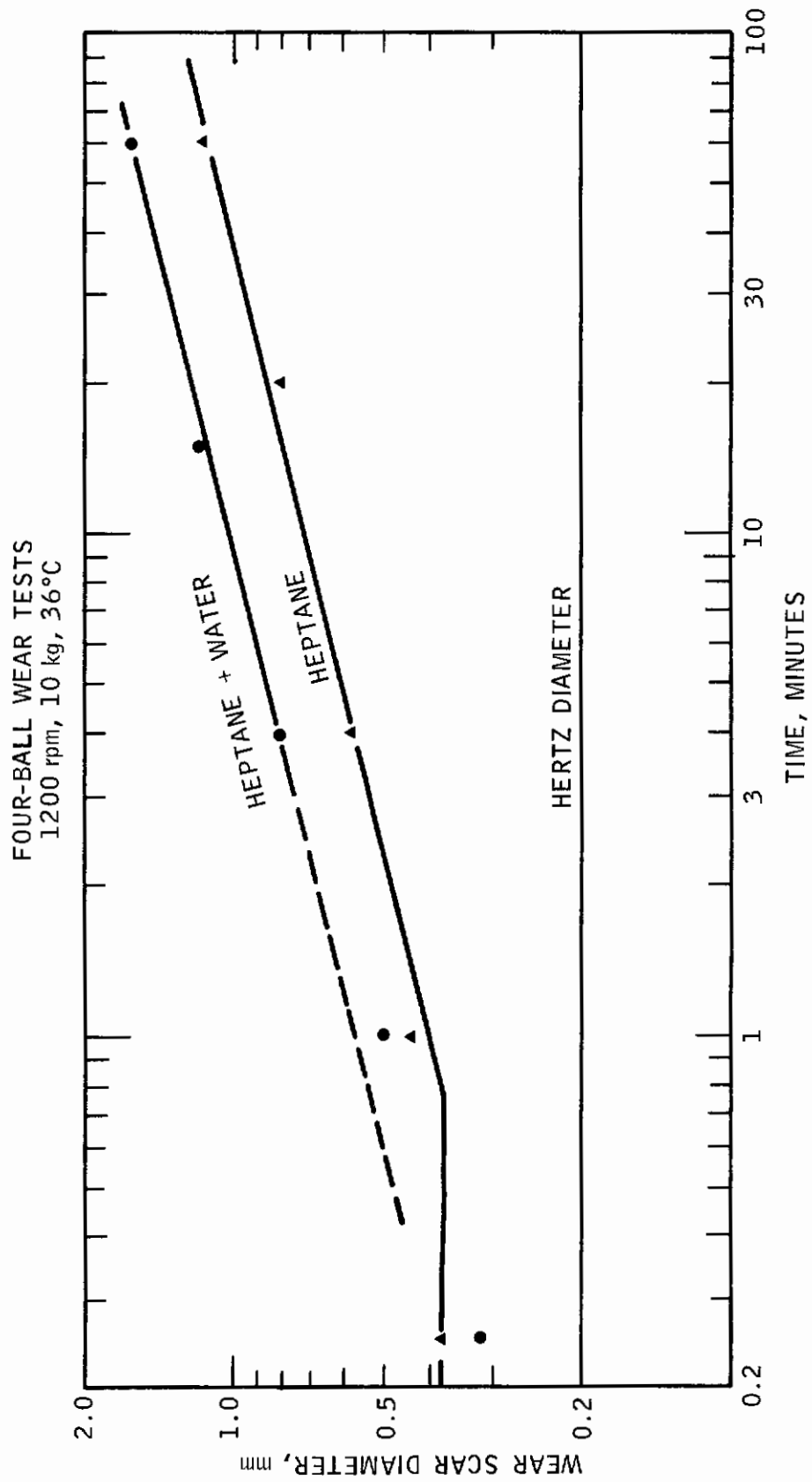
FIGURE 8 - EFFECT OF WATER ON WEAR FOR HEPTANE: FOUR-BALL TEST

TABLE XI

EFFECT OF ATMOSPHERIC MOISTURE ON WEAR OF BAYOL 35

Ball-on-Cylinder Tests (1000 gm Load, 240 rpm, 160°F., 32 min.)

Atmosphere	% RH	Coef. of Friction	Wear Scar Dia., mm
Argon	0	0.13	0.28
Dry Air	0	0.14	0.41
Open Air	26	0.24*	0.59
Wet Air	100	0.23*	0.65

* Friction trace very erratic.

TABLE XII

FRICTION AND WEAR OF COMMERCIAL FUELS IN VARIOUS ATMOSPHERES

Ball-On-Cylinder Tests (160F, 240 rpm, 32 min)

| | 240g Load | | | | 480g Load | | | | 1000g Load | | | |
| | Argon | | Air | | Argon | | Air | | Argon | | Air | |
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Wear Scar Dia, mm												
Bayol 35	0.24	0.23	0.26	0.33	0.24	0.23	0.40	0.63	0.25	0.24	0.41	0.75
JP-5	0.20	0.21	0.21	0.44	0.25	0.25	0.35	0.44	0.30	0.39	0.44	0.56
RAF-176-64	0.17	0.21	0.23	0.31	0.26	0.23	0.34	0.38	0.28	0.33	0.44	0.48
PW-523	0.19	0.22	0.39	0.50	0.30	0.25	0.42	0.58	0.24	0.27	0.56	0.67
JP-4 (at 120F)	0.20	0.20	0.21	0.26	0.20	0.21	0.22	0.54	0.24	0.28	(c)	(c)
Coeff. of Friction												
Bayol 35	0.13	0.10	0.14	0.12	0.15	0.12	0.19	0.18	0.17	0.18	0.14	0.28[a]
JP-5	0.14	0.16	0.32	0.21	0.14	0.15	0.23	0.18	0.19	0.17	0.60[a]	0.52[a]
RAF-176-64	0.06	0.12	0.20	0.12	0.12	0.12	0.15	0.16	0.12	0.14	(a)	0.16[a]
PW-523	0.19[b]	0.19[b]	0.11	0.27	0.15[b]	0.16[b]	0.11	0.19	0.13[b]	0.15[b]	0.38[a]	0.30[a]
JP-4 (at 120F)	0.12	0.15	0.11	0.12	0.12	0.15	0.14	0.17	0.24	0.17	(c)	(c)

Notes:

(a) Friction trace erratic.

(b) A defect of the spring was found after tests; friction readings may be in some error.

(c) Tests discontinued due to the excessive friction.
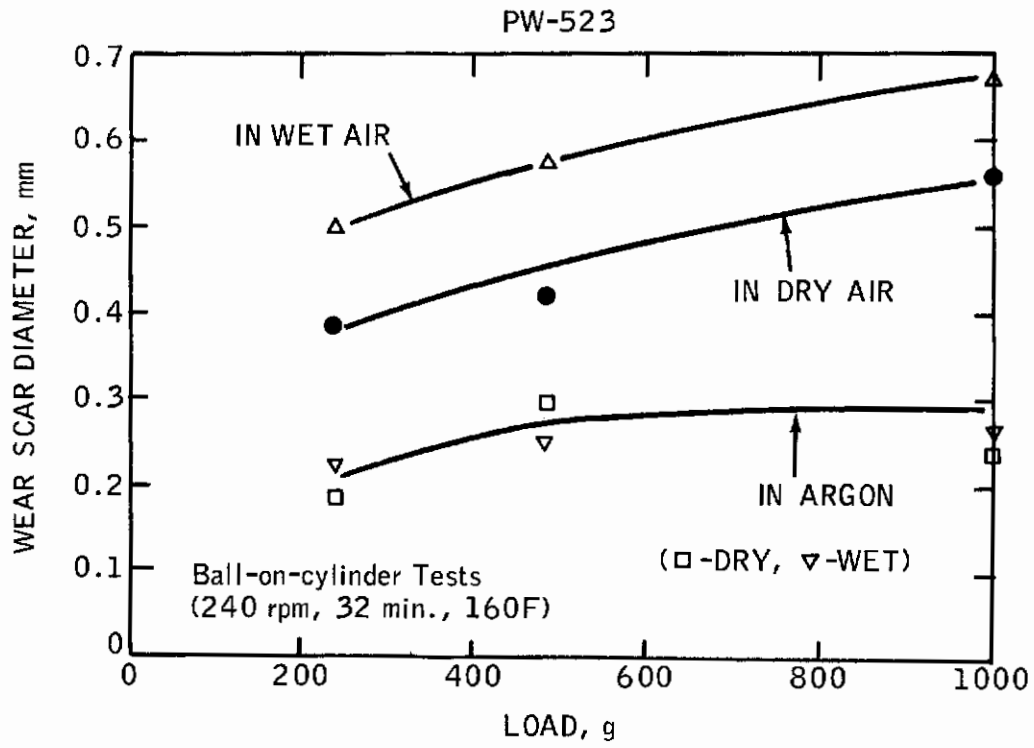
FIGURE 9 - EFFECT OF ATMOSPHERE ON WEAR OF PW-523
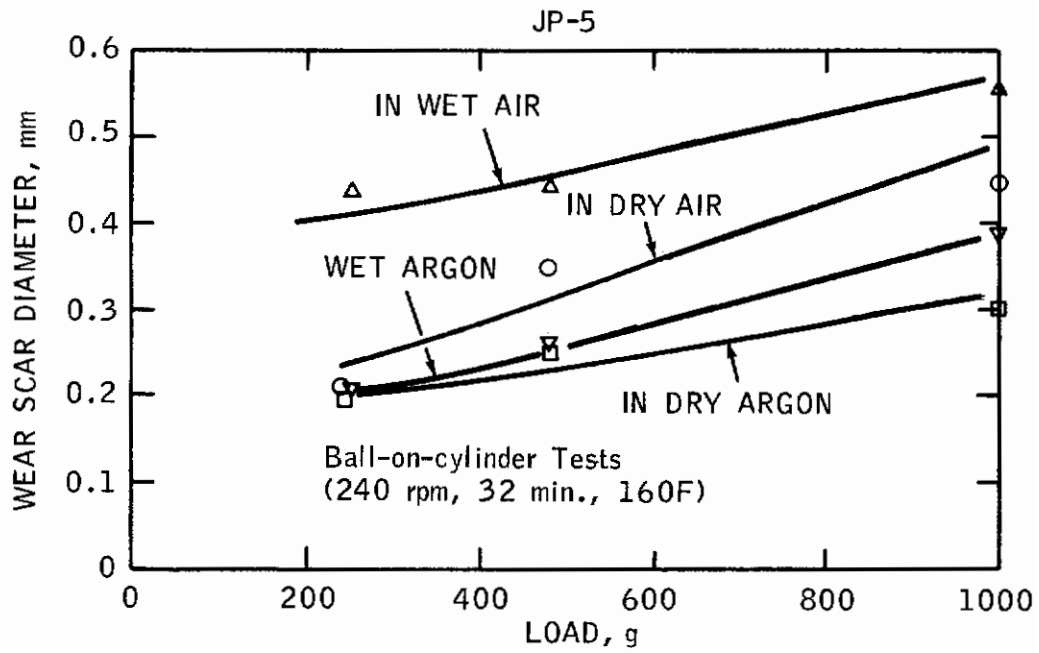
FIGURE 10 - EFFECT OF ATMOSPHERE ON WEAR OF JP-5
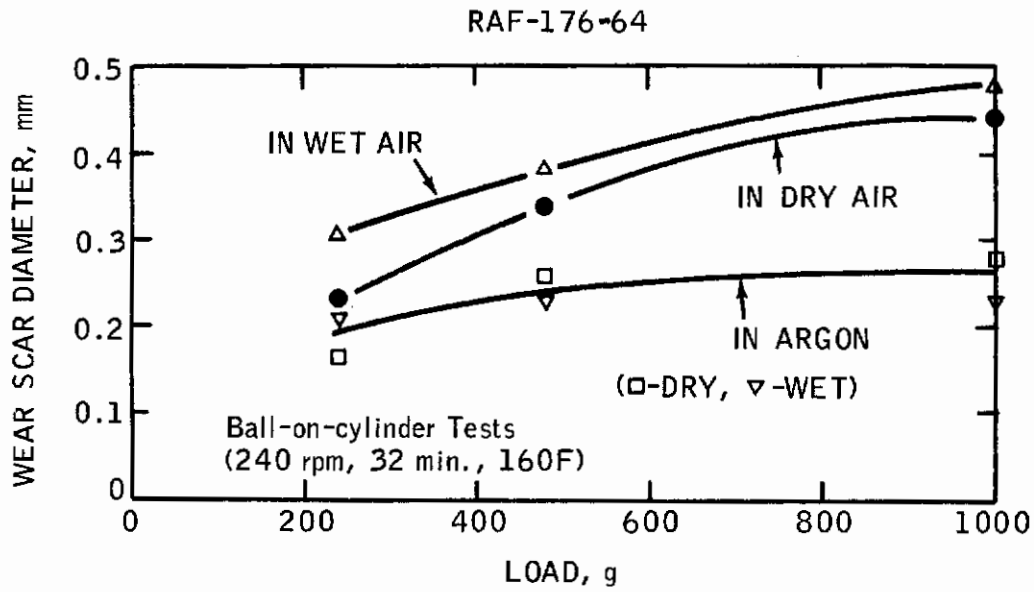
RAF-176-64

FIGURE 11 - EFFECT OF ATMOSPHERE ON WEAR OF RAF-176-64

JP-4
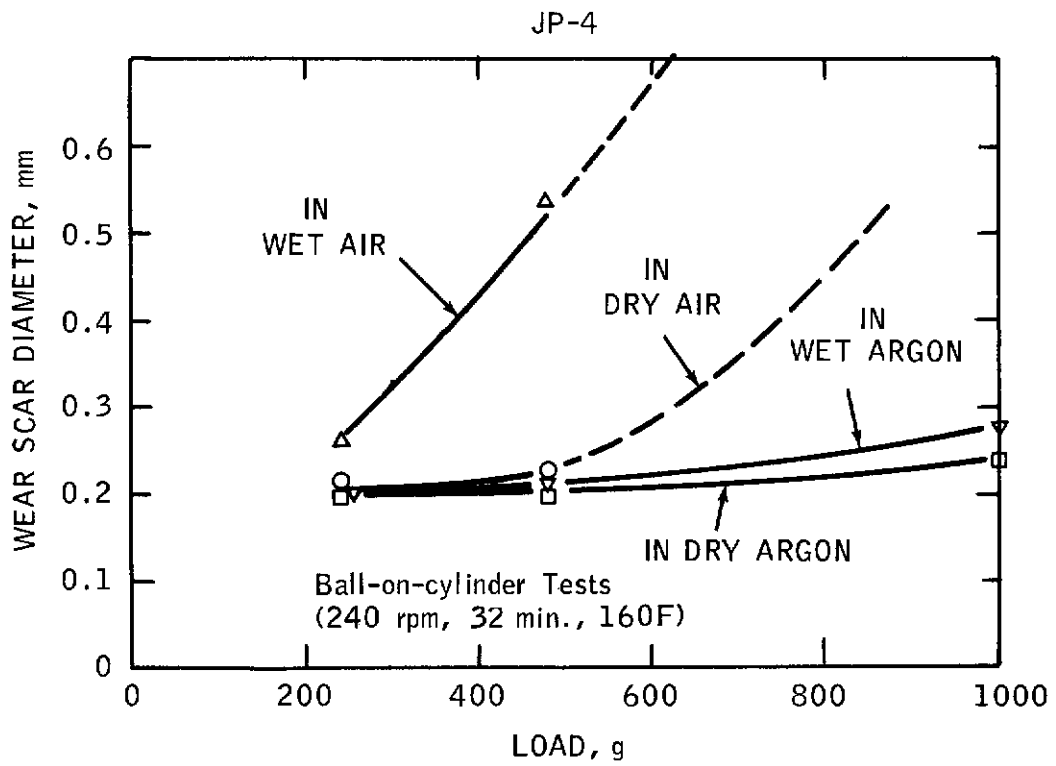
FIGURE 12 - EFFECT OF ATMOSPHERE ON WEAR OF JP-4
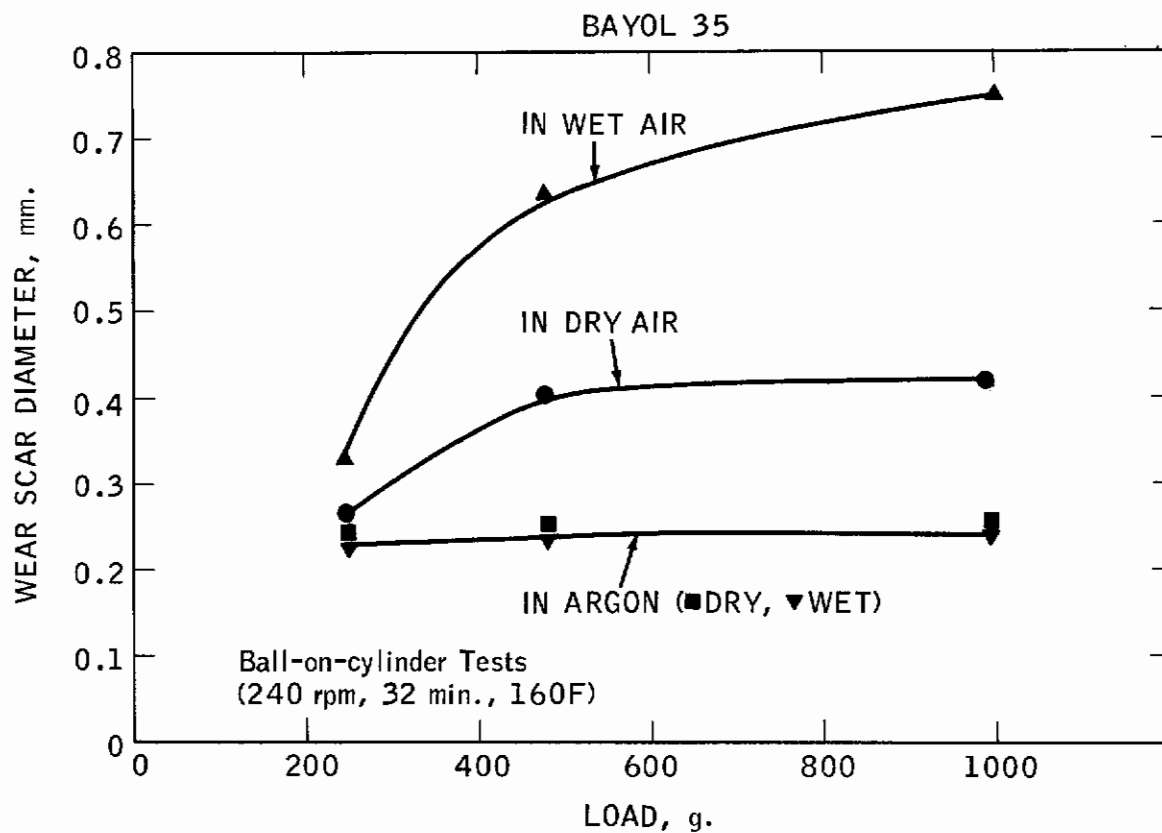
BAYOL 35

FIGURE 13 - EFFECT OF ATMOSPHERE ON WEAR OF BAYOL 35

1000g load. This difference, although not highly significant, is rather anomalous. JP-4, which has a lower viscosity than the other fuels, could not be run at 1000g in air because of excessive friction. At lower loads, it gave fairly low wear and friction.

The effect of oxygen and water will be further shown in Section VIII, which deals with higher temperature tests.

E. Pure Hydrocarbons

Because of the effect noted in Section II that heavy aromatics had unusual lubricity characteristics, several pure hydrocarbons were evaluated, covering all chemical types. The major conclusion from this work is that condensed-ring aromatics (i.e. derivatives of naphthalene, anthracene and phenanthrene) are unique in their friction and wear behavior.

1. Paraffins and Purified Paraffins

Ball-on-cylinder tests were also run on four paraffinic hydrocarbons ranging from C_6 (hexane) to C_{16} (cetane), viscosity 0.31 cp to 3.5 cp/77F. Hexane and octane were chromatographic grade reagent; dodecane was a reagent of 99%+ purity (olefin free) and cetane was of ASTM purity (olefin free 97.5% C_{16}). Tests were carried out at room temperature and various atmospheres. Table XIII shows the results of two series of tests. In the first series the hydrocarbons were tested as received; in the second series, they were passed through a silica-gel column before tests. This treatment removes the last traces of polar materials.

As shown in Figure 14, wear for the as-received compound decreased with an increase in viscosity. However, this might be due to differences in relative purity, the lower viscosity compounds being more pure than the higher. After silica-gel treatment, the differences in wear among these hydrocarbons became much less. This indicates that corrosive wear is more sensitive to the presence of trace polar components than to viscosity differences. This would be expected.

These data also point out that the effect of higher temperature is more than a viscosity-thinning effect. The viscosities of octane and hexane simulates those of jet fuels at about 230F and 350F, respectively. As seen from Figure 14, there was no appreciable difference of wear between these two fuels and dodecane which is in the jet fuel range.

2. Light Hydrocarbons

Six other hydrocarbons, as shown in Table XIV, were selected to represent six different chemical structures: paraffin, isoparaffin, naphthene, alkyl naphthene, aromatic, and alkyl aromatic. These hydrocarbons were chromatographic grade reagent, having a viscosity of about 0.7 cs which simulates the viscosity of jet fuels at about 200F. These tests were made at room temperature and in various atmospheres. The results indicate that these light hydrocarbons, regardless of their molecular structure, give the highest wear in wet air, high wear in dry air, and the lowest wear in argon. No anomalous phenomenon was observed in testing these aliphatic one-ring hydrocarbons.

3. Two-Ring Hydrocarbons

Table XV shows the results from ball-on-cylinder tests on various two-ring hydrocarbons. These hydrocarbons represent three different types of poly-

TABLE XIII

EFFECT OF VISCOSITY AND PURITY OF PARAFFINIC HYDROCARBONS

(Ball-on-Cylinder Tests, 240 g, 240 rpm, 32 min, 77F)

Hydrocarbons	Viscosity cp @ 77F	Coeff. of Friction			Wear Scar, mm		
		Dry Argon	Dry Air	Wet Air	Dry Argon	Dry Air	Wet Air
Hexane, C_6	0.31	0.15	0.22	0.23	0.29	0.62	0.95
Octane, C_8	0.49	0.14	0.19	0.22	0.22	0.45	0.75
Silica Gel Treated		0.14	*	*	0.18	0.71	0.89
Dodecane, C_{12}	1.37	0.10	0.14	0.15	0.17	0.39	0.43
Silica Gel Treated		0.10	*	*	0.16	0.70	0.84
Cetane, C_{16}	3.42	0.10	0.14	0.15	0.20	0.24	0.38
Silica Gel Treated		0.10	*	*	0.23	0.52	0.66

*Friction very erratic.

BALL-ON-CYLINDER TESTS
(240g, 32 min., 240 rpm)
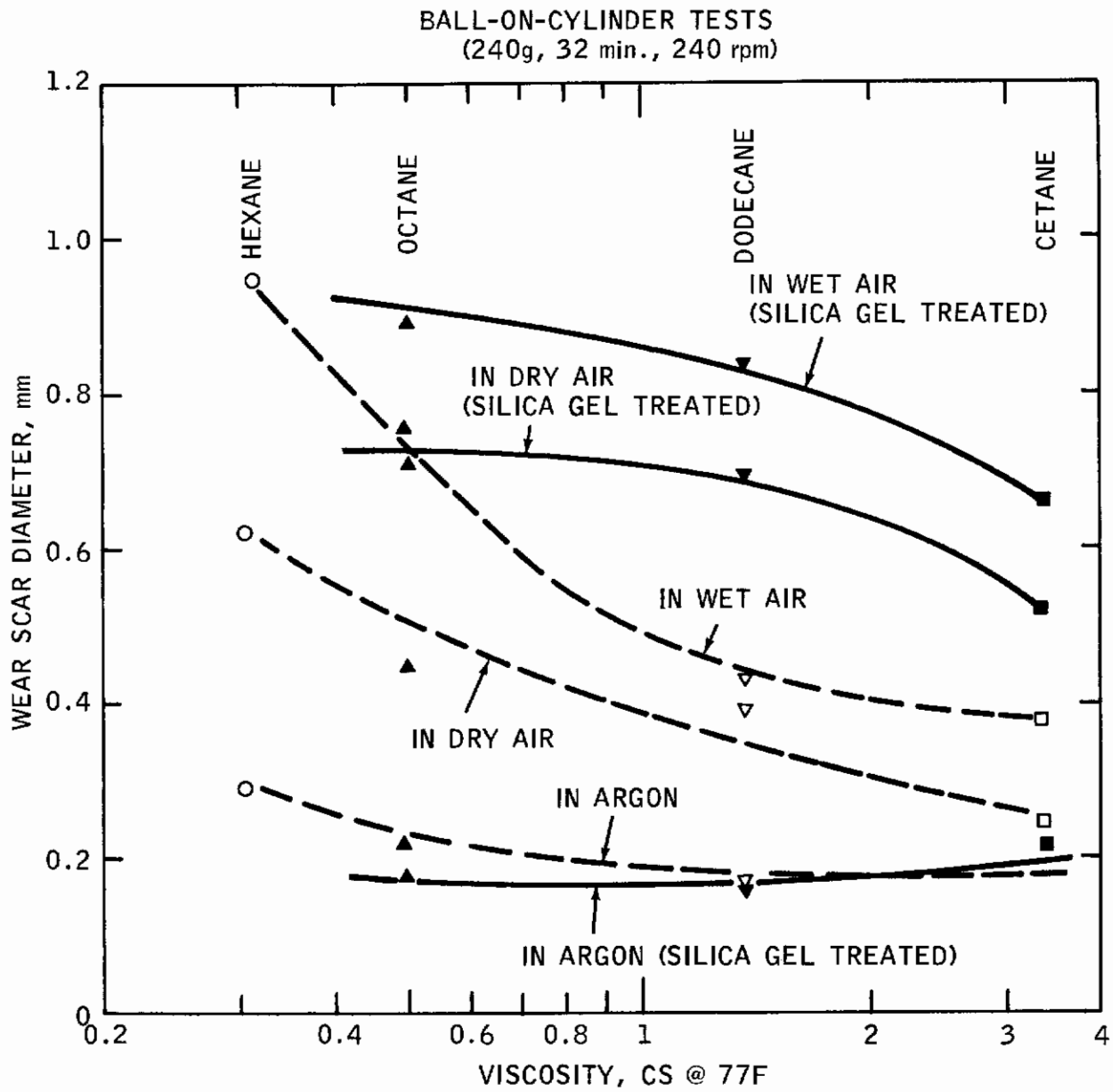
FIGURE 14 - EFFECT OF VISCOSITY AND PURITY OF PARAFFINS

TABLE XIV

EFFECT OF HYDROCARBON TYPE

(Ball-On-Cylinder Tests, Steel-On-Steel; 240 g Load, 240 rpm, 32 Min, 80°F)

Cylinder No.	Hydrocarbons	Vis. cs @ 77°F	Coefficient of Friction			Wear Scar, mm		
			Argon	Dry Air	Wet Air	Argon	Dry Air	Wet Air
203	n-Octane	0.74	0.13	0.20	0.20	0.21	0.45	0.74
356	2,2,4 Trimethyl-pentane	0.69	0.13	0.26	0.22*	0.23	0.76	0.85
203	Cyclohexane	1.13	0.12	0.20	0.20*	0.19	0.74	0.82
203	Methylcyclopentane	0.61	0.13	0.25	0.55*	0.25	0.73	0.92
203	Benzene	0.68	0.15	0.19	0.23*	0.23	0.52	0.92
203	Toluene	0.63	0.12	0.16	0.23*	0.22	0.49	0.85

* Friction trace erratic.

TABLE XV

EFFECT OF TWO-RING HYDROCARBONS

(Ball-On-Cylinder Tests, Steel-On-Steel, 1000 gm Load, 240 rpm, 32 Min, 80°F)

Cylinder No.	Hydrocarbons	Molecular Formula	Vis. cs @ 77°F	Coefficient of Friction			Wear Scar, mm		
				Argon	Dry Air	Wet Air	Argon	Dry Air	Wet Air
330	Decalin		2.87	0.12	0.14	0.16*	0.26	0.35	0.42
295	Isopropyl-bicyclohexyl		9.46	0.11	0.11	0.10	0.24	0.24	0.35
303	Dimethano-decalin		11.50	0.11	0.11	0.10	0.21	0.29	0.41
330	Phenyl-cyclohexane		2.70	0.13	0.14	0.16	0.31	0.33	0.50
303	Tetralin		2.10	0.13	0.16	0.19	0.25	0.42	0.68
303	Indane		1.52	0.13	0.13	0.17	0.30	0.31	0.42
323	Diphenyl-methane		2.90	0.12	0.12	0.17	0.29	0.43	0.62
303	Methyl-naphthalene		2.65	0.17	0.11	0.13	0.82	0.33	0.36
323	Indene		1.71	**	0.15*	0.14	0.93 (1.05)	0.72 (0.90)	0.33 (0.35)

* Friction trace erratic.

nuclear compounds with various degrees of unsaturation. In the first group, both rings are saturated; in the second group, one ring is saturated, the other aromatic; in the third group, both rings are aromatic.

These compounds showed the same general behavior as the lower-viscosity compounds, giving the lowest wear in dry argon and the highest wear in wet air. However, they did not appear to be so sensitive to atmosphere; wear in wet air was about double that in dry argon, whereas with the lower-viscosity compounds it was about four times higher. Part of this difference may be due to a difference in purity: these hydrocarbons were technical grade reagent rather than chromatographic grade.

Two important exceptions to the above behavior were noted. Methyl naphthalene and indene both gave high wear in dry argon and much lower wear in wet air. This behavior has been extensively investigated and is reported separately in Section VI.

4. Olefins

Ball-on-cylinder tests were made on various olefins, including aliphatic alkenes, cycloalkenes, and olefinic aromatics. The results are presented in Table XVI. The most striking difference is that the olefins give much lower wear in dry air than in wet air, as shown in Figure 15. In dry air, the alkenes gave less wear than the alkanes, but in wet air there was no appreciable difference. A direct comparison of wear for the corresponding pairs is shown below:

| | Wear Scar, mm | | |
Hydrocarbon	Argon	Dry Air	Wet Air
Octane	0.21	0.62	0.74
Octene-1	0.19	0.33	0.86
Cyclohexane	0.24	0.73	0.79
Cyclohexene	0.31	0.31	0.75
2,2,4-Trimethyl-pentane	0.23	0.76	0.85
2,5-Dimethyl-1,5-hexadiene	0.23	0.25	0.94

Table XVI also shows that olefinic cycloalkenes give less wear not only in dry air but also in wet air. It is noteworthy that bicyclo-(2,2,1)-heptadi(2,5)ene and methyl styrene gave less wear in both dry and wet air than aliphatic alkanes and alkenes, and that this advantage was retained at a higher load (1000 gm vs 240 gm). This indicates the chemical structure of the unsaturated groups may be important for reduction of corrosive wear.

It is known that olefinic hydrocarbons are more readily oxidized than paraffinic hydrocarbons and their oxidation rates are dependent upon the bond structure. According to the published data of oxidation rates for some hydrocarbons (refer to Scott, G., "Atmospheric Oxidation and Antioxidants," Elsevier Publiching Company, Amsterdam, 1965), the relative molar rate for α-methyl styrene and octene-1 is 200:2.4. It seems that the difference in reactivity toward oxygen may be a contributing factor for their difference in reducing the corrosive wear. The relative oxidation rates for these hydrocarbons were estimated by

TABLE XVI

EFFECT OF OLEFINIC HYDROCARBONS

(Ball-On-Cylinder Tests, Steel-On-Steel, 240 rpm, 32 Min, 77°F)

Cylinder No.	Hydrocarbons	Vis. cs @ 77°F	Load gm	Coefficient of Friction			Wear Scar, mm		
				Argon	Dry Air	Wet Air	Argon	Dry Air	Wet Air
181	n-octane	0.74	240	0.13	0.20	0.20*	0.21	0.62	0.74
181	2,2,4 Trimethyl-pentane	0.69	240	0.13	0.26*	0.22*	0.23	0.76	0.85
213	Cyclohexane	1.13	240	0.13	0.22	0.20*	0.24	0.73	0.79
181	Octene-1	0.66	240	0.13	0.18	0.22*	0.19	0.33	0.86
181	2,5 Dimethyl-1,5-hexadiene	0.63	240	0.13	0.16	0.27*	0.23	0.25	0.94
213	Cyclohexene	0.76	240	0.22	0.23	0.22*	0.31	0.31	0.75
323	Bicyclo(2,2,1)heptadi(2,5)ene	0.93	240	0.15	0.16	0.18*	0.25	0.38	0.47
213	4-Vinyl cyclohexene	0.79	240	0.11	0.12	0.19*	0.18	0.19	0.32
234	Bicyclo(2,2,1)heptadi(2,5)ene	0.93	1000	0.21*	0.19*	0.13*	0.24	0.40	0.39
234	α-Methyl styrene	0.95	1000	0.15*	0.14*	0.18*	0.28	0.28	0.44
234	Ar-Methyl styrene	0.87	1000	0.14	0.11	0.17*	0.42	0.25	0.44

* Friction trace erratic.
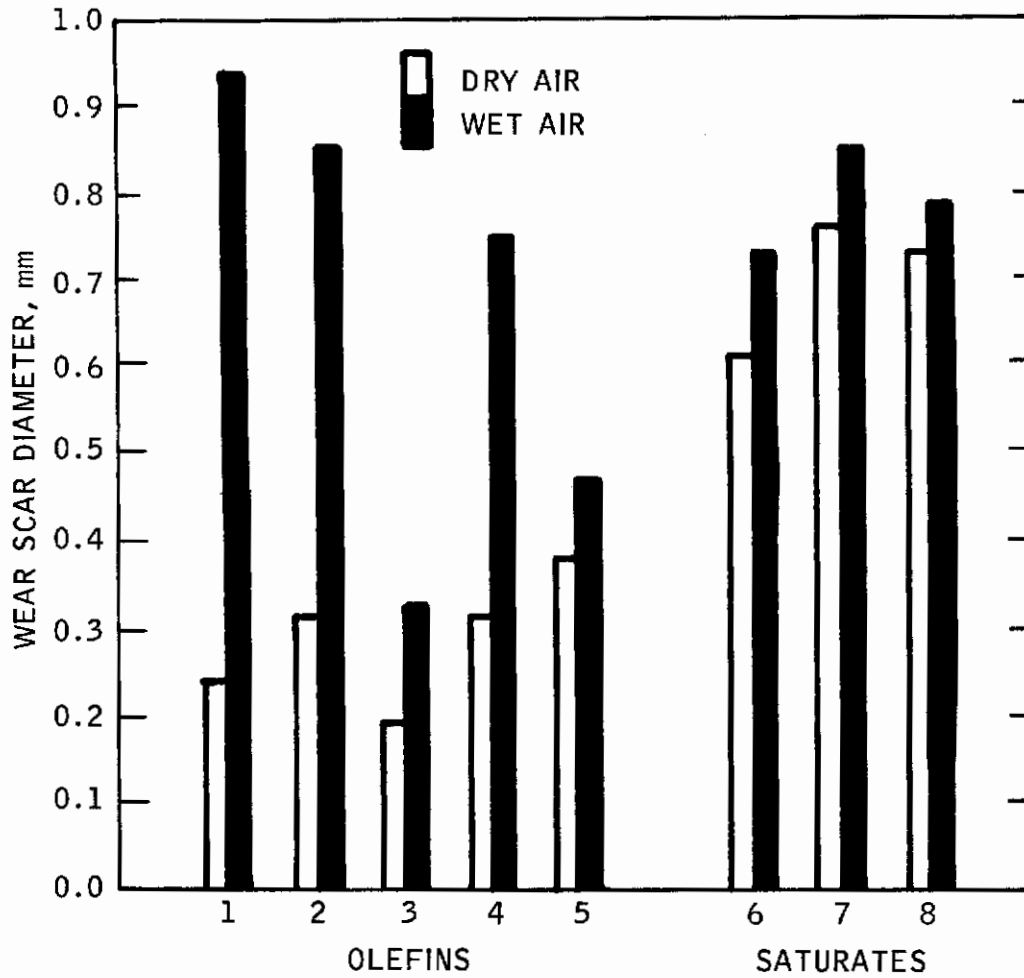
Legend:

1) 2-5 dimethyl-1,5-hexadiene
2) octene-1
3) 4-vinyl-cyclohexane
4) cyclohexene
5) bicyclo(2,2,1)-heptadi(2,5)ene
6) octane
7) 2,2,5-trimethylpentane
8) cyclohexane

FIGURE 15 - WEAR IN DRY AIR AND WET AIR FOR LIGHT HYDROCARBONS

Boland's empirical rule (refer to Boland, J. L., Trans. Faraday Soc., 46, 1950) and are shown below together with some published experimental data:

| Hydrocarbon | Relative Oxidation Rate[1] | | Wear Scar Diameter, mm |
	Calculated	Experimental	@ 240 g in Wet Air
Octene-1	1	1	0.86
2,5-Dimethyl-1,5-hexadiene	2.6	2.5*	0.94
Cyclohexene	11.1	10.3	0.75
4-Vinyl-cyclohexene	350	--	0.32
Bicyclo(2,2,1)-heptadi(2,5)ene	1160	--	0.47 (0.39)**
α-Methyl-styrene	--	83	0.44**
Alkane (n-decane)	--	0.1	--

---

(1) From G. Scott (See text)

 * Experimental data for diallyl
** Wear at 1000 g load

Note that the olefins that have the highest oxidation rate are the most effective in reducing corrosive wear. It is conceivable that there may be less corrosive wear in hydrocarbons having higher oxidative reactivity, because of either their competitive reaction with oxygen to ease the oxygen attack to the metal surface, or more probably, the formation of polar components in oxidation for wear protection.

VI

WEAR BEHAVIOR OF CONDENSED-RING AROMATICS

In Section II it was reported that heavy aromatics were the compounds responsible for the good lubricity of jet fuels. In Section V, methylnaphthalene and indene were shown to be unique, giving very high wear in dry inert atmospheres. As a result, the behavior of condensed-ring aromatics has been studied at some length. Most of this work has been done with 1-methylnaphthalene, which is a liquid at room temperature.

Two separate phenomena involving the condensed-ring aromatics have been investigated: (1) the high wear found with the pure compounds in the absence of water and oxygen, and (2) the low wear found with mixtures of these materials and paraffins. Although the data have been amply confirmed in each case, no satisfactory explanation is available as yet that accounts for all the experimental data.

A. High Wear in Dry Inert Atmospheres

1. Experimental Data

The first tests on methylnaphthalene were a comparison with Bayol 35 in dry nitrogen and room air. Methylnaphthalene and Bayol 35 have almost the same viscosity, so that the comparison is that between a wholly condensed-ring aromatic and a wholly non-aromatic fuel.

Table XVII presents the results of two series of tests. In the first series, three loads and two atmospheres were used. In room air, Bayol 35 and methylnaphthalene gave roughly the same wear. In dry nitrogen, however, the two fuels behaved quite differently. Wear of methylnaphthalene was double what it was in air; wear of Bayol 35 was cut in half.

In the second series, three atmospheres were used, argon being the inert gas. The results duplicate the first series. Bayol 35 gives high wear in air; methylnaphthalene gives high wear in inert atmospheres.

Several other naphthalene derivatives have been evaluated in dry argon at 100F. These data are given in Table XVIII. Not all of these were hydrocarbons; two contained chlorine. But all showed high wear similar to 1-methylnaphthalene. In contrast, the aliphatic compounds, such as dicyclopentadiene, gave low wear.

2. Mechanism

The most likely explanation of the high wear of condensed-ring aromatics in dry, inert atmospheres is that scuffing is occurring. This conclusion was reached somewhat reluctantly because the loads are far below those necessary to cause scuffing with paraffinic hydrocarbons. For example, in Figure 16 is a comparison between the four-ball performance of methyl naphthalene in argon vs that of cetane in air. Cetane scuffed at about 60-80 Kg whereas methylnaphthalene apparently started to scuff at less than 5 Kg.

TABLE XVII
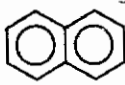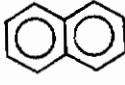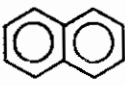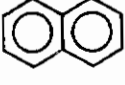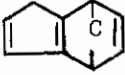
COMPARISON OF CONDENSED-RING AROMATIC WITH PARAFFINIC FUEL

Ball-on-Cylinder Tests (240rpm, 32min, 85F)

	240g		480g		1000g	
	Methyl Naphthalene	Bayol 35	Methyl Naphthalene	Bayol 35	Methyl Naphthalene	Bayol 35
In Room Air	0.27	0.28	0.34	0.30	0.43	0.55
In Dry Nitrogen	0.49	0.19	0.62	0.20	0.83	0.25
In Dry Argon	---	---	---	---	0.70	0.25
In Dry Air	---	---	---	---	0.33	0.41
In Wet Air	---	---	---	---	0.36	0.75

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TABLE XVIII

WEAR AND FRICTION
FOR POLYNUCLEAR AROMATICS IN ARGON

(Ball-On-Cylinder Tests, 1000g, 100F, Steel-On-Steel, 240rpm, 32min)

Hydrocarbon	Molecular Formula	Coefficient of Friction	Wear Scar Diameter, mm
1-Methylnaphthalene		0.17	0.59
2-Methylnaphthalene		0.15	0.76
1-Chloronaphthalene		0.11	0.43
1-Chloromethylnaphthalene		0.14	0.58
Dicyclopentadiene		0.14	0.27
Methylcyclopentadiene		0.14	0.27
Bayol 35		0.19	0.26

FOUR-BALL WEAR TESTS
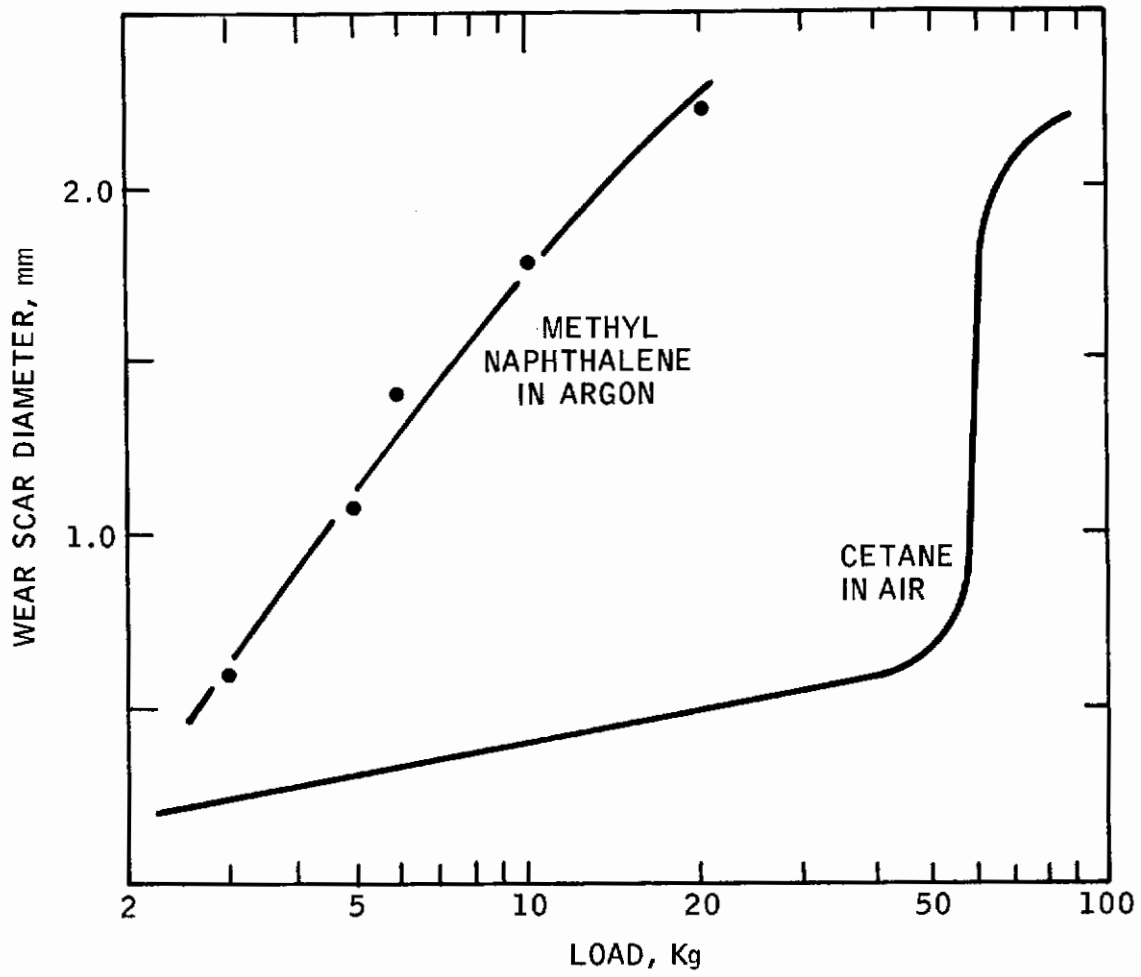
FIGURE 16 - COMPARISON OF SCUFFING OF CETANE IN AIR
METHYL NAPHTHALENE IN ARGON

However, three pieces of evidence point to scuffing as the phenomenon involved. Table XIX gives ball-on-cylinder data for methylnaphthalene under dry atmospheres of various oxygen contents. The load and speed were constant at 1 Kg and 240 rpm. As shown in Figure 17, when the oxygen level was reduced to 1 ppm (about 1% oxygen in the atmosphere), wear rose abruptly in a manner typical of scuffing. (In comparison, Bayol 35 showed no signs of scuffing at < 0.01% oxygen, as already shown in Figure 6. Even octane showed no scuffing, although its viscosity is only one-fifth that of methylnaphthalene.)

Second, when run over a wide load range, both 1-methylnaphthalene and 2-methylnaphthalene showed typical scuffing curves as illustrated in Figure 18 (Data in Table XX). The transition load is about 400 g. (In comparison, the transition load of Bayol 35 was greater than the limit of ball-on-cylinder machine, > 4000 g.)

Third, the wear debris from methylnaphthalene runs is metallic iron, typical of scuffing failure. In comparison, the wear debris from the high-wear runs of Bayol 35 in air is largely iron oxide.

The question still remains: Why do condensed-ring aromatics scuff so easily? Several hypotheses have been advanced and these are being investigated. Apparently these compounds alter the surface in some way so that the film normally responsible for some scuffing resistance is removed. Whether this film is iron oxide, adsorbed oxygen, or some other material, has not yet been determined. Nor has the mechanism by which the condensed-ring aromatics removes this film. However, this film is somehow involved with oxygen, since at higher oxygen concentrations, no scuffing is observed.

B. Synergism Between Paraffins and Condensed-Ring Aromatics

The antiwear effect of heavy aromatics in paraffinic hydrocarbons has been amply confirmed.

1. Four-Ball Tests

Mixtures of Bayol 35 and methylnaphthalene were run both in dry argon and in room air. As shown in Figure 19, a pronounced synergism was found in each case: mixtures gave lower wear than either component alone. As little as 5% of either component in the other gave a pronounced reduction in wear. The lowest wear was attained at 20-50% methylnaphthalene.

The effect of dissolved water is shown in Figures 20 and 21. In air, the water caused more corrosive wear with Bayol 35, but decreased the wear of methylnaphthalene. In argon, the water eliminated all differences between the hydrocarbons. Scuffing with methylnaphthalene disappeared, wear with Bayol 35 decreases, and the synergistic effect of the 70/30 mixture no longer was found. Thus, there is a triple interaction between hydrocarbon type, oxygen availability and humidity.

2. Ball-On-Cylinder Tests

The synergistic behavior of mixtures of Bayol 35 and methylnaphthalene were already shown in Section II. Other tests are shown in Figure 22. It is interesting to note that although the wear curve shows a minimum at the 70/30 mixture, the friction curve steadily decreases as the amount of methylnaphthalene increases.

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TABLE XIX

EFFECT OF DISSOLVED OXYGEN IN METHYL NAPHTHALENE

(Ball-On-Cylinder Tests, 1000g,   80°F, 240 rpm, 32 Min)

Atmosphere % O_2	O_2 in Fuel ppm	Wear Scar Diameter mm	Coefficient of Friction
0.06	0.06	0.80	0.10*
0.28	0.27	0.86	0.13*
0.52	0.50	0.87	0.17*
0.76	0.72	0.86	0.11*
1.02	0.96	0.67	0.11*
2.10	2.00	0.46	0.11
4.13	3.94	0.28	0.11
8.00	7.60	0.27	0.11
21.00 (Dry Air)	20.00	0.26	0.11

* Friction trace erratic.
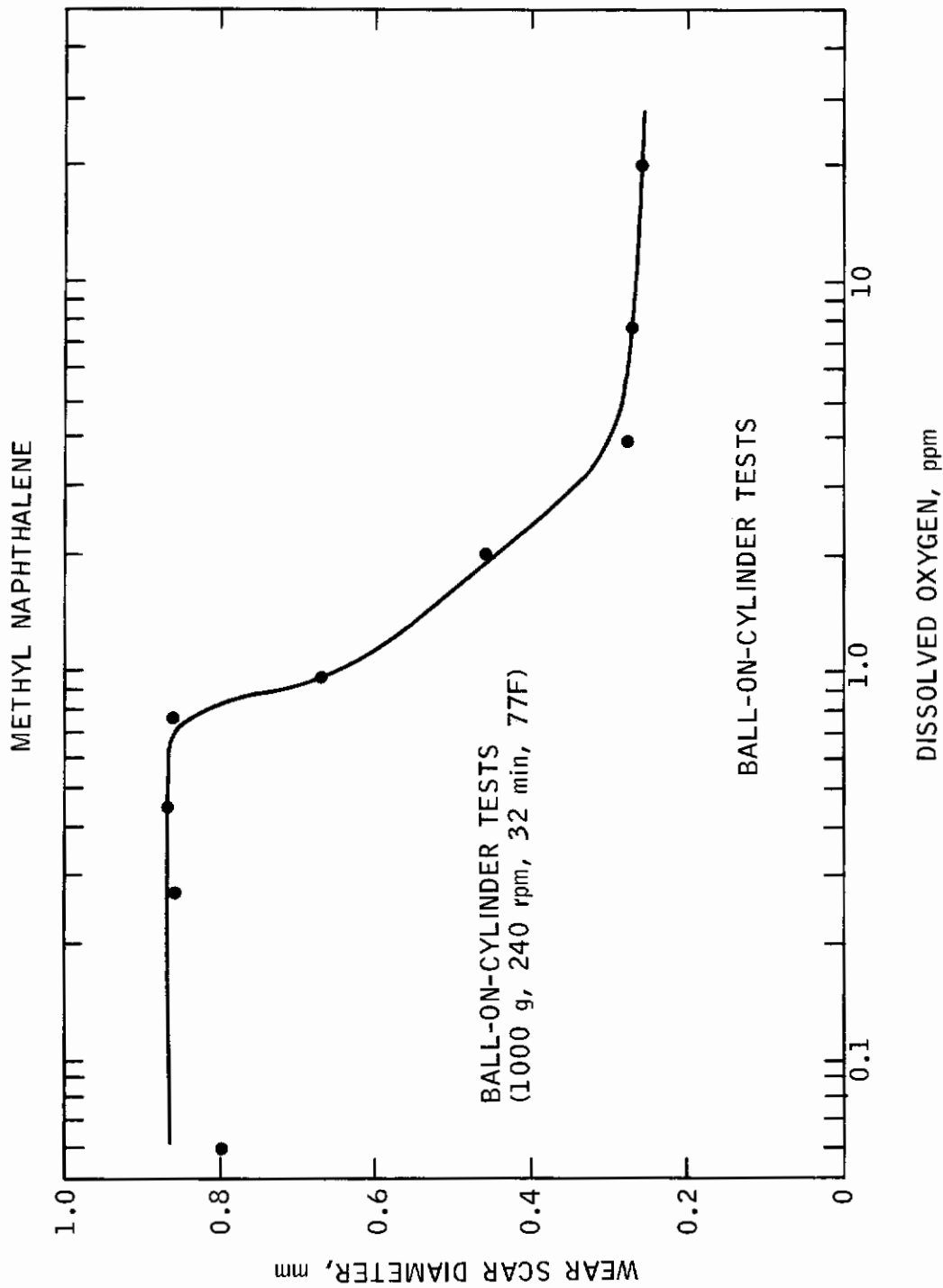
FIGURE 17 - THE EFFECT OF DISSOLVED OXYGEN ON WEAR FOR METHYL-NAPHTHALENE
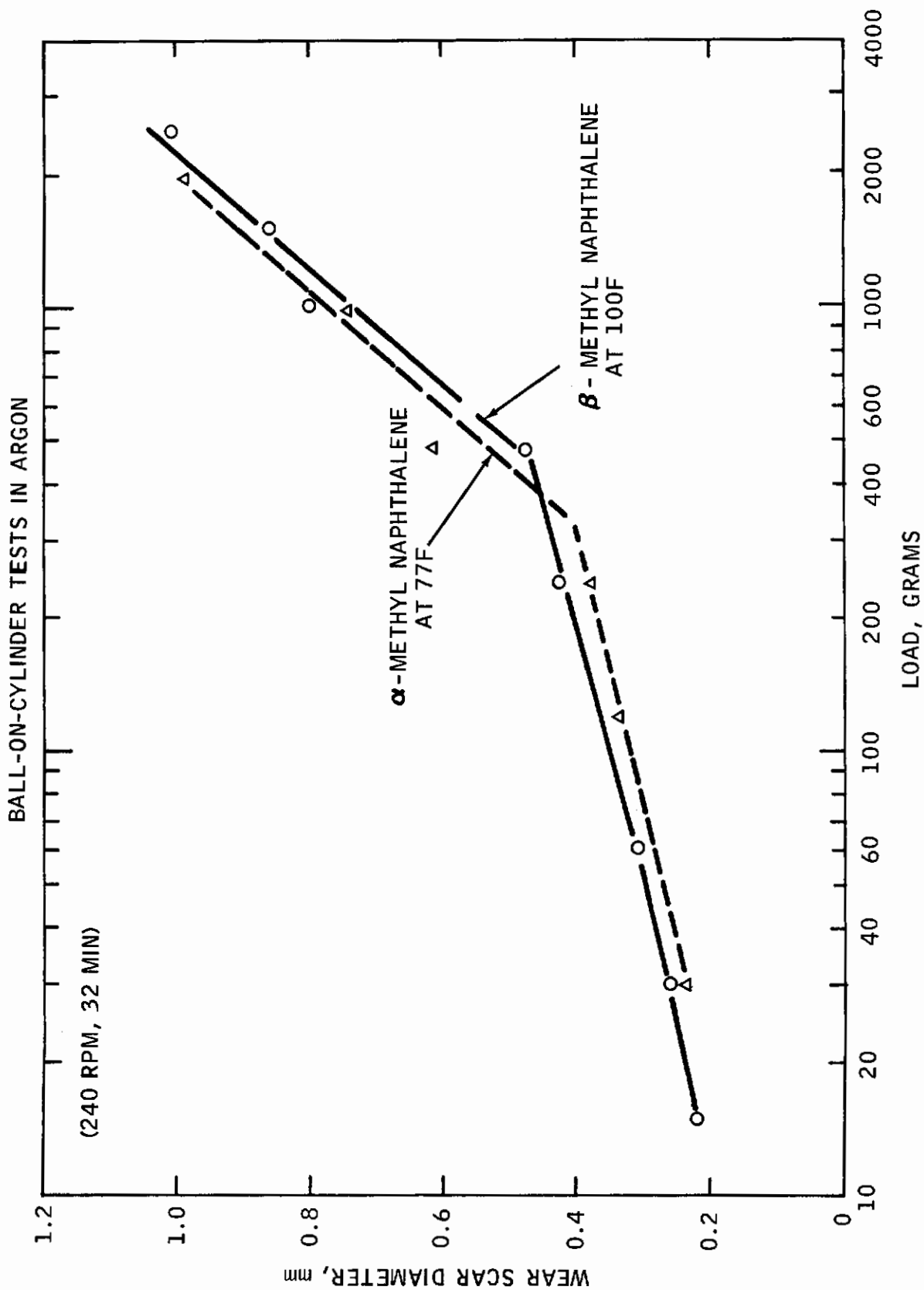
FIGURE 18 - SCUFFING BEHAVIOR OF METHYL-NAPHTHALENES IN ARGON

FOUR-BALL WEAR TESTS
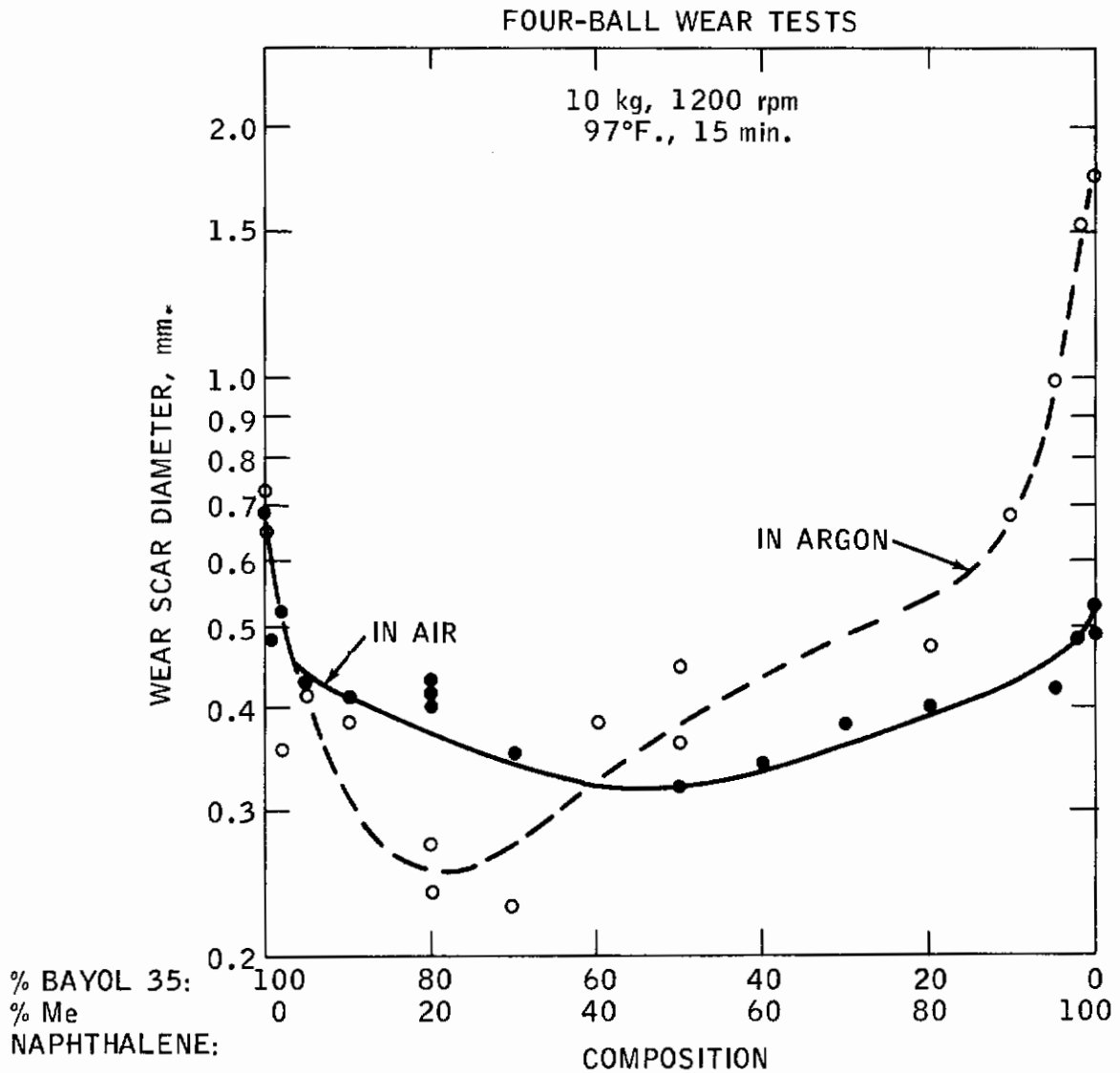
FIGURE 19 - SYNERGISM BETWEEN PARAFFINIC BAYOL 35 AND METHYL-NAPHTHALENE

- 65 -
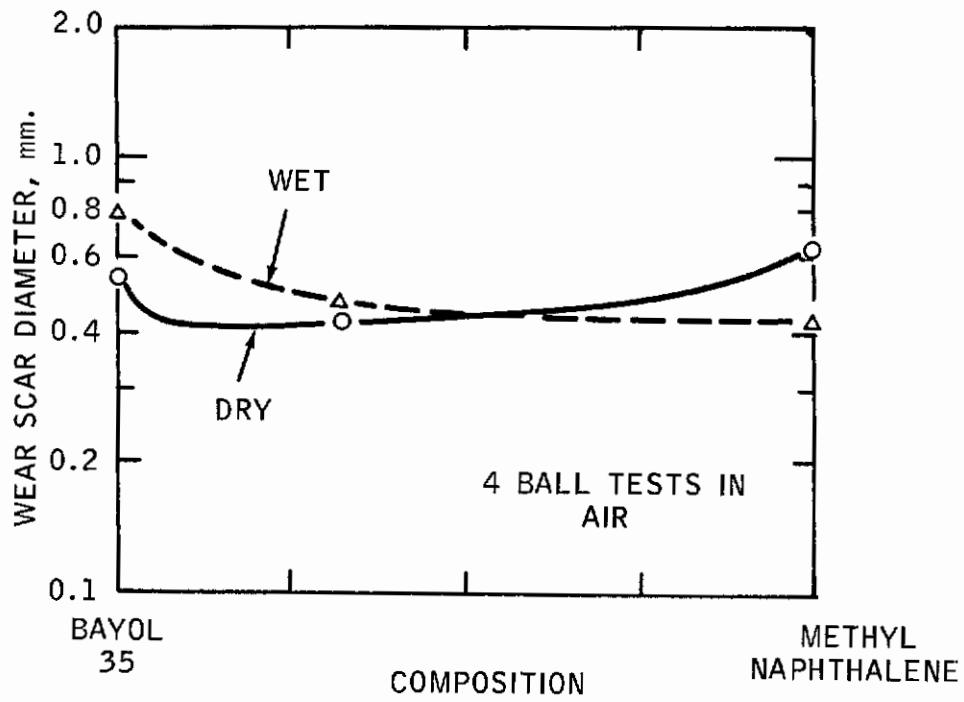
FIGURE 20 - EFFECT OF HUMIDITY IN AIR ON WEAR OF HYDROCARBON MIXTURES
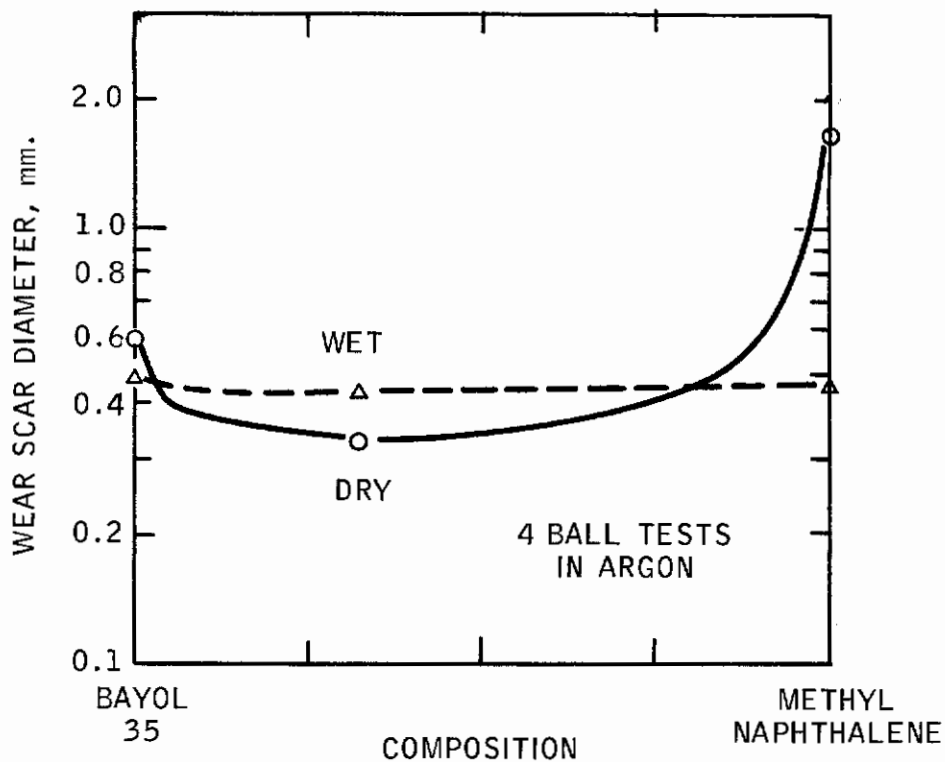
FIGURE 21 - EFFECT OF HUMIDITY IN ARGON ON WEAR OF HYDROCARBON MIXTURES
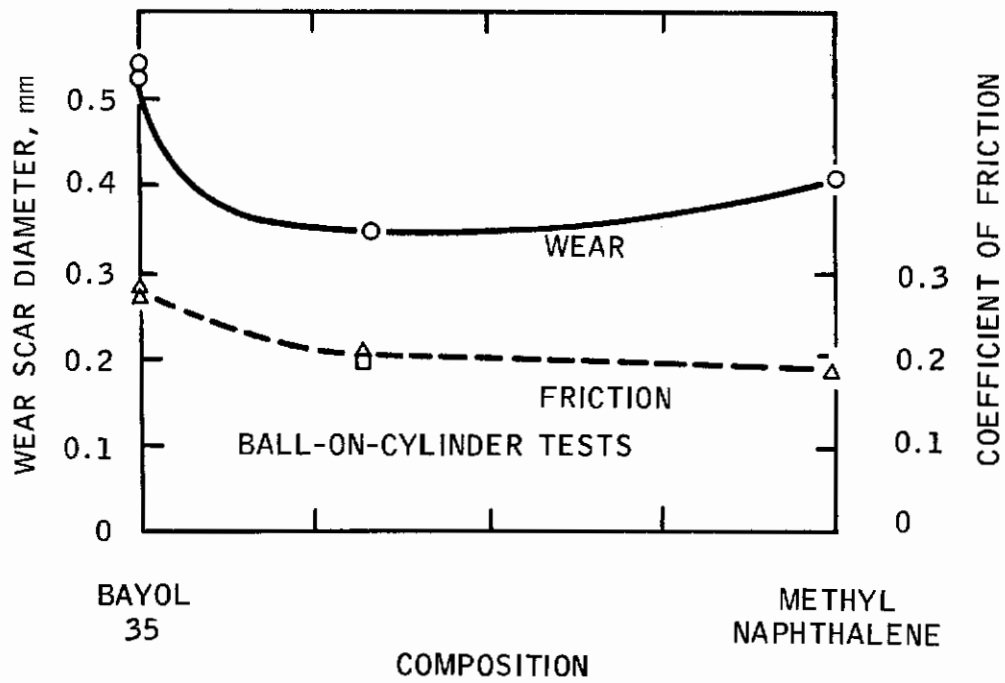
FIGURE 22 - SYNERGISM BETWEEN BAYOL 35 AND METHYL-NAPHTHALENE

TABLE XX

EFFECT OF LOAD ON WEAR FOR
METHYL NAPHTHALENE IN ARGON

(Ball-On-Cylinder Test, 240 rpm, 32 min, Steel-On-Steel)

Load gms	Coefficient of Friction		Wear Scar, mm	
	α-Methyl Naphthalene	β-Methyl Naphthalene	α-Methyl Naphthalene	β-Methyl Naphthalene
15	- -	0.06	- -	0.22
30	0.06	0.07	- -	0.26
60	- -	0.09	- -	0.32
120	0.08	0.12	0.35	0.35
240	0.10	0.14	0.38	0.43
480	0.11	0.14	0.63	0.48
1000	0.16	0.17	0.75	0.80
1500	- -	0.18	- -	0.86
2000	0.14	- -	0.95	- -
2500	- -	very erratic	- -	1.02

In another series of tests, the highly-purified sample of 1-methyl naphthalene was compared to the less-pure sample and to 2-methylnaphthalene, all as 30% blends in Bayol 35. As shown in Table XXI, all three materials were equivalent. The 30% belnds all gave lower wear than the pure aromatics in argon, and much lower wear than Bayol 35 in air. That is, the blends combined the best features of each component. However, in these tests, the blends were not better than both components but merely equal to the best; i.e. there was no synergism.

Blends containing 5% (by weight) of various olefinic or aromatic hydrocarbons in Bayol 35 were tested in the ball-on-cylinder device under various atmospheres. Results are shown in Table XXII. In a non-oxidative atmosphere (argon), the blending of these hydrocarbons did not appreciably affect friction or wear. In air, those hydrocarbons that had given lower wear than paraffins (Tables XIV-XVI) also gave somewhat lower wear in blends. Only a few hydrocarbons showed improved lubricity in both dry and wet air.

| | Wear Scar, mm | |
5% Additive in Bayol 35	Dry Air	Wet Air
None	0.62	0.79
1-Methyl-naphthalene	0.29	0.48
Indane	0.25	0.37
Indene	0.25	0.33
Vinyl-cyclohexene	0.30	0.39

It is interesting to note that these hydrocarbons are either olefins or two-ring aromatics.

In this series of tests at the 5% level, 2-methylnaphthalene was not equivalent to 1-methylnaphthalene as it was at 30%. To check this, tests were run in the modified four-ball tester on several aromatic compounds blended in Bayol 35.

3. Modified Four-Ball Tests

The modified four-ball tester with hydraulic loading was used to check the performance of several aromatics: 1- and 2-methylnaphthalene, naphthalene, diphenyl methane and butyl benzene. These compounds were run in the pure state and at 5 and 10% blends in Bayol 35. A temperature of 175F was maintained to insure that the blends containing naphthalene (m.p. 167F) were above its melting point. Some of the compounds were also run at room temperature. Data are given in Table XXIII.

The results show that all the condensed-ring aromatics are effective antiwear compounds in wet air. There may be some differences at different temperatures; for example, 1-methylnaphthalene appears to be better than other compounds at 77F (both here and in ball-on-cylinder tests), but the differences disappear at higher temperatures.

In contrast, as observed before, n-butylbenzene is completely ineffective. The data on diphenylmethene is anomalous: although it is not a condensed-ring aromatic, it appears to be equally effective. The good blending characteristics of heavy aromatics may therefore not be limited to condensed-ring compounds only. However, since the mechanism of the behavior of heavy aromatics is still completely unknown, this behavior cannot be considered too surprising.

TABLE XXI

COMPARISON OF CONDENSED-RING AROMATICS IN
BALL-ON-CYLINDER TESTS

(240rpm, 1000g, 32min)

	Wear Scar Dia., mm	
% Aromatic in Bayol 35	Dry Argon	Wet Air
100% 1-methylnaphthalene (pure)	0.58	0.31
100% 1-methylnaphthalene (impure)	0.75	0.36
30% 1-methylnaphthalene (pure)	0.26	0.39
30% 1-methylnaphthalene (impure)	0.28	0.39
30% 2-methylnaphthalene	0.30	0.40
100% Bayol 35	0.28	0.72

TABLE XXII

EFFECT ON WEAR OF BLENDING VARIOUS HYDROCARBONS IN BAYOL 35

(Ball-On-Cylinder Tests, 1000g, 240rpm, 32min, 80F, Steel-On-Steel)

Cylinder No.	% Additive in Bayol 35	Coefficient of Friction			Wear Scar, mm		
		Argon	Dry Air	Wet Air	Argon	Dry Air	Wet Air
321	5% Naphthalene	0.10	0.14	0.17	0.27	0.56	0.58
	5% 1-Methyl-naphthalene	0.12	0.13	0.15	0.27	0.29	0.48
	5% 2-Methyl-naphthalene	0.10	0.12	0.15	0.27	0.58	0.58
327	5% Decalin	0.12	0.14	0.18*	0.25	0.73	0.58
	5% Tetralin	0.12	0.12	0.17	0.25	0.53	0.62
314	5% Indane	0.12	0.12	0.15	0.22	0.25	0.37
	5% Indene	0.11	0.11	0.14	0.23	0.25	0.33
	5% Diphenylmethane	0.13	0.15	0.17	0.25	0.45	0.52
263	5% Vinyl-cyclohexene	0.13	0.12	0.16	0.24	0.30	0.39
	5% Phenyl-cyclohexane	0.13	0.14	0.18	0.25	0.44	0.57
183	5% α-Methyl-styrene	0.12	0.13	0.17	0.25	0.39	0.65
	5% Biphenyl	0.13	0.13	0.17	0.25	0.47	0.63
	5% Isopropyl-bicyclohexyl	0.10	0.13	0.16	0.27	0.62	0.59
190	5% Dodecane	0.11	0.15	0.16	0.22	0.53	0.60
	5% Diethyl-cyclohexane	0.11	0.15	0.16	0.21	0.65	0.65
	5% 2,5-Dimethyl-1,5-Heptadiene	0.13	0.13	0.17	0.22	0.35	0.58
	None	0.12	0.15	0.19*	0.26	0.62	0.79

* Friction trace erratic

TABLE XXIII

PERFORMANCE OF AROMATIC BLENDS IN FOUR-BALL MACHINE
(5kg, 1200rpm, wet air)

	Wear Scar Diameter, mm	
% Aromatic in Bayol 35	175F	77F
None	0.63	0.73
5% 1-methylnaphthalene	0.49	0.44
5% 2-methylnaphthalene	0.50	0.48
5% naphthalene	0.46	---
5% diphenylmethane	0.50	0.50
5% n-butylbenzene	0.68	---

VII

EFFECT OF TEMPERATURE ON FRICTION AND WEAR

A. Four-Ball Tests

        In the previous report, four-ball data had shown that for high-purity
materials the principal effect of temperature was its effect on viscosity. When
pure hydrocarbons or high-purity fuels were compared at the same viscosity, their
wear characteristics were the same. On the other hand, when polar impurities were
present, the effect of temperature was greater than that predicted from viscosity
alone. It appeared that differences in fuels were magnified at higher tempera-
tures.

        This work has been expanded to cover all but two of the commercial fuels
examined previously. The two exceptions were JP-4 and light naphtha, both of
which were too volatile to be run at higher temperature.

        The four-ball wear performances of these fuels at 300F are tabulated in
Table XXIV. Figure 23 shows their log-log plots of WSD vs. time. From these
curves, the 60-minute WSD values are extrapolated and tabulated in Table XXV along
with their absolute viscosity at 300F. The calculated 60-minute WSD and absolute
viscosity at 97F are also included in Table XXV for convenient comparison.

        In general, the wear results at 300F show a much wider spread. The
relative order of severity of wear at 97F is retained at 300F, with 75LN-LV as the
exception. Unlike the other fuels, 75LN-LV reaches a wear scar size of about 1 mm
in a few minutes and shows practically no further increase in wear. Of the other
seven fuels, AFFB-3-65 shows highest wear. In the absence of wear results on
naphtha, this is consistent with the 97F wear results. The two highly-refined
fuels, PW-523 and Bayol 35, are indistinguishable in their wear performance and
their wear is only slightly lower than that of AFFB-3-65. Diesel fuel shows not
only the lowest wear but also the least increase in wear due to temperature as
compared with the rest.

        The effect of temperature is therefore to increase the spread between
the fuels. All fuels get worse but the fuels already poor in lubricity are the
most affected. This is probably because these fuels, being highly-refined and low
in polar components, are more sensitive to the decrease in viscosity and increase
in volatility caused by temperature.

B. Ball-On-Cylinder Tests

        Several preliminary series of runs were made at higher temperature.
However, the results were so contradictory that it was feared that excessive
oxidation was occurring even at 160F. Accordingly the procedure for the ball-
on-cylinder test was modified as follows:

        (1) The test fuel was not circulated--to reduce agitation.
        (2) The fuel was preheated to the desired temperature in argon
             which was replaced by air just before the run--to decrease
             and control the oxidation time.
        (3) The air was introduced above the fuel rather than bubbling
             through it--to reduce the contact of oxygen and fuel.

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TABLE XXIV

FOUR BALL WEAR RESULTS FOR JET FUELS AT 300F

Test Fuel Minutes:	Wear Scar Diameter, mm									
	0.25	0.50	1.0	2.0	4.0	7.0	10.0	15.0	30.0	60.0
Diesel Fuel	0.46		0.43		0.44			0.49	0.53	0.65
RAF-176-64	0.50		0.50		0.62			0.78		
JP-5	0.60		0.65		0.67			0.91		1.28
75LN-LV	0.72		0.74	0.95	0.98	1.01	0.98	1.06		
RAF-173-61	0.78		0.96		0.88			1.22		
PW-523			0.92		1.24			1.56		
Bayol 35			0.99		1.26			1.58		
AFFB-3-65				1.12				1.86		
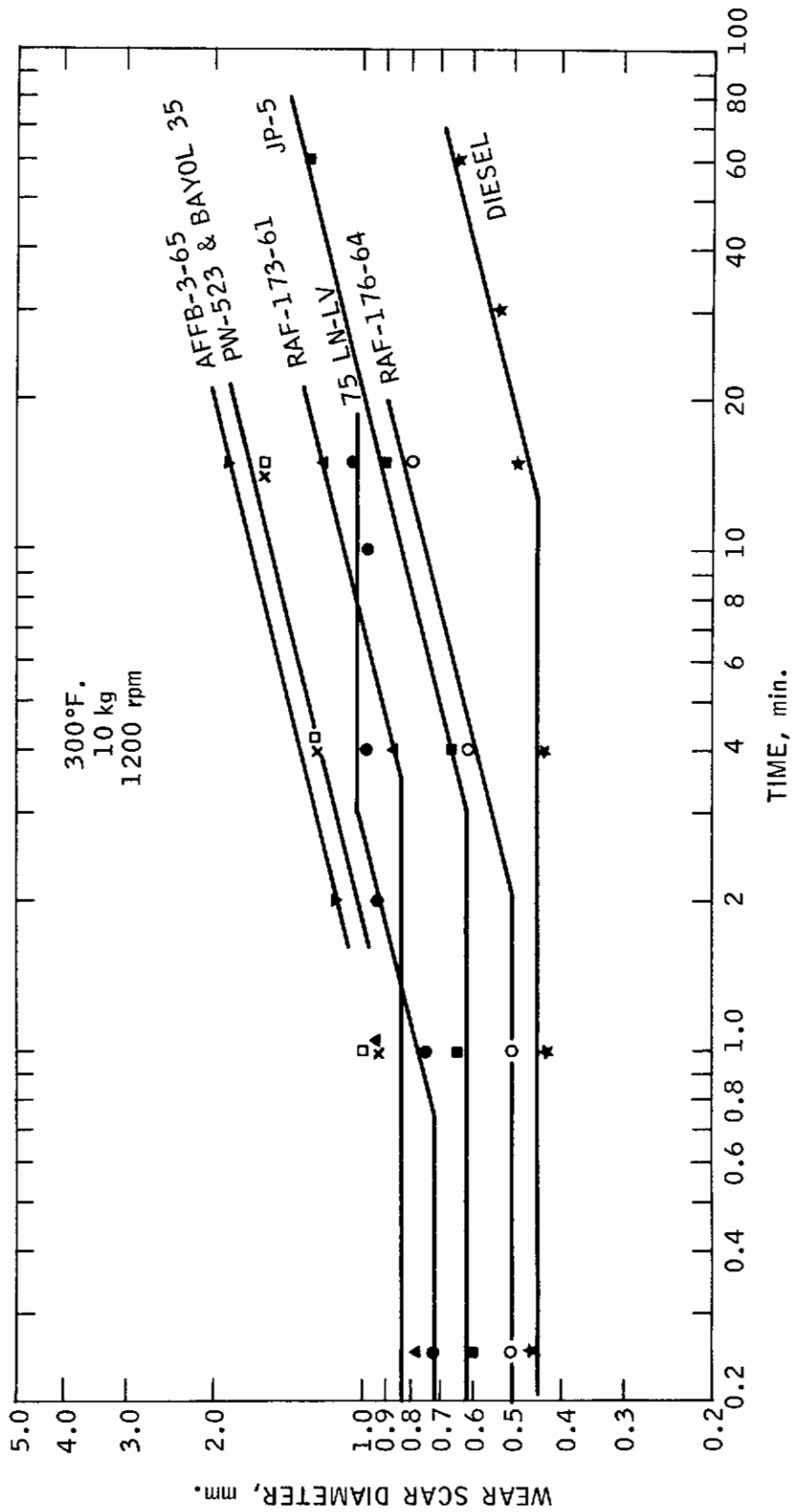
FIGURE 23 - WEAR OF JET FUELS AT 300F IN FOUR-BALL MACHINE

TABLE XXV

EFFECT OF TEMPERATURE ON FOUR-BALL PERFORMANCE OF JET FUELS

(10kg, 1200rpm)

Fuel	Calc 60min WSD/ 300F, mm	Vis/300F, cp	Calc 60min WSD/ 97F mm	Vis/97F cp
AFFB-3-65	2.61	0.298	1.04	0.98
PW-523	2.39	0.345	0.86	1.21
Bayol 35	2.39	0.429	0.80	1.88
RAF-173-61	1.72	0.432	0.81	1.70
JP-5	1.31	0.351	0.70	1.21
RAF-176-64	1.18	0.331	0.61	1.09
75-LN-LV	(1.02)	0.313	0.70	1.04
Diesel Fuel	0.66	0.508	0.52	2.18

Under these conditions, the lubricity of several commercial fuels at various temperatures from 160F to 350F was investigated.

The effect of reducing oxidation is a substantial increase in wear as shown below.

Wear Scar Diameter, mm

(Ball-on-cylinder Tests: 240g, 160F, 32 min)

	Bayol 35		PW-523	
	Dry Air	Wet Air	Dry Air	Wet Air
Recirculating System	0.26	0.33	0.39	0.50
Modified System	0.63	0.75	0.58	0.77

The modified system reduces oxidation and gives more severe wear.

In the first series of tests, using the modified system, room air was used, i.e. humidity was not controlled. Three commercial fuels were evaluated. The results, as shown in Table XXVI and Figure 24, indicate that the highly-refined PW-523 gives higher friction and wear than the currently marketed fuels, consistent with data obtained earlier. The higher wear with highly-refined fuels is found at all temperatures.

Two highly-refined fuels, Bayol 35 and PW-523 were then tested in controlled atmospheres at temperatures from 160 to 350F. It was immediately noted that at the higher temperatures, friction was much higher and more erratic. In many cases, the tests had to be terminated to avoid damaging the apparatus. In fact, a relatively low load of 240g had to be used in order to get comparable results at all temperatures; higher loads gave excessive scuffing at high temperatures.

Data from these runs are given in Table XXVII. In argon, wear increased with temperature for both fuels. This is clearly a temperature effect, for oxidation was nil, as evidenced by the low acidity values. In air, wear was lower when oxidation was high, indicating that the oxidation products were acting as good lubricity agents. Under the most severe conditions (high temperature and wet air) friction was often so great in the first few minutes of test (before oxidation products could build up) that the tests could not be continued.

The conclusion is that higher temperatures give increased wear and friction, especially in air. Some of the effect is to decrease viscosity, but the greater part appears to be its effect in promoting corrosive wear which can lead to excessive friction and early failure.

C. Vickers Vane Pump Tests

1. Tests in Inert Atmospheres

Vickers vane pump tests were run at higher temperatures on several commercial fuels in a nitrogen atmosphere. The test data are shown in Table XXVIII. Wear was very low in all cases. Since the viscosity of the fuels is considerably reduced at these higher temperatures, the pressure could only be maintained at 150

TABLE XXVI

EFFECT OF TEMPERATURE ON COMMERCIAL FUELS: BALL-ON-CYLINDER TEST
(240g, room air, 240rpm, 32 min, Steel-on-Steel)

Temperature °F	PW-523		RAF-176-64		JP-5	
	CoFr	WSD,mm	CoFr	WSD,mm	CoFr	WSD,mm
160	0.16	0.62	--	0.29	0.11	0.42
240	0.18	0.50	0.14	0.37	0.15	0.29
300	0.20	0.67	--	--	--	--
350	--	--	0.14	0.32	0.11	0.40

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BALL-ON-CYLINDER TESTS
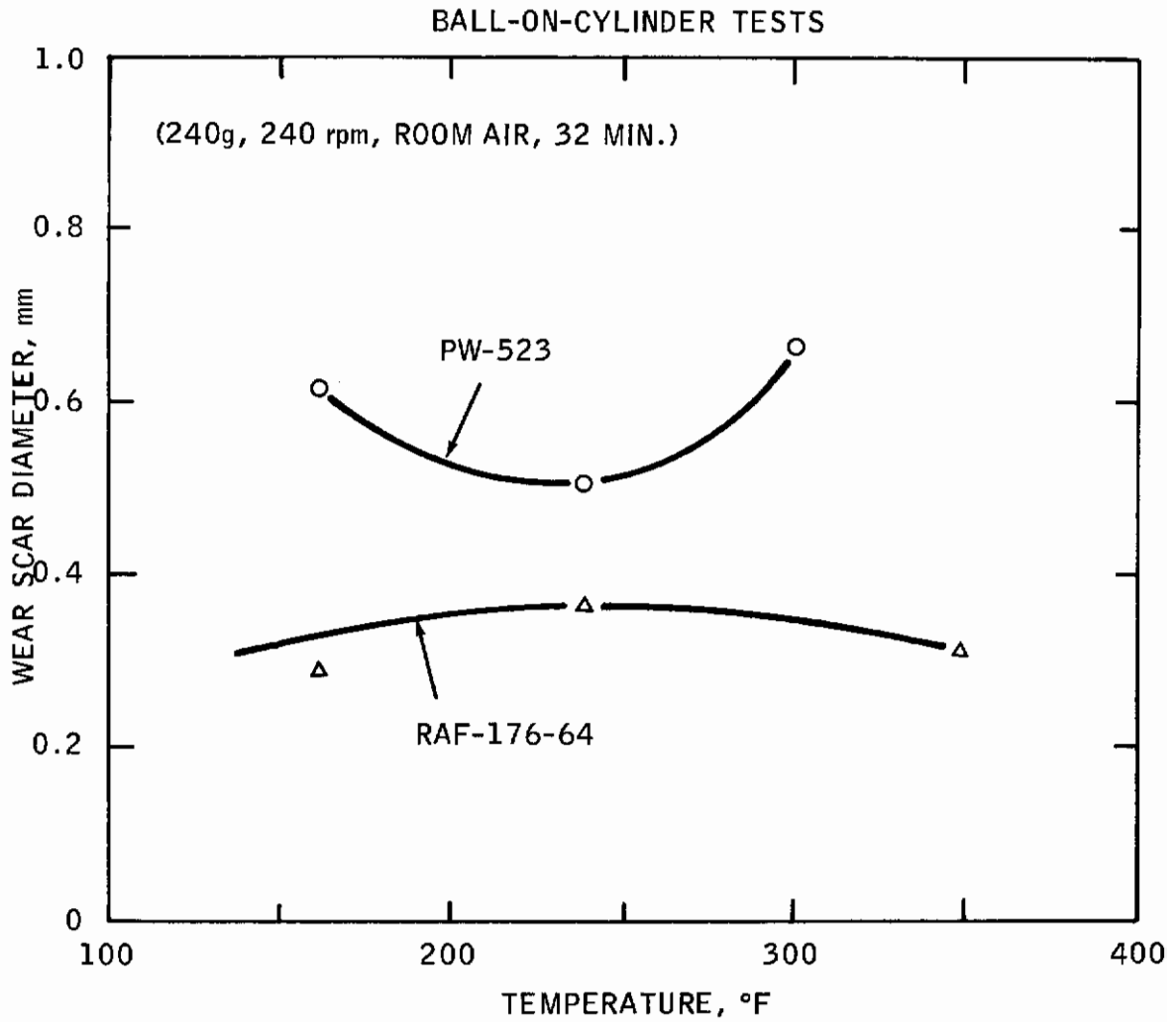
FIGURE 24 - COMPARISON OF HIGHLY-REFINED AND COMMERCIAL FUEL
AT ELEVATED TEMPERATURE

TABLE XXVII

EFFECT OF TEMPERATURE ON HIGH-PURITY FUELS: BALL-ON-CYLINDER TEST

(240g, 240rpm, 32 Min)

Fuel	Temp. °F.	Coefficient of Friction			Wear Scar Diameter, mm			Acidity, ppm KOH		
		Argon	Dry Air	Wet Air	Argon	Dry Air	Wet Air	Argon	Dry Air	Wet Air
Bayol 35	160	0.15	0.20	0.20	0.24	0.63	0.75	< 0.1	< 0.1	< 0.1
	240	0.16	0.19	0.21	0.27	0.58	0.72	< 0.1	< 0.1	< 0.1
	300	0.15	0.19	*	0.30	0.48		< 0.1	33.8	
	350	0.16	0.18	*	0.28	0.38		< 0.1	122.0	
PW-523	160	0.19	0.17	0.23	0.25	0.58	0.77	< 0.1	< 0.1	< 0.1
	240	0.16	0.20	0.30	0.26	0.40	0.73	< 0.1	< 0.1	0.2
	300	0.16	0.18	0.26	0.34	0.57	0.62	< 0.1	1.0	64.0
	350	0.18	0.19	**	0.36	0.36	0.45	< 0.1	174.1	127.3

* Tests discontinued after 10 minutes due to excessive friction.

** Friction very erratic

TABLE XXVIII

VICKERS VANE PUMP TESTS ON COMMERCIAL FUELS IN NITROGEN

Fuel Tested	Bayol 35		PW-523		JP-5		RAF-176-64	RAF-173-61	
Sump Temperature, °F	240	300	240	300	240	300	240	240	300
Vis @ Sump Temp, cp	0.6	0.43	0.46	0.33	0.46	0.35	0.44	0.6	0.44
Pressure, psig	150	110	148	90	125	100	145	125	110
$H \times 10^6$*	1.16	1.13	0.9	1.06	1.07	0.98	0.88	140	1.16
Pump Rate, gpm	0.49	0.23	0.42	0.3	0.30	0.23	0.47	0.27	0.23
Vol Eff. %	24	13	23	17	17	13	26	15	13
Wear, mg									
Wt Loss of Vanes	1	1	1	0	2	5	1	1	1
Wt Loss of Ring	23	42	78	59	64	74	63	17	6
Surface Roughness, CLA									
Vanes, Initial	20	24	17	4	21	20	21	21	23
Final	31	74	24	27	19	22	26	34	26
Ring, Initial	12	8	15	13	19	16	10	11	11
Final	7	12	12	12	10	13	18	9	9

$$* H = \text{A modified Sommerfeld No.} = \frac{(Vis)(rpm)}{(Pressure)}, \quad (Dimensionless)$$

psig or lower due to excessive internal leakage. Although the low wear might be ascribed to a lower severity due to the lower pressure, this does not seem to be correct. The severity of the test depends on both load and fuel viscosity. It may be expressed numerically by a dimensionless group, $\frac{\mu N}{P}$, where μ is the fuel viscosity, N is rotation speed to the pump, and P is the pressure. The pressure is equivalent to the load to press the vanes against the ring. The values of $\frac{\mu N}{P}$ were from 0.9 to 1.4 x 10^6; this may be compared to a value of 1.1 x 10^6 for PW-523 at 90F and 350 psi. Since, under these latter conditions, PW-523 gave very high wear in air, it is concluded that the low values in nitrogen shown here are a result of inerting and not lower pressures. That is, temperatures up to 225F can be employed with no wear occurring if the pump is blanketed with an inert gas.

Another way was also used to investigate the temperature effect on wear without complication of viscosity variation. Three highly-refined paraffinic/naphthenic oils, Bayol 35, Bayol 55 and Bayol 70, were tested in a Vickers vane pump at such temperatures that they all had the same viscosity. All the tests were made in a nitrogen atmosphere. Since Bayol 35 at 90F gave very low wear, its test results are well suited to serve as a reference for comparison. Any appreciable increase in wear for Bayol 55 and Bayol 70 at higher temperatures should be attributable to the effect of the bulk fuel temperature. However, as shown in Table XXIX, Bayol 55 at 185F and Bayol 70 at 225F also gave very low wear.

2. Tests in Air

When the atmosphere was air rather than nitrogen, the tests at higher temperatures gave anomalous results. Table XXX presents data for five fuels at 240F under conditions of nitrogen, dry air, and wet air. The highly-refined fuels -- Bayol 35, PW-523, RAF-173-61--showed more wear in air than in nitrogen, although the increase was not as great as observed earlier at lower temperatures. The commercial fuels JP-5 and RAF-176-64 showed no such increase; wear was low in all atmospheres.

It seemed likely that these differences were due to oxidation of the fuel at the higher temperature. A study of the effect of oxidation was therefore carried out.

D. Effect of Oxidation on Fuel Lubricity

1. Paraffinic Fuels Show Oxidation Effect

To study the effect of oxidation, a series of tests was made on PW-523 and Bayol 35. These tests were carried out by heating the fuels to 240F or 400F in nitrogen. After the temperature became steady, air was introduced to replace nitrogen. Samples were taken at time intervals of one hour, two hours, and four hours, and were cooled in nitrogen. These oxidized fuel samples were used for ball-on-cylinder tests and chemical analyses. The test results are shown in Table XXXI. An increase of acidity for PW-523 was detected after its being oxidized at 240F for one hour and this was accompanied by a decrease in wear. As shown in Figure 25, the decrease of wear is a close function of the increase of oxidation time. A difference in acidity for Bayol 35 was not detectable after oxidation at 240F for four hours. The wear decreased slowly with the increase of oxidation time as shown in Figure 26. At 400F, both fuels were oxidized rapidly

TABLE XXIX

VICKERS' VANE PUMP TESTS
(IN N_2 ATMOSPHERE)

Fuel Tested	Bayol 35	Bayol 55	Bayol 70	PW-523	Column Treated JP-5
Sump Temperature, °F	90	184	225	90	90
Outlet Temperature, °F	100	194	225	105	98
Vis. @ Sump Temp., cp	2.08	2.04	2.06	1.34	1.28
@ Outlet Temp., cp	1.83	1.86	2.06	1.15	1.18
Pressure, psig	350	350	350	350	350
Pumping Rate, gpm	0.72	0.75	0.88	0.41	0.80
Vol. Eff., %	40	42	46	23	44
Wear, mg					
Wt. Loss of Vanes	3.3	10	11	0	5
Wt. Loss of Ring	0	36	16	31	17
Surface Roughness,					
CLA,					
Vanes, Initial	20	21	20	24	21
Final	38	20	23	22	23
Ring, Initial	13	10	17	12	45
Final	8	15	21	8	36

TABLE XXX

VICKERS VANE PUMP TESTS IN VARIOUS ATMOSPHERES

(Sump Temperature, 240°F)

	Bayol-35			PW-523			JP-5			RAF-176-64			RAF-173-61	
	N_2	Dry Air	Wet Air	N_2	Dry Air	Wet Air	N_2	Dry Air	Wet Air	N_2	Dry Air	Wet Air*	N_2	Dry Air
Pressure, psig	150	145	150	148	150	150	125	130	130	145	155	150	125	120
Pumping Rate, gpm	0.49	0.23	0.28	0.42	0.44	0.49	0.30	0.39	0.38	0.47	0.29	0.44	0.27	0.28
Vol Eff., %	27	13	16	23	24	27	17	22	21	26	16	24	15	16
Wear, mg														
Wt Loss of Vanes	1	80	162	1	58	70	2	3	5	1	3	5	1	8
Wt Loss of Ring	23	1851	2941	78	180	239	64	15	17	63	64	46	17	441
Surface Roughness														
Vanes, Initial	20	19	24	17	20	18	21	22	14	21	20	26	21	21
Vanes, Final	31	>200	>200	24	>200	76	19	22	15	26	11	26	34	22
Ring, Initial	12	8	12	15	10	10	19	12	11	10	12	18	11	14
Ring, Final	7	>200	>200	12	40	29	10	13	11	18	15	9	9	10

* Run stopped at 12 hours due to a leakage in the system.

TABLE XXXI

EFFECT OF OXIDATION OF FUELS

(Ball-On-Cylinder Tests, Steel-On-Steel, 1000 g Load,)
(240 rpm, 32 Min, Open Air, 80°F   )

Fuel	Oxidation Temp °F	Time Hr	Acidity, ppm/KOH	Coeff. of Friction	Wear Scar Diameter mm
PW-523	-	0	< 0.2	0.20*	0.71
PW-523	240	1	0.55	0.20	0.52
PW-523	240	2	0.77	0.22	0.48
PW-523	240	4	3.75	0.19	0.36
PW-523	240	24	32.6	0.19	0.32
PW-523	400	1	37.2	0.19	0.30
PW-523	400	2	130.1	0.18	0.26
PW-523	400	4	960.0	0.18	0.28
PW-523	-	0	< 0.2	0.19*	0.64
Bayol 35	-	0	< 0.2	0.22*	0.80
Bayol 35	240	1	< 0.2	0.22*	0.80
Bayol 35	240	2	< 0.2	0.21*	0.75
Bayol 35	240	4	< 0.2	0.21*	0.66
Bayol 35	240	24	85.5	0.19	0.36
Bayol 35	400	1	80.0	0.19	0.32
Bayol 35	400	2	172.9	0.17	0.27
Bayol 35	400	4	785.0	0.16	0.26
Bayol 35	-	0	< 0.2	0.21*	0.80

* Friction trace erratic.
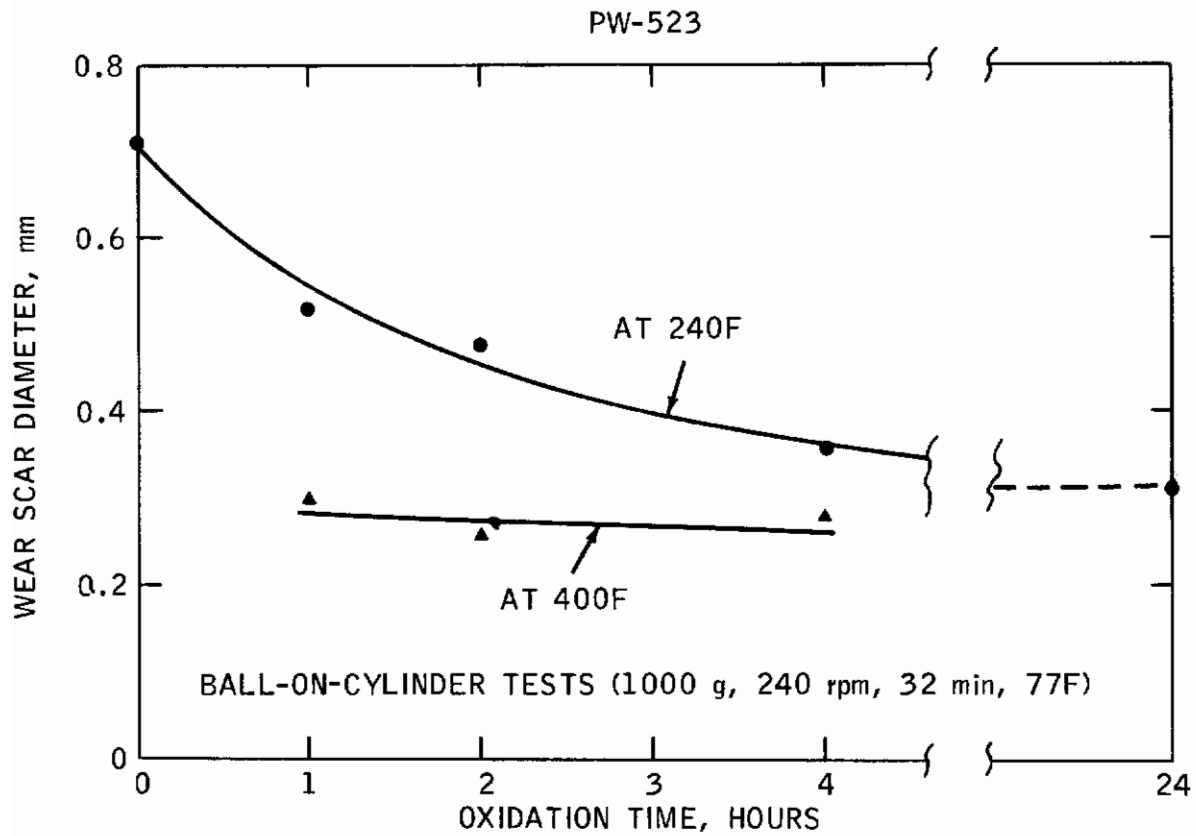
PW-523

FIGURE 25 - WEAR VS OXIDATION TIME FOR PW-523 AT 240F AND 400F

- 88 -
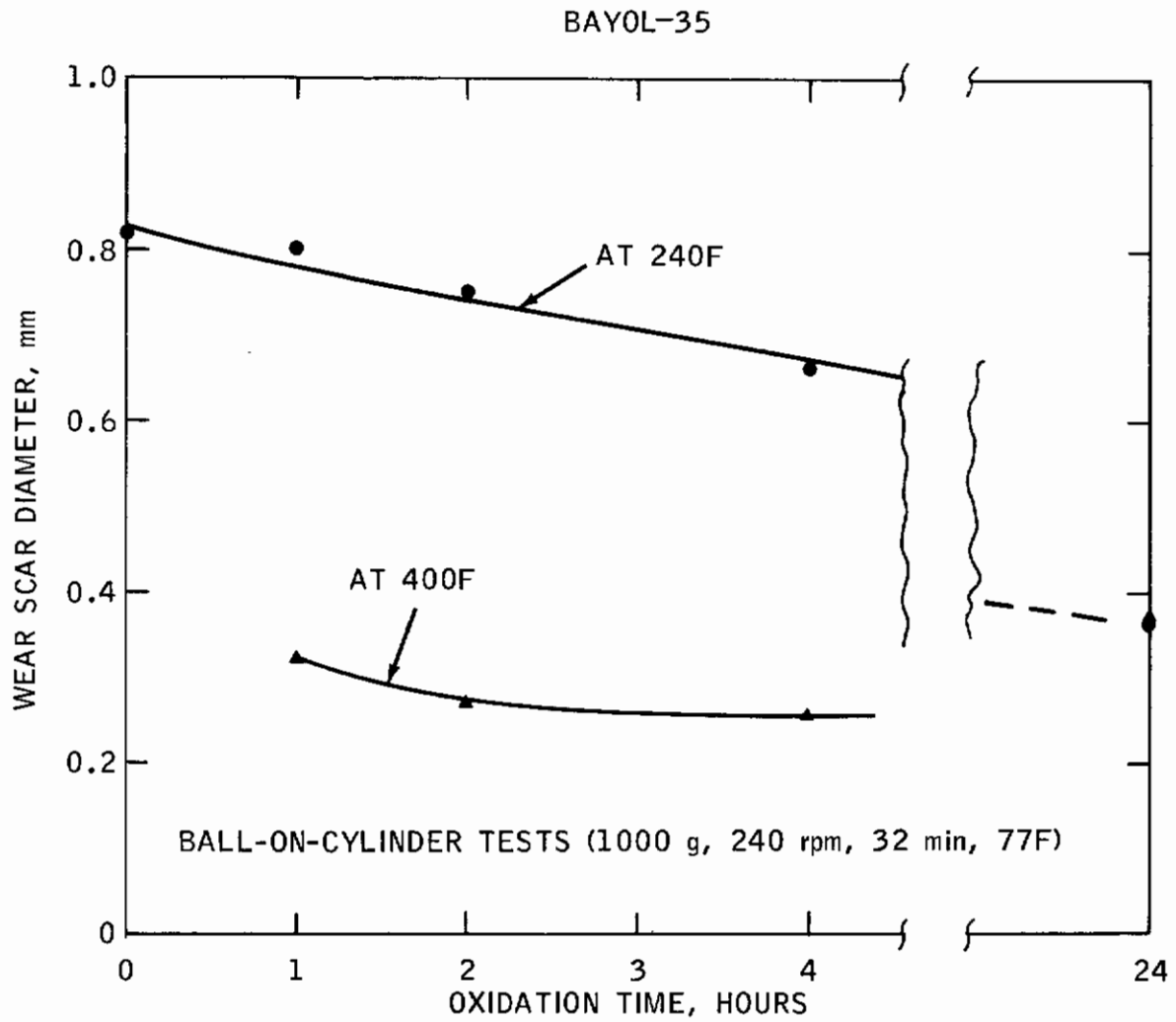
BAYOL-35

FIGURE 26 - WEAR VS OXIDATION TIME FOR BAYOL 35 AT 240F AND 400F

and the wear was consistently at a low level. The Neut. No. may be considered representative of the extent of oxidation. A plot of wear versus Neut. No. is shown for PW-523 in Figure 27. It appears that a low severity of wear may be attained at a Neut. No. of about 100 ppm KOH. This is in surprisingly good agreement with previous tests that had shown that about 30 ppm of oleic acid was equally effective.

Ball-on-cylinder tests were also made on other commercial fuels before and after 24-hour pump tests at 240F. The results are shown in Table XXXII. It is clearly seen that the high-refined fuels were more oxidized than the other commercial fuels and the extent of the wear reduction was correspondingly greater.

2. Thin Layer Chromatography Indicates the Formation of Polar Components in Oxidation

For investigating the chemical change in oxidation, thin layer chromatography was used to examine the fuels. Thin layer chromatography is essentially a type of adsorption chromatography where the adsorbent is a thin layer of a solid, such as silica gel, deposited on a plate support. The sample to be analyzed is placed near one end of the plate and is resolved by a solvent (developer) passing through the layer by capillary action. The trace components are adsorbed at different spots and can be made visible by a treatment with certain indicators.

Figure 28 shows the thin layer chromatogram for these commercial fuels before and after pump tests at 240F. These analyses were carried out using 5 μl sample of a solution of 10% fuel in pentane. Isooctane was used as the developer; phospho-molybdic acid as the indicator. It shows clearly that a new polar component was produced in oxidation for all the highly-refined fuels. For other commercial fuels, the polar component was present originally and was only slightly increased.

The sample of PW-523 from oxidation tests at 240F and 400F were also analyzed by thin layer chromatography as shown in Figure 29. The size and intensity of these polar spots increased distinctly with temperature and oxidation time. The quantitative evaluation of the chromatogram by a densitometer was tried. For samples oxidized at 400F, the intensity ratio of these spots for one hour, two hours, and four hours was approximately 1:2:5. For further identification of these polar components, a large sample was prepared on the thin layer plate and the adsorbed spots were removed from the plate and dissolved in methanol. This sample will be analyzed by IR, GC, and mass spectroscopy.

3. Oxidation Rather Than Thermal Decomposition is Contributing Factor to Lubricity

To confirm that it was an oxidative change and not merely thermal decomposition that caused the improved lubricity, ball-on-cylinder tests were made on Bayol 35 which had been heated at 400F in nitrogen or in air for two hours. The results are shown in Table XXXIII. It is obvious that heating alone did not have any appreciable effect to the fuel lubricity. The chemical change of fuels, which showed the effectiveness on friction and wear, is clearly oxidation.

None of these findings is in any sense surprising. Oxidized hydrocarbons are known to be good lubricity agents and these tests have merely confirmed this fact. The data do point out that the effect of temperature can be easily masked if oxidation is occurring simultaneously and that differences between hydrocarbons may be more a difference in oxidative stability rather than a difference in native lubricity.
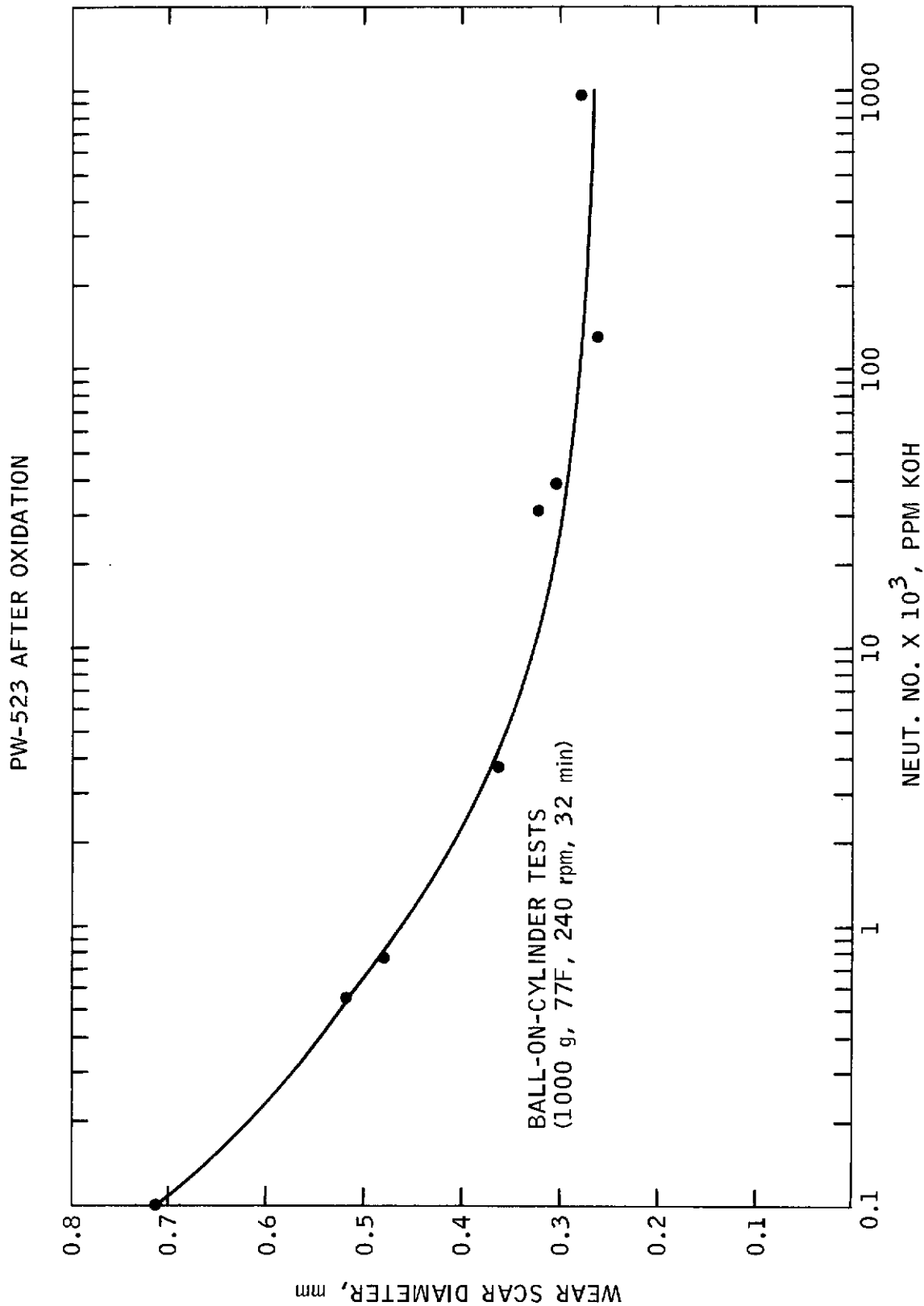
FIGURE 27 - WEAR VS NEUT. NO. FOR PW-523 AFTER OXIDATION

TABLE XXXII

FUELS AFTER PUMP TEST AT 240°F IN OPEN AIR

(Ball-On-Cylinder Tests, Steel-On-Steel, 1000 g, 240 rpm, 32 Min, 77°F)

Fuel	Vis. cp @ 77°F	Neut. No. ppm KOH	Coef. of Friction	Wear Scar mm
Bayol-35				
Before Pump Test	2.416	< 0.2	*	0.62
After Pump Test	2.376	85.5	0.14	0.35
RAF-173-61				
Before Pump Test	2.151	0.3	0.18	0.54
After Pump Test	2.063	48.7	0.15	0.28
PW-523				
Before Pump Test	1.513	< 0.2	0.16	0.63
After Pump Test	1.510	37.9	0.16	0.35
JP-5				
Before Pump Test	1.466	0.8	0.21	0.45
After Pump Test	1.461	9.7	0.15	0.28
RAF-176-64				
Before Pump Test	1.310	9.5	0.17	0.29
After Pump Test	1.336	13.8	0.16	0.28

* Run stopped at 14 min because of excessive friction.

THIN LAYER CHROMATOGRAM
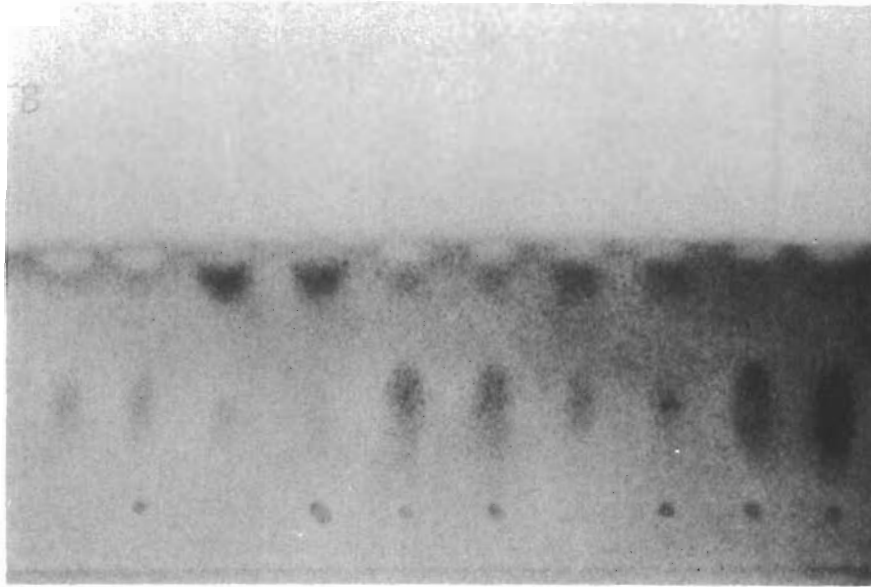
b   a   b   a   b   a   b   a   b   a

PW-523   Bayol 35   JP-5   RAF-173   RAF-176

SOLUTION;   10% FUEL IN PENTANE
SAMPLE SIZE: $5 \mu l$
DEVELOPER: ISOOCTANE
INDICATOR: PHOSPHOMOLYBDIC ACID

FIGURE 28 - THIN LAYER CHROMATOGRAM OF FUELS
BEFORE AND AFTER OXIDATION

PW-523

THIN LAYER CHROMATOGRAM
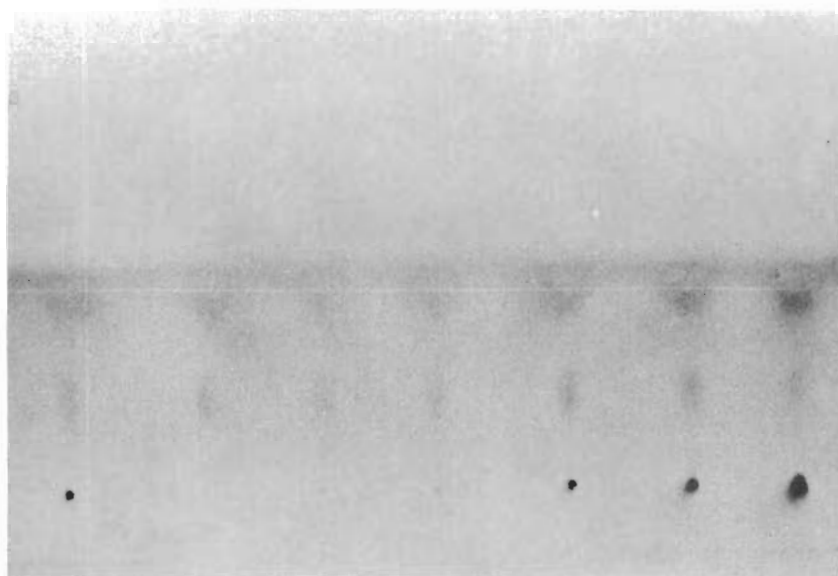
400F	240F	240F	240F	400F	400F	400F
1 Hr.	1Hr.	2 Hr.	4 Hr.	1 Hr.	2 Hr.	4 Hr.

SOLUTION: 10% IN PENTANE
SAMPLE SIZE: 5 μl
DEVELOPER: ISOOCTANE
INDICATOR: PHOSPHOMOLYDBIC ACID

FIGURE 29 - THIN LAYER CHROMATOGRAM FOR PW-523 AFTER OXIDATION

TABLE XXXIII

EFFECT OF OXIDATIVE AND THERMAL STABILITY

(Ball-On-Cylinder Tests - Bayol-35, 1000 g, 77°F, 240 rpm, 32 Min)

	No Heating	Heated @ 400°F in Argon	Heated @ 400°F in Air
Vis. @ 77°F, cs.	3.079	3.060	3.144
Neut. No. ppm KOH	< 0.3	< 0.3	394
New Compounds in TLC	0	0	1

Ball-On-Cylinder Tests

● Coeff. of Friction

	No Heating	Heated @ 400°F in Argon	Heated @ 400°F in Air
in Argon	0.12	0.12	0.12
in Dry Air	0.14	0.13	0.11
in Wet Air	0.16*	0.14*	0.11

● Wear Scar, mm

	No Heating	Heated @ 400°F in Argon	Heated @ 400°F in Air
in Argon	0.26	0.22	0.23
in Dry Air	0.56	0.53	0.27
in Wet Air	0.70	0.72	0.41

* Friction trace erratic.

4. Methylnaphthalene Shows no Oxidation Effects

In contrast, the effect of oxidizing methylnaphthalene was essentially nil. Table XXXIV presents data on the effect of first oxidizing 1-methyl naphthalene in air and then running a ball-on-cylinder test on the oxidized sample. After one hour at 400F, considerable oxidation had taken place, as evidenced by the increase in acidity and the appearance of polar compounds in TLC. However, these compounds had no effect on lubricity. Scuffing still occurred in argon, and wear actually increased somewhat in dry air, although it showed a slight de- crease in wet air. This is in agreement with the effect of oleic acid, which also did not improve the lubricity of 1-methyl naphthalene in argon. See Section VIII. The thin layer chromatogram for 1-methyl naphthalene before and after oxidation is shown in Figure 30.

TABLE XXXIV

EFFECT OF THERMAL AND OXIDATIVE STABILITY

(Methyl Naphthalene)

	No Heating	After Heated At 400°F in Argon	After Heated At 400°F in Air
Vis. @ 77°F, cs	2.628	2.636	2.764
Neut. No. x 10^3, ppm KOH/gm	7.0	8.8	314.7
New Components in *TLC	0	0	3
**Ball-On-Cylinder Tests:			
Coeff. of Friction			
in Argon	0.14	0.13	0.08
in Dry Air	0.10	0.09	0.09
in Wet Air	0.14	0.12	0.10
Wear Scar, mm			
in Argon	0.70	0.73	0.75
in Dry Air	0.35	0.40	0.49
in Wet Air	0.43	0.41	0.35
% Metallic Contact			
in Argon	100	100	100
in Dry Air	98.3	86.4	76.8
in Wet Air	100	100	100

* Thin-Layer Chromagraph
** 1000 gm Load, 240 rpm, 80°F, 32 Min

THIN LAYER CHROMATOGRAM

		(3)
(1)	(2)	METHANOL
NO	400°F	EXTRACT
TREATMENT	IN AIR	OF (2)

FIGURE 30 - THIN LAYER CHROMATOGRAM FOR 1-METHYL NAPHTHALENE
BEFORE AND AFTER OXIDATION AT 400F

VIII

LUBRICITY ADDITIVES

The previous report showed a substantial effect for lubricity additives and corrosion inhibitors even in concentrations as low as 15 ppm. In this present report, several separate additive studies have been carried out: (1) concentration studies with corrosion inhibitors and special lubricity additives, (2) effect of oxygen and water on effectiveness of oleic acid, (3) lubricity of antioxidants, (4) lubricity of anti-icing additives, (5) the effect of temperature on additive effectiveness, and (6) a comparison of additive fuels in ball-on-cylinder test and fuel-control mechanism.

A. Concentration Studies

Several additives shown to be good previously were studied in the ball-on-cylinder machine in room air. Concentrations varied from 5 ppm to 1% (10,000 ppm).

Table XXXV gives complete data on five additives used in jet fuels: ER-3, 4, 5, 12, and oleic acid. ER-3, ER-5, and oleic acid resemble each other in their effect on friction and wear. ER-4 acts differently; it reacts with the surface to form an electrically-insulating layer that has anti-friction properties but often causes an increase in wear. ER-12 is a proprietary additive of different composition to any of these and is quite effective as an anti-wear additive in lubricants. In these tests it was intermediate between ER-3 and ER-4.

The results have been plotted only for ER-3 and ER-4. Figure 31 gives the coefficient of friction for ER-3. The dotted curve is for the friction near the beginning of the test (4-minute mark); the solid curve is the friction at the end of the test (32 minutes). A comparison of these two lines tells whether friction increased or decreased during the test.

It will be seen that friction drops steadily as the concentration of ER-3 is increased. Although only 5 ppm is enough to give an improvement, the friction at 1% is appreciably less than at 0.1%. Also it takes 0.1% to give a test where the friction does not increase as the test proceeds. In other words, a little bit is good, but a lot is better.

In contrast, as shown in Figure 32, ER-4 is not effective up to 15 ppm. In fact it actually increases friction markedly, both in level and in erraticness of the trace. Friction increased steadily during the test. At 25 ppm, friction was even higher for a few minutes; then metallic contact suddenly began to drop and with it friction dropped also. At 32 minutes the coefficient of friction had dropped from 0.30 to 0.16. Further increases in concentration brought the friction down still more. Metallic contact decreased rapidly as soon as the test was started. The minimum was reached at 100 ppm. Higher concentrations gave slightly higher friction again.

The difference between the two additives is seen in Figure 33 which is a replot of the 32-minute friction. It is postulated that ER-4 reacts with the surface to give an insulating film. If the concentration is too low to form a complete film, the reaction roughens the surfaces and causes an increase in friction. Once a complete film is formed, friction is at a minimum.

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TABLE XXXV

EFFECT OF ADDITIVE CONCENTRATION IN BALL-ON-CYLINDER TEST

(240rpm, 240g, 32min, steel-on-steel)

Cyl	ppm Additive in Iso-octane	WSD, mm	CoFr @ 4min	CoFr @ 32min	% Metallic Contact
583	0	0.65	0.17	0.21	100
	5 ER-4	0.80	0.18	0.25	"
	10 "	0.79	0.19	0.27	"
	15 "	0.80	0.20	0.29	"
	25 "	0.71	0.20	0.16	75
	50 "	0.29	0.16	0.15	50
	0	0.65	0.19	0.21	100
	5 ER-3	0.34	.0.16	0.19	"
	10 "	0.31	0.15	0.18	"
	15 "	0.30	0.16	0.19	"
	0	0.69	0.20	0.24	"
562	5 Oleic Acid	0.34	0.13	0.18	95+
	10 " "	0.32	0.13	0.17	"
	15 " "	0.28	0.13	0.15	"
	5 ER-12	0.66*	0.21	--	100
	10 "	0.41	0.15	0.17	90
	15 "	0.46	0.17	0.18	93
	5 ER-5	0.40	0.18	0.23	100
	10 "	0.42	0.18	0.21	"
	15 "	0.36	0.18	0.21	"
560	5 ER-12	0.62	0.17	0.20	98
	10 "	0.38	0.14	0.16	99
	15 "	0.46	0.15	0.15	92
	50 "	0.37	0.13	0.13	53
	200 "	0.34	0.12	0.13	42
	1000 "	0.26	0.14	0.14	100
	0	0.46*	0.23	--	100
584	0	0.68	0.18	0.21	95+
	10 ER-3	0.32	0.15	0.18	"
	100 "	0.36	0.14	0.17	"
	1000 "	0.25	0.13	0.14	"
	10,000 "	0.27	0.12	0.12	"
	0	0.51	0.17	0.20	100
	10 ER-4	0.77	0.19	0.25	"
	100 "	0.27	0.14	0.15	"
	1000 "	0.38	0.15	0.15	"
	10,000 "	0.32	0.16	0.16	"
	0	0.66	0.19	0.20	--
	15 ER-4 } 10 ER-3	0.36	0.16	0.15	--

*Test terminated before 32 minutes because of excessive friction.
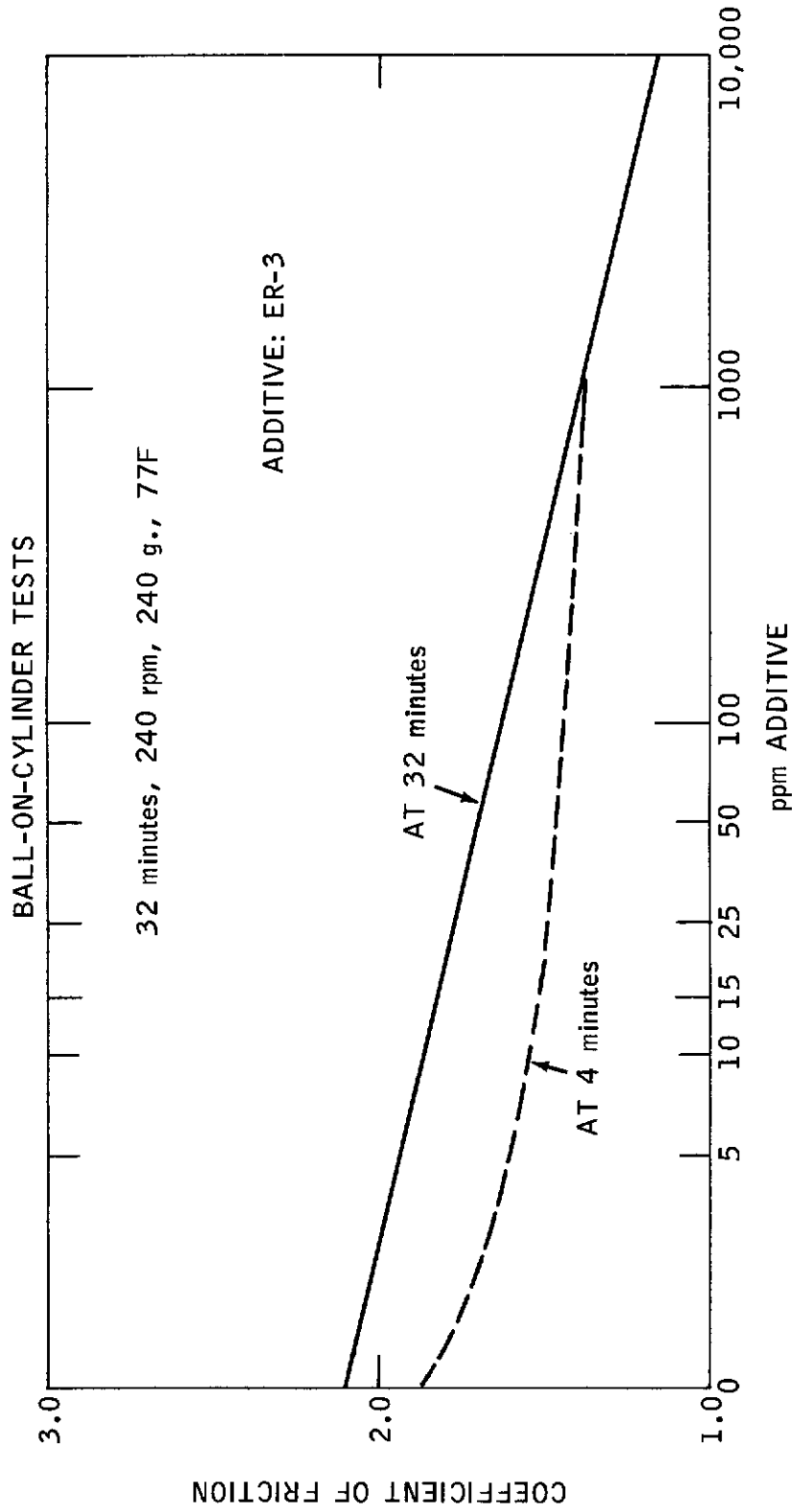
FIGURE 31 - FRICTION VS ADDITIVE CONCENTRATION FOR ER-3 IN BALL-ON-CYLINDER APPARATUS

BALL-ON-CYLINDER TESTS

32 minutes, 240 rpm, 240 g., 77F
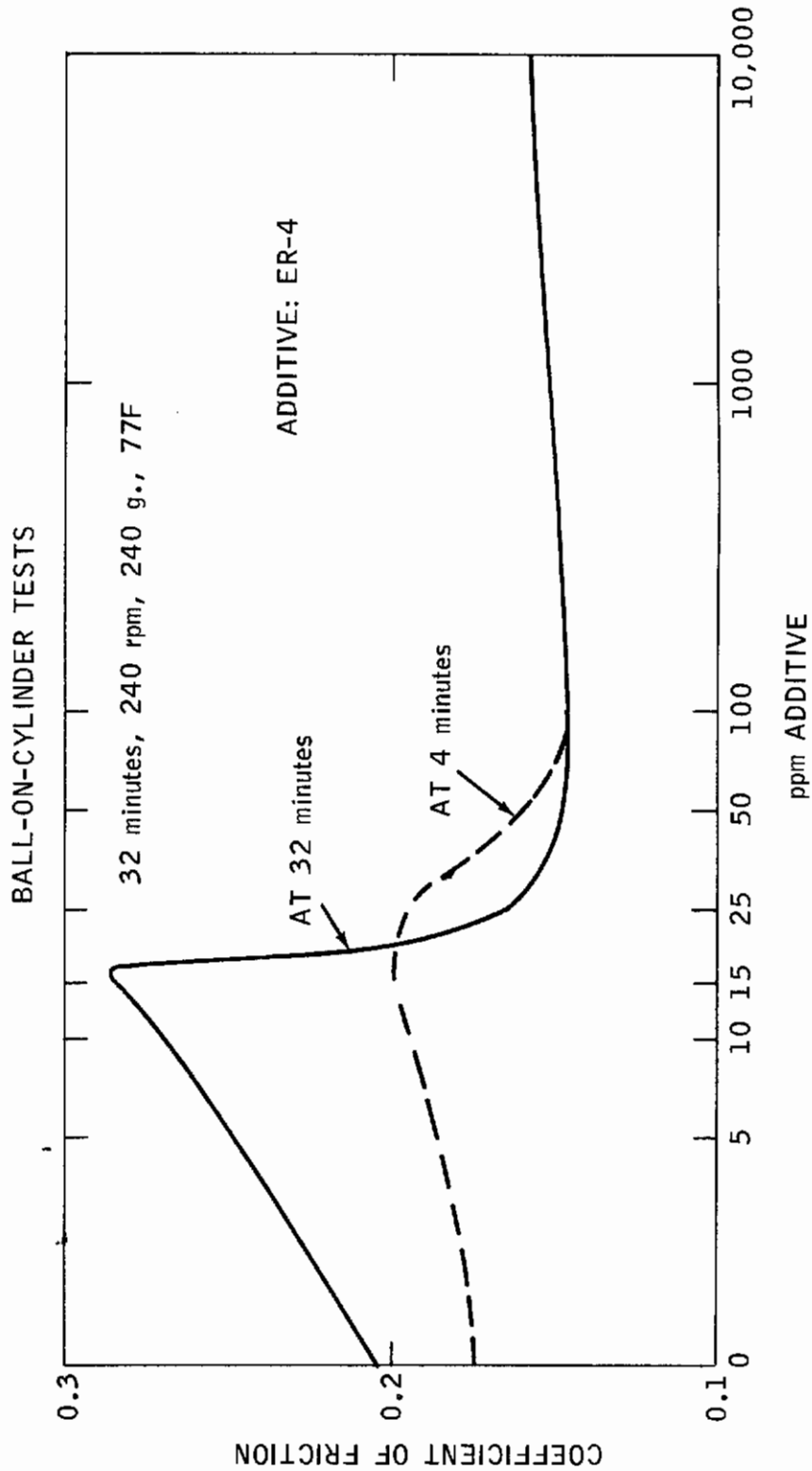
ADDITIVE: ER-4

FIGURE 32 - FRICTION VS ADDITIVE CONCENTRATION FOR ER-4 IN BALL-ON-CYLINDER APPARATUS

BALL-ON-CYLINDER TESTS

32 minutes, 240 rpm, 240 g., 77F
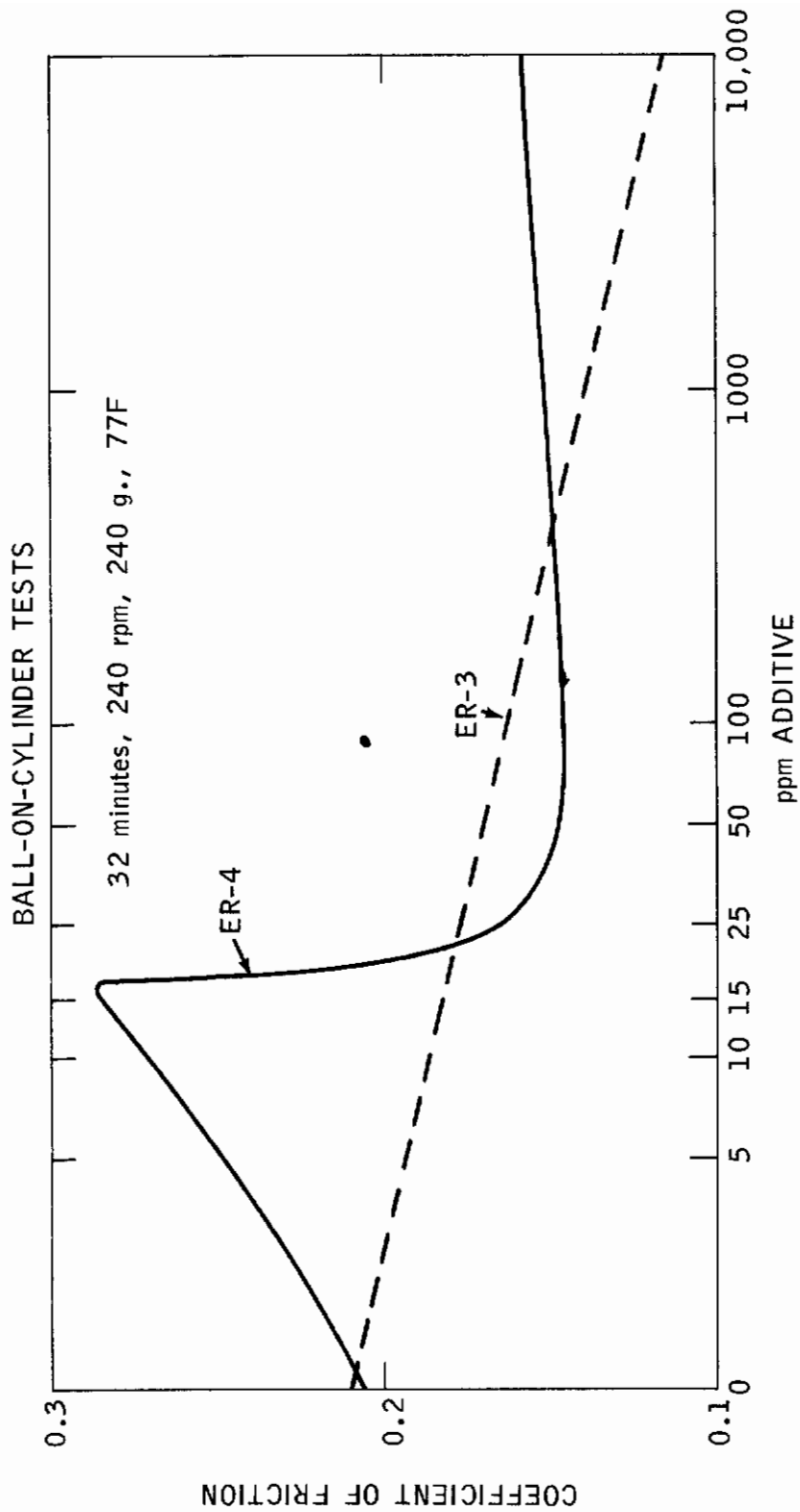
FIGURE 33 - COMPARISON OF ER-3 AND ER-4 IN BALL-ON-CYLINDER APPARATUS

ER-3, on the other hand, merely adsorbs on the surface, decreasing friction and wear in proportion to its concentration. More information on the behavior of these additives will be forthcoming when they are tested in different hydrocarbons and different atmospheres.

The wear data in Table XXXV parallels the friction data very closely and has not been plotted. The principal difference is that for ER-3, only 5 ppm is enough to drop the wear scar from 0.67 to 0.34 mm. Further additives then decrease it only to 0.25 mm. Wear is thus more responsive to traces of the additive than is friction.

One interesting run was a combination of 15 ppm ER-4 and 10 ppm ER-3. Since these two additives react so differently, they might behave synergistically. Such was the case. Metallic contact dropped much faster than with even 25 ppm ER-4 alone and friction was lower than for either component alone even at 25 ppm. Wear, however, was somewhat higher.

B. Effect of Oxygen and Water on
Effectiveness of Oleic Acid

1. Ball-on-Cylinder Tests

Bayol 35 containing 50 ppm oleic acid and various oxygen contents was tested at 160F and 1000 g load. The results, as shown in Table XXXVI and Figure 34, show clearly the effectiveness of oleic acid in reducing wear and friction and that there is only a slight increase of friction and wear when the oxygen content is increased.

In the absence of oxygen, the wear and friction are already so low with pure Bayol 35 that the addition of oleic acid has almost no effect. This suggests that one of the roles of oleic acid is to exclude oxygen from the surface.

2. Four-Ball Tests

Because Bayol 35 (paraffinic) and methylnaphthalene (aromatic) behaved so differently toward oxygen concentration in the four-ball test, it was decided to learn how oleic acid would affect the results. Blends of 50 ppm oleic acid in both Bayol 35 and methylnaphthalene were run in both argon and air, both wet and dry. Results are given in Table XXXVII and in Figures 35, 36 and 37.

It appears that oleic acid is most effective in reducing corrosive wear and has little effect elsewhere. In Bayol 35 in air, oleic acid cut wear in half as shown in Figure 35. Essentially, it reduced the WSD to a low level of about 0.37 mm regardless of the humidity. One can speculate that oleic acid is functioning as a corrosion inhibitor, forming a protective film on the surface that resists oxygen attack.

In argon, oleic acid again maintained wear at a low level. As shown in Figure 36, it reduced the relatively high wear in dry argon, but did not further reduce the lower wear in wet argon.

In methylnaphthalene, oleic acid is completely ineffective. It did not reduce the very high wear in dry argon, and it had only minor effects in the other cases, where the wear was already low. This is perhaps not too surprising for it has been reported in the literature that organic acids work best when oxide films are present.

TABLE XXXVI

EFFECT OF OLEIC ACID ON WEAR AND FRICTION OF BAYOL 35

Ball-on-Cylinder Tests (240rpm, 32min, 160F, 1000g)

O_2 in Fuel, ppm	Wear Scar Diameter, mm		Coefficient of Friction	
	Bayol 35	50ppm Oleic Acid in Bayol 35	Bayol 35	50ppm Oleic Acid in Bayol 35
52 (in Air)	0.57	0.31	0.27*	0.13
17	0.41	0.23	0.16*	0.12
5.0	0.30	0.23	0.16*	0.12
0.7 (in N_2)	0.21	0.20	0.14	0.11

* Friction trace erratic.
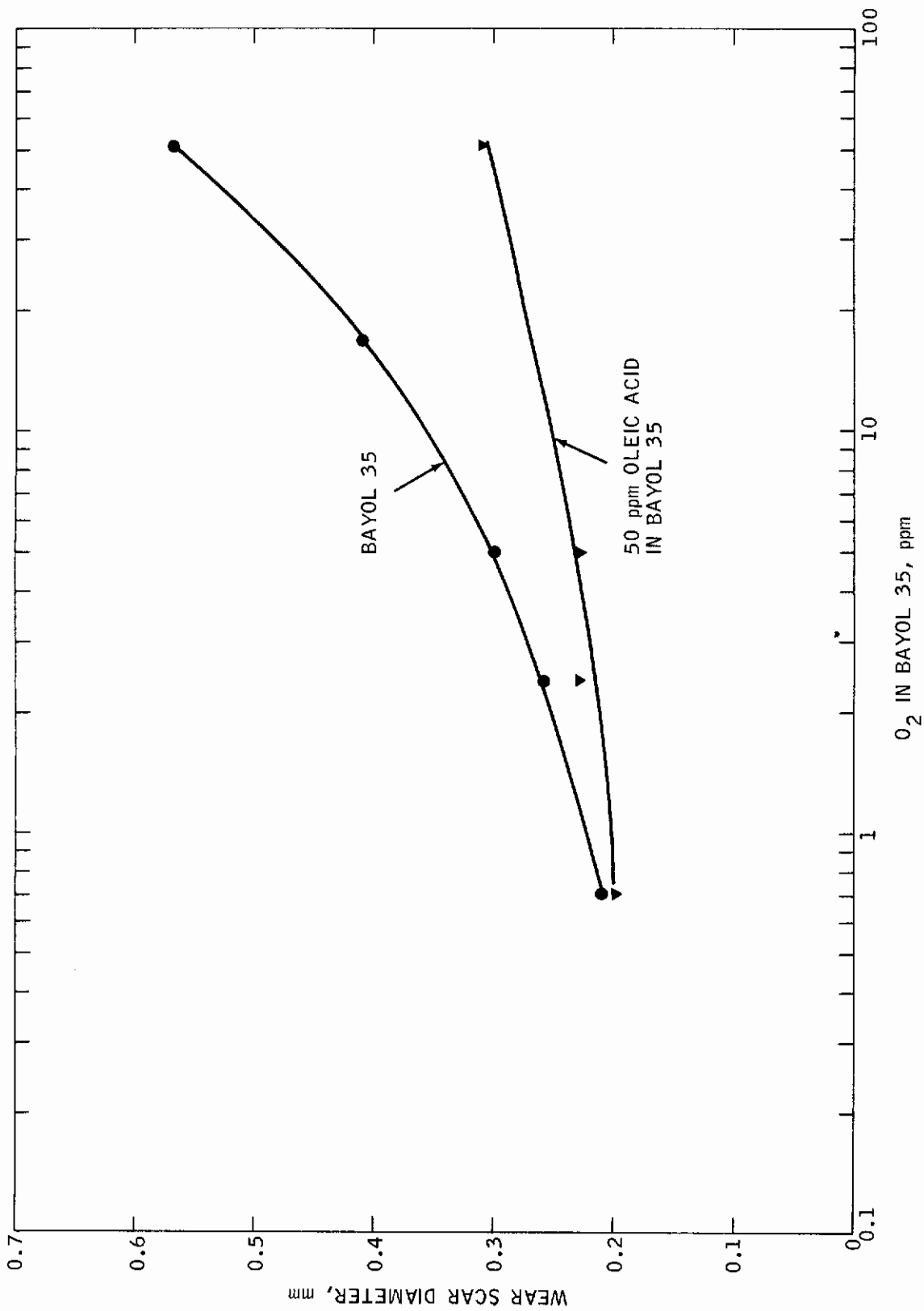
FIGURE 34 - WEAR VS OXYGEN CONCENTRATION FOR BAYOL 35 AND
BAYOL 35 CONTAINING 50 ppm OLEIC ACID
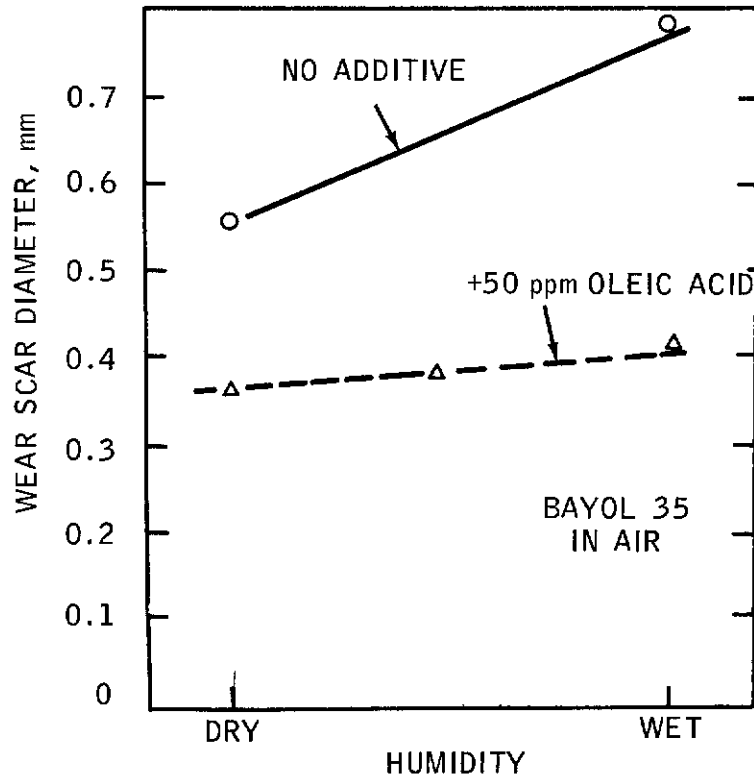
FIGURE 35 - EFFECT OF OLEIC ACID ON WEAR OF BAYOL 35 IN AIR - FOUR-BALL TEST
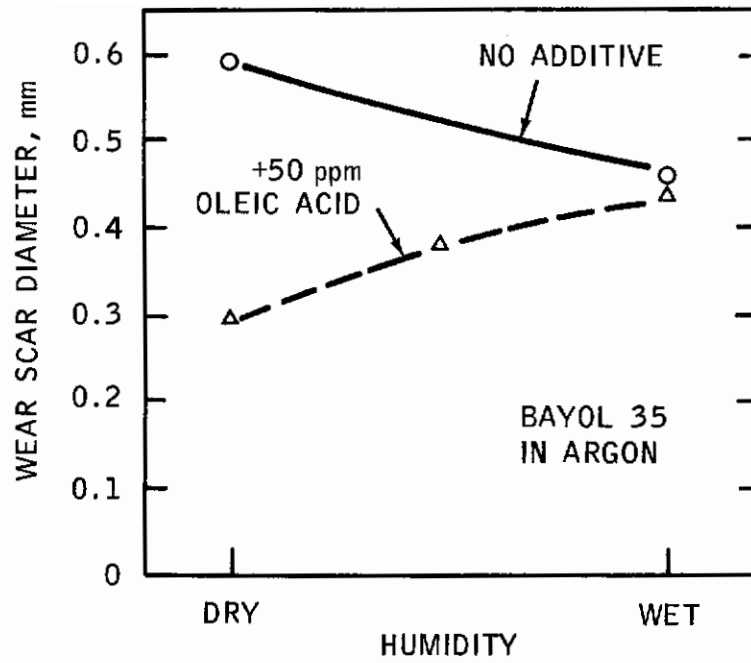
FIGURE 36 - EFFECT OF OLEIC ACID ON WEAR OF BAYOL 35 IN ARGON - FOUR-BALL TEST

- 108 -
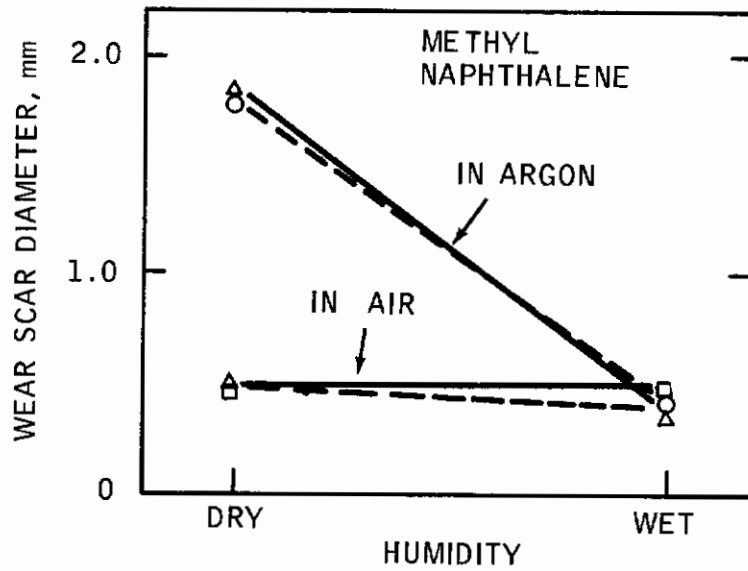
FIGURE 37 - EFFECT OF OLEIC ACID ON WEAR OF METHYL NAPHTHALENE IN ARGON AND AIR
FOUR-BALL TEST
(Dashed Lines Represent 50 ppm Oleic Acid)

TABLE XXXVII

EFFECT OF OLEIC ACID ON WEAR

4-Ball Wear Tests: 1200 rpm, 36C, 10 Kg, 15 min

		Wear Scar Diameter, mm					
		Bayol 35			Me Naphthalene		
ppm Oleic Acid	Atmosphere	Dry	Moist	Wet	Dry	Moist	Wet
0	Argon	0.58	---	0.46	1.78	---	0.43
50	Argon	0.30	0.38	0.44	1.81	1.76	0.36
0	Air	0.56	---	0.79	0.48	---	0.46
50	Air	0.37	0.38	0.42	0.53	0.47	0.38

C. Effect of Antioxidants on Wear

1. Four-Ball Tests

Oxygen obviously has a strong effect on wear, increasing it with Bayol 35 (paraffinic) and decreasing it with methylnaphthalene (aromatic). It also appears that the primary attack of oxygen is on the metal to form FeO, and not on the fuel to form oxidation products which then attack the metal. However, to check this, a few runs were made using two common antioxidants: phenyl-alpha-naphthyl-amine (PAN) and 4,4'-methylene-bis-(2,6 di-t-butyl phenol) (MDTBP). Both antioxidants were run at 1% concentration in Bayol 35 and methylnaphthalene. This is far above the usual concentration in jet fuels, but was used to magnify any effects. Runs were made in air and argon, wet and dry.

The results are given in Table XXXVIII, but they are not very conclusive. PAN reduces the wear of Bayol 35 in all cases but this is exactly what would be expected from adding a heavy aromatic hydrocarbon, which is what PAN is. The effect seems more probably the effect of PAN's aromaticity rather than its antioxidant character. PAN had no effect on the wear of methylnaphthalene in argon; nor would it be expected to. MDTBP reduced the wear of methylnaphthalene in dry argon; it behaves like water in this respect. But again, this cannot be due to its antioxidant qualities.

The only effects that could be connected in any way with antioxidation are the decrease in wear with Bayol 35 in wet air, and with methylnaphthalene in dry air. Both additives are effective under these conditions.

2. Ball-on-Cylinder Tests

Ball-on-cylinder tests were carried out on Bayol 35 containing 0.1% MDTBP, and various contents of dissolved oxygen at 160F and 1000 g loads. The results are presented in Table XXXIX and plotted in Figure 38 along with similar data on Bayol 35 alone, and Bayol 35 containing oleic acid. It is obvious that this antioxidant is ineffective in improving the lubricity of the base fuel. This confirms that the oxygen attack is at the metal surface rather than oxidation of the fuel.

D. Effect of Anti-Icing Additive
   (AIA) on Lubricity

Anti-icing additive is used in jet fuels to lower the freezing point of any suspended water. It consists of 99.6% Cellosolve (methyl ester of ethylene glycol) and 0.4% glycerine; it is used in 0.1% concentration in jet fuel.

An evaluation of fuels containing AIA was made in the ball-on-cylinder device. It appears that AIA is quite sensitive to humidity although for the most part it does not have much of an effect on either friction or wear. In general, AIA acts as a lubricity agent (although not a very good one) in dry air, reducing both friction and wear. In wet air, however, it merely accentuates the effect of water. Water itself, as has been shown before, accelerates corrosive wear giving higher friction and wear. AIA helps dissolve more water and therefore gives still more friction and wear. At low humidities then, AIA is somewhat beneficial while at high humidities it is somewhat detrimental.

Table XL presents two sets of ball-on-cylinder tests; one with isooctane as a base fuel, the other with Bayol 35. It can be seen that AIA has an anti-wear effect in the absence of water and a pro-wear effect in the presence of water.

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TABLE XXXVIII

EFFECT OF ANTIOXIDANTS ON WEAR
4-Ball Tests: 1200 rpm, 36C, 10kg, 15 min

Antioxidant	Base Fuel	Wear Scar Diameter, mm			
		In Argon		In Air	
		Dry	Wet	Dry	Wet
None	Bayol 35	0.58	0.46	0.56	0.79
1% PAN[*]	"	0.42	0.41	0.40	0.46
1% MDTBP[**]	"	0.52	0.50	0.56	0.59
None	Methyl Naphthalene	1.78	0.43	0.62	0.43
1% PAN	"	1.81	0.41	0.48	0.38
1% MDTBP	"	0.85	0.46	0.46	0.40

* PAN = Phenyl-alpha-naphthylamine

** MDTBP = 4,4'-methylene-bis-(2,6 di-t-butyl phenol)

TABLE XXXIX

EFFECTIVENESS OF ANTIOXIDANT

0.1% MDTBP in Bayol 35

(Ball-on-Cylinder Tests - 160F, 1000g, 240 rpm)

Atmosphere	ppm O_2	Coefficient of Friction	Wear Scar Diameter, mm
Argon	0.4	0.14	0.22
2% O_2 in Argon	6	0.22	0.29
7.3% O_2 in Argon	21	0.22	0.38
Air	59	*	0.65

* Erratically high.
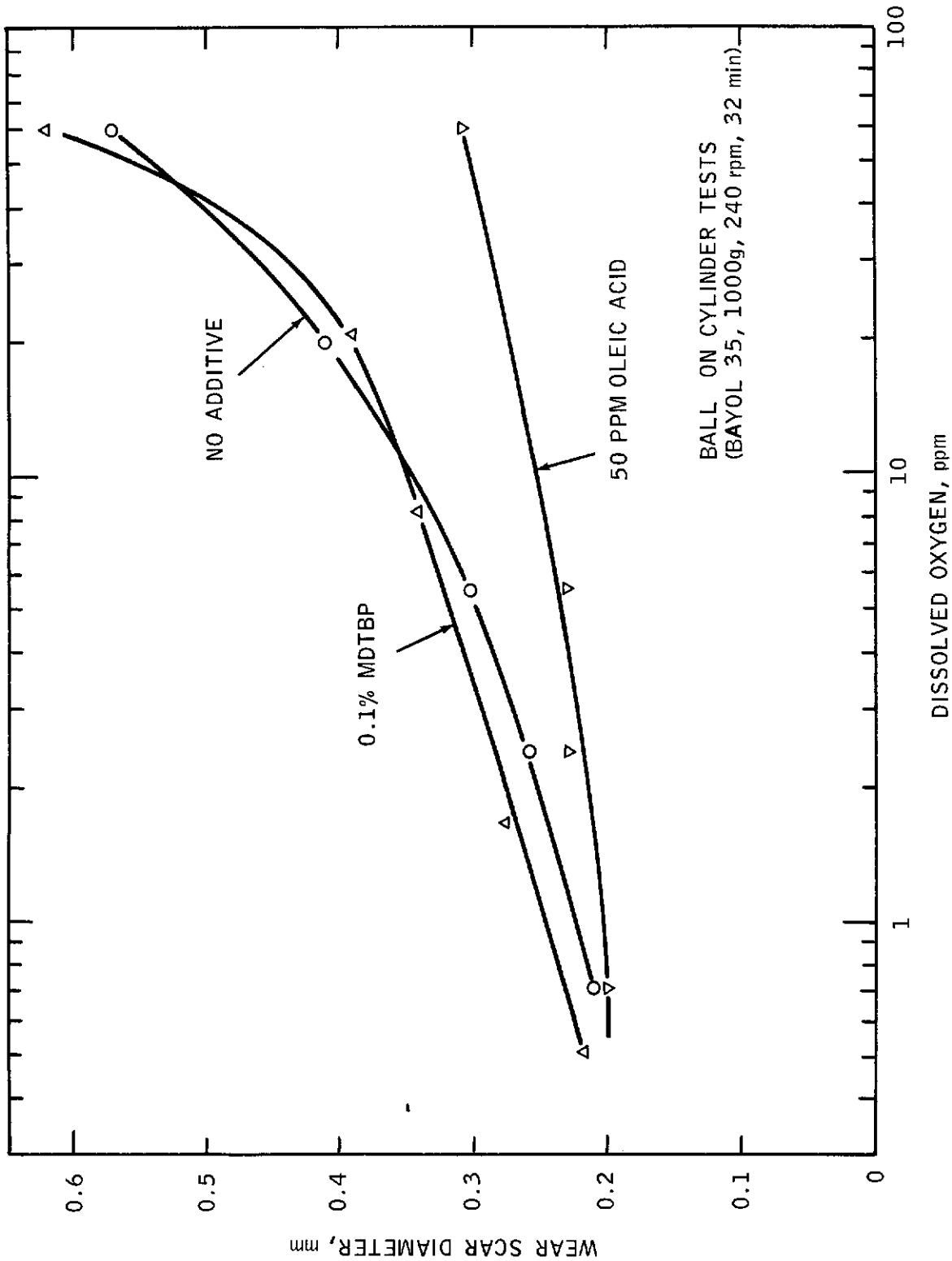
FIGURE 38 - EFFECT OF OLEIC ACID AND ANTI-OXIDANT MDTBP ON WEAR - BALL-ON-CYLINDER TEST

TABLE XL

EFFECT OF AIA: BALL-ON-CYLINDER TESTS

(240 rpm, 32 min, 77F)

	Argon		Air	
	Dry	Wet	Dry	Wet
	Wear Scar Diameter, mm			
Isooctane	0.27	0.32	0.75	0.95
+ 0.10% AIA*	0.26	0.45	0.45	1.00
Bayol 35	0.34	0.31	0.65	0.77
+ 0.10% AIA*	0.21	0.31	0.32	0.82
	Coefficient of Friction			
Isooctane	0.13	0.22	0.23	0.24
+ 0.10% AIA	v. High	0.19**	0.17**	0.25**
Bayol 35	0.10	0.14	0.16	0.13
+ 0.10% AIA	0.10	0.12**	0.13**	0.14

---

* 99.6% Methyl Cellosolve
   0.4% Glycerine

** More erratic.

AIA gives a 50% reduction in wear scar diameter in dry air (10-15 fold reduction in wear rate) but gives a 5% increase in wear scar in wet air (25% increase in wear rate). Note that the effect of either oxygen or water is generally much greater than the effect of AIA. The friction data, also presented in Table XL, shows that coefficient of friction for Bayol 35 alone was 0.16, for Bayol 35 + AIA it cycled irregularly between 0.10 and 0.16. In wet air, AIA actually gives more friction.

Table XLI gives data on AIA in isooctane containing lubricity additives. These tests were run in room air with uncontrolled humidity. The effect of AIA was quite minor, the wear increasing slightly, the friction decreasing slightly. The lubricity additives have reduced the wear to a much lower level than in Table XL so that AIA does not have much effect.

Table XLII gives wear data on the effect of Cellosolve alone and also with the trace of glycerine included in AIA. Both isooctane and Bayol 35 were the base fuels. As can be seen in the table, with one exception there was no effect for adding the trace of glycerine, and the exception appears to be due to irreproducibility. In all cases, however, both Cellosolve and AIA reduced wear, although there was little effect on friction. These data correlate best with the dry air data of Table XL.

The final set of data were obtained on a low volatility fuel furnished by Wright-Patterson Air Force Base. This fuel contained AIA and was extracted as follows: Equal volumes of fuel and distilled water were shaken for two minutes in a separatory funnel, allowed to stand several minutes and the water layer drawn off. This was repeated a second time. The extracted fuel was compared to the unextracted fuel at two loads and under four atmospheric conditions: (a) in room air, (b) in wet air, (c) blown dry with dry air and run in dry air, (d) blown dry and run in room air after equilibrating for three days.

The results were consistent in all cases as shown in Table XLIII. The unextracted fuel gives less wear, the effect being more pronounced in wet air than in dry. The friction traces show almost no differences in any of the eight comparisons. These data agree with the data in Table XLI, AIA reducing wear. They do not agree with the data in wet air which showed AIA to increase wear, both with and without lubricity additives. One can only speculate as to the reason for the differences. Perhaps other additives in the fuel are having an overriding effect; perhaps the extraction removes more than just the AIA. The overall conclusion remains the same. AIA is a lubricity agent but a poor one.

Summarizing all these data, AIA has much less effect on lubricity than do heavy aromatics, corrosion inhibitors, lubricity additives or atmospheric oxygen and humidity. The results shown in Table XL are believed to be the most definitive. These data were obtained last chronologically and separate the effect of additive and atmosphere most clearly.

TABLE XLI

EFFECT OF AIA WITH LUBRICITY ADDITIVES: BALL-ON-CYLINDER TESTS

(240 rpm, 32 min, 77F, in Air)

Additive in Isooctane	60 g		240 g	
	WSD, mm	CoFr	WSD, mm	CoFr
None	0.62	Erratic	0.72	Erratic
15 ppm ER-5	0.26	0.17	0.32	0.18
15 ppm ER-5 + 0.1% AIA	0.28	0.14	0.35	0.16
15 ppm ER-3			0.31	0.19
15 ppm ER-3 + 0.1% AIA			0.32	0.18

TABLE XLII

EFFECT OF COMPONENTS OF AIA: BALL-ON-CYLINDER TESTS

(240 rpm, 32 min, 77F)

	Wear Scar Diameter, mm		
	60 g	240 g	1000 g
Isooctane	0.57	0.80	--
+ 0.10% Methyl Cellosolve	0.55	0.54	--
+ 0.10% AIA	0.54	0.55	--
Bayol 35	--	0.41	0.64
+ 0.10% Methyl Cellosolve	--	0.36	0.52
+ 0.10% AIA	--	0.42	0.53

TABLE XLIII

EXTRACTION OF AIA: BALL-ON-CYLINDER TESTS

(240 rpm, 32 min, 77F)

	Dry Air		Room Air		Wet Air	
	240 g	1000 g	240 g	1000 g	240 g	1000 g
Extracted Low Volatility Fuel	--	--	0.32	0.37	0.32	0.43
Low Volatility Fuel (With AIA)	--	--	0.26	0.33	0.29	0.38
Extracted Low Volatility Fuel (Blown With Dry Air)	0.30	0.35	0.31	0.37	--	--
Low Volatility Fuel (With AIA) (Blown With Dry Air)	0.29	0.34	0.29	0.37	--	--

E. The Effect of Temperature
    on Additive Response

          The effectiveness of jet fuel additives at 50 ppm concentration were
tested at various temperatures. The base fuel was Bayol 35 containing 0.1% MDTBP,
an antioxidant having been found to have no antiwear effect. The results are
shown in Table XLIV and Figure 39. ER-2, ER-3 and ER-5 showed the decrease of ef-
fectiveness with the increase of the temperature. At 350F, their effectiveness was
either lost or masked by the oxidized product. The behaviors of ER-1 and ER-4 are
different from these three additives. ER-1, showing no antiwear effect at 160F
and 240F, gave the lowest wear at 350F among all additives. ER-4 showed a minimum
wear at 240F. The reason for these anomalous phenomena is unknown.

          The effectiveness of ER-1, ER-3 and ER-4 was also tested in the Vickers'
vane pump at 240F and in wet air. The results, as shown in Table XLV, confirmed
those from ball-on-cylinder tests ER-3 and ER-4 give an antiwear effect but ER-1
was ineffective at 240F.

          These experimental results indicate that the effectiveness of additives
at high temperature is quite unpredictable and deserves further investigation.

F. Comparison of Additive Fuels in Ball-On-Cylinder
    Test and Full-Scale Fuel Control Mechanism

          A request was received to run four fuels in the ball-on-cylinder device
to compare with tests run in a fuel control mechanism by the manufacturer of the
mechanism. The rubbing surfaces here are steel. The manufacturer's tests con-
sisted of four successive runs as follows: a JP-4, JP-4 + 20 ppm ER-4, JP-4 + 20
ppm ER-4 + 1000 ppm ER-5, and Stoddard solvent. They found that JP-4 gave a con-
tinuously increasing friction; the ER-4 halted the increase but did not reduce the
friction; the ER-4/ER-5 gave low friction throughout; Stoddard solvent was as good
as the preceding run.

          Ball-on-cylinder tests on the same four fuels are reported in Table XLVI.
Runs were made on both steel and anodized aluminum systems. Several differences
were noted.

          ● With steel, 20 ppm ER-4 showed a definite improvement in wear and fric-
             tion; with anodized aluminum it made things worse. In the previous
             section of this report, it was found that in isooctane, 20 ppm ER-4 is
             borderline in performance, lower concentrations giving actually higher
             friction and wear. Also in previous work with JP-4 fuels, ER-4 was found
             to increase wear. The good performance with this fuel was therefore
             rather surprising. It was as if a greater amount of ER-4 than 20 ppm were
             present, or as if another additive had also been added.

          ● The addition of 1000 ppm ER-5 did not make much improvement in friction
             and wear over the ER-4 alone. In comparison with the base fuel, the
             improvement caused by the ER-5 is about what would be expected, but this
             again makes the performance of ER-4 alone to appear surprisingly good.

● Stoddard solvent was as bad as the JP-4, whereas in the fuel-control test it was as good as the additive run just before. The most likely explanation of this discrepancy is that in the fuel-control tests the previous run on ER-5 so conditioned the metal surfaces that good performance was continued even after the fuel had been changed. To check the possibility of "carry-over", runs were made on the ball-on-cylinder rig in which the fuel was changed but the ball and track were not. A pronounced carry-over was observed: friction remained at a low level for over three minutes (750 revolutions). During that time, metallic contact slowly increased back to 100%, indicating that the protective layer was being worn away. The same effect was noted with anodized aluminum where the friction with JP-4 was much less following a run with ER-5 than it was before.

TABLE XLIV

EFFECT OF ADDITIVES AT VARIOUS TEMPERATURES

(Ball-On-Cylinder Tests, 480g, Room Air, 240 rpm, 32 min)

Base Fuel: 0.1% MDTBP in Bayol 35

	Wear Scar Diam, mm			Coefficient of Friction			Acidity After Test, ppm KOH	
Additive:	160F	240F	350F	160F	240F	350F	160F	350F
None	0.85 (0.78)	0.67 (0.77)	0.51	0.18 (0.18)	0.15 (0.17)	0.15	<0.1 (<0.1)	6.7
50 ppm ER-1	0.72 (0.80)	0.78	0.46 (0.43)	0.16 (0.18)	0.16	0.15 (0.12)	<0.1 (<0.1)	6.7 (4.9)
50 ppm ER-2	0.35	0.36	0.55	0.17	0.16	0.12	4.9	11.0
50 ppm ER-3	0.40	0.43	0.56	0.16	0.17	0.14	0.8	6.7
50 ppm ER-4	0.78 (0.77)	0.52 (0.38)	0.72	0.16 (0.13)	0.13 (0.12)	0.17	3.6 (5.3)	25.0
50 ppm ER-5	0.42	0.38	0.57	0.16	0.16	0.17	2.8	11.0

BALL-ON-CYLINDER TESTS
(480g₁, 240 rpm, 32 MIN, ROOM AIR, STEEL-ON-STEEL)
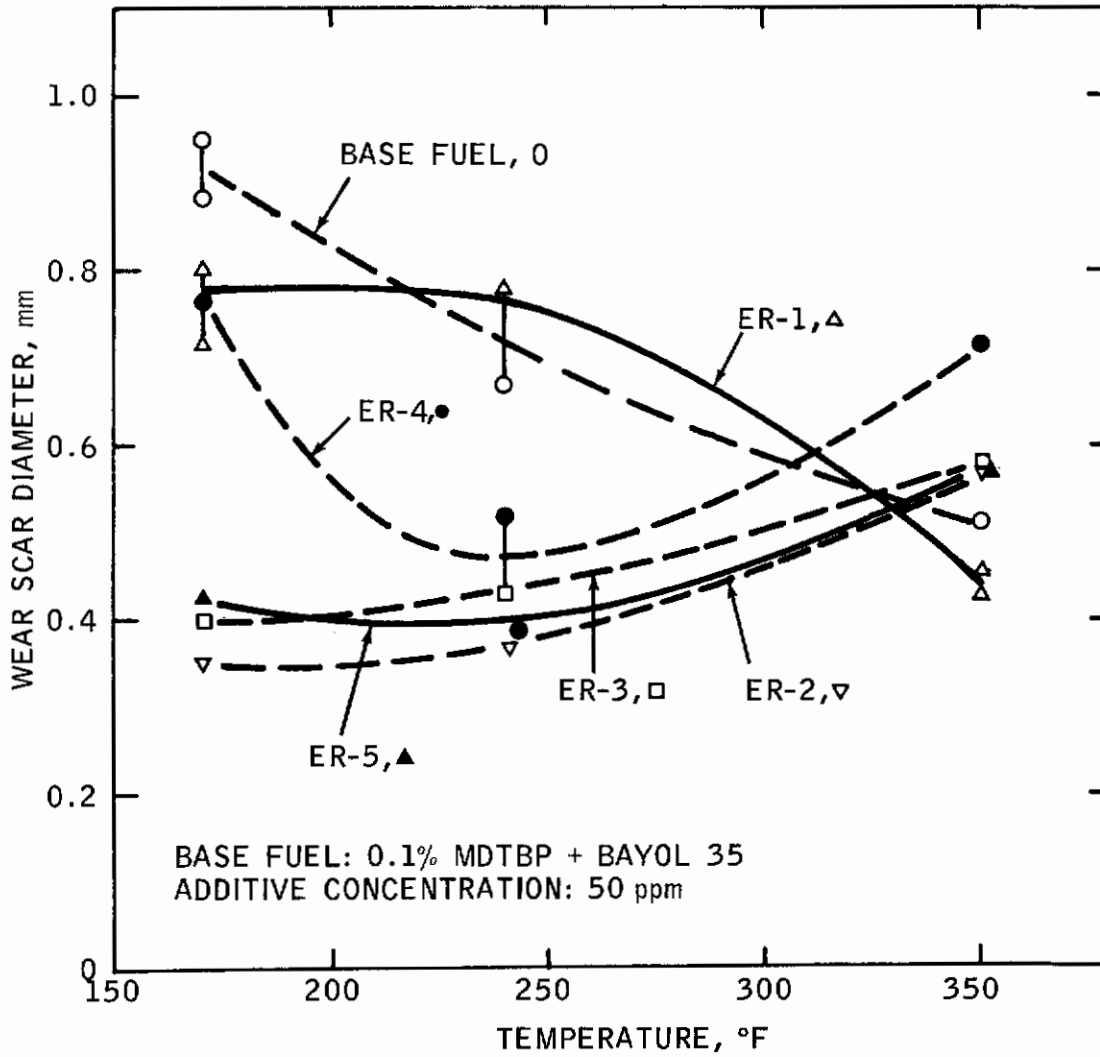
FIGURE 39

EFFECT OF TEMPERATURE ON ADDITIVE RESPONSE

TABLE XLV

EFFECT OF TEMPERATURE ON ADDITIVE EFFECTIVENESS: VICKERS VANE PUMP TESTS

(Sump Temperature, 240F; Wet Air, 4 Hours)

Base Fuel: Bayol 35 Containing 0.1% MDTBP

Additive:	None	50 ppm ER-1	50 ppm ER-3	50 ppm ER-4
Pressure, psig	150	150	150	150
Pumping Rate, gpm	0.27	0.22	0.43	0.42
Vol. Eff., %	15	12	24	23
Wear, mg				
Wt. Loss of Vanes	22	29	0	1
Wt. Loss of Ring	473	360	5	0
Surface Roughness, μ inch				
Vanes, Initial		9	15	9
Final	>200	80	12	12
Ring, Initial	27		12	23
Final	>200	136	9	13

TABLE XLVI

COMPARISON OF BALL-ON-CYLINDER WITH FUEL CONTROL MECHANISM TESTS

Ball-on-Cylinder Tests (32min, 77F, 240rpm)

Fuel No	Fuel	Steel-on-Steel 60g		Steel-on-Steel 240g		Anodized Al 60g		Mfg. Tests in Fuel Control Mechanism
		WSD, mm	Coeff. Friction	WSD, mm	Coeff. Friction	WSD, mm	Friction	
1	JP-4	0.24	0.19	0.29	0.18	0.44	0.41 High	Friction high and in-creasing
2	JP-4 + 20ppm ER-4	0.19	0.18	0.22	0.15	0.62	0.53 V. High	Friction high but level
3	JP-4 + 20ppm ERA + 1000ppm ER-5	0.22	0.17	0.23	0.14	0.33	0.30 V. Low	Friction low
4	Stoddard Solvent	0.24	0.21	0.29	0.18	0.45	0.36 Medium	" "
5	JP-4 Fuel D	0.25	0.25	--	--	--	-- --	--

IX

EFFECT OF METALLURGY

Essentially all of the data obtained so far have been obtained on a steel-on-steel system. This system is subject to corrosive wear, and indeed this kind of wear is the most serious investigated. The corrosion leads to the formation of iron oxide particles, which are themselves abrasive, and the abrasion can bring on a "mild" form of scuffing.

If the surfaces are not subject to corrosion--or at least resistant to it--then corrosive wear is greatly reduced. Other kinds of wear then predominate. In particular scuffing is more likely to occur. Scuffing is the result of the failure of the thin films normally on metal surfaces. For steel surfaces the most probable film is iron oxide. This film is continuously being reformed during the wear process as a result of the presence of oxygen and water.

For stainless steels and other non-corrodible metals, the iron oxide film can reform only with difficulty. Therefore, where a mild steel surface will undergo corrosive wear, a stainless surface will tend to scuff.

The work on different metallurgies has been delayed pending the arrival and debugging of a new four-ball machine. This machine was designed primarily for lubricant testing and was not suitable for working at the low loads required for fuels testing. The data reported here are therefore only the preliminary work on metallurgy as a major variable.

In the first series of tests, three steels were used. Two were the same composition, AISI 52100, but differed in hardness, one being the 63-66 R_c usually used, the other being annealed to about 25 R_c. The third was a 440 stainless steel. Data are in Table XLVII. Both of the chrome steels showed higher wear in air than in argon, indicating that corrosive wear was controlling. Interestingly enough, wear was higher with the hard balls. This is believed to be due to the smaller contact area and greater unit loads, which tend to promote scuffing. The abrasive iron oxide particles in the contact region therefore were promoting "mild" scuffing.

The stainless steel gave lower wear throughout, particularly in air. This is obviously because corrosive wear was much less. The loads were low enough so that scuffing did not occur.

In the second series of tests, the additional variable of fuel type was included. A series of blends of the paraffinic Bayol 35 and the aromatic 1-methylnaphthalene were tested under four different atmospheres on both chrome and stainless steel.

As can be seen in Table XLVIII, the tendency to scuff increased as the percent 1-methylnaphthalene increased. This was true for both steels, indicating that qualitatively they were behaving the same. However, the stainless steel tended to scuff more easily. In dry argon and in dry air, with 52100 steel, scuffing was only with 100% 1-methylnaphthalene, whereas with stainless steel the 95% blend scuffed as well. In wet argon the 52100 steel did not scuff at all, whereas both the 95% and 100% 1-methylnaphthalene scuffed with stainless.

In wet air no scuffing failures occurred, but it is interesting that with 52100 the highest wear occurred with 100% Bayol 35, whereas with stainless it was with 100% 1-methylnaphthalene. That is, 52100 steel tended to undergo corrosive wear, stainless steel tended to scuff.

These tests indicate that the wear and friction behavior is further complicated by metallurgy, but that the complications may not be too confusing. What is necessary in correlating laboratory data with the field is some knowledge as to whether the limiting condition is scuffing, corrosion, or abrasion.

TABLE XLVII

EFFECT OF STEEL TYPE ON WEAR

(Four-Ball Tests: Bayol 35, 5 kg, 1200 rpm, 77F, 15 min)

Steel Type	Hardness, R_c	Wear Scar Diam, mm		
		Argon	Dry Air	Wet Air
Chrome (AISI 52100)	63-66	0.28	0.50	0.63
Chrome (AISI 52100)	~25	0.30	0.41	0.47
Stainless (Type 440)	55-60	0.21	0.20	0.31

TABLE XLVIII

INTERACTION BETWEEN FUEL COMPOSITION AND STEEL TYPE

	Wear Scar Diameter, mm							
	Dry Argon		Wet Argon		Dry Air		Wet Air	
	52100	440	52100	440	52100	440	52100	440
Fuel	Steel	Stainless	Steel	Stainless	Steel	Stainless	Steel	Stainless
Bayol	0.23	0.22	0.35	0.26	0.51	0.24	0.59	0.46
5% ⍺-MN	0.24	0.31	0.52	0.39	0.48	0.27	0.50	0.43
30 ⍺-MN	0.27	0.32	0.44	0.34	0.45	0.41	0.44	0.36
95 ⍺-MN	0.57	1.80	0.43	1.17	0.45	1.98	0.46	0.57
⍺-MN	1.22	1.72	0.40	1.26	1.45	1.30	0.44	0.86

X

MATHEMATICAL MODEL FOR CORROSIVE WEAR

A mathematical model for corrosive wear in the ball-on-cylinder device has been constructed. Nomenclature is given in Table XLIX. Figure 40 shows the model. The wear region between the ball and cylinder was assumed to be two smooth parallel plates, with a uniform clearance, ξ. The lower plate--the moving cylinder--brings in fresh oil by viscous drag. The oil is assumed to be saturated with the dissolved gases (oxygen and/or water) at the inlet. The gases then diffuse to the stationary surface (the ball) where they react to form iron oxide. The reaction is assumed to be instantaneous and the reaction product immediately removed by rubbing. The other simplifying assumptions are:

(1) Diffusion is at a steady state and two-dimensional, i.e.

$$\frac{\delta c}{\delta t} = 0 \qquad \frac{\delta c}{\delta z} = 0$$

(2) The fluid is Newtonian and incompressible and there is no slip at the wall.

(3) Wear occurs only at the upper surface (ball) where the oxygen is consumed to reach an equilibrium concentration, C_1. There is no mass transfer at the lower boundary.

The equation of diffusion thus becomes:

$$\frac{\delta}{\delta y} \left(D \frac{\delta c}{\delta y}\right) = u_o \left(1 - \frac{y}{\xi}\right) \frac{\delta c}{\delta x} \qquad [1]$$

With boundary conditions as:

$$C(0, y) = C_o \qquad\qquad 0 \leq y \leq \xi$$

$$C(x, \xi) = C_1 \qquad\qquad x > 0$$

$$\frac{\delta c}{\delta y}(x, 0) = 0 \qquad\qquad x \geq 0$$

By means of the similar approach for Graetz' problem, the solution of Equation [1] becomes an eigen-value and eigen-function problem and is found to be:

$$C(x,y) = (C_o - C_1) \left[\sum^{\infty} B_n \psi_n \left(\frac{y}{\xi}\right) \exp\left(\frac{-\beta_n^2 Dx}{\xi^2 u_o}\right) \right] + C_1 \qquad [2]$$

The values of β_n^2, $\psi_n\left(\frac{y}{\xi}\right)$ and B_n have been obtained by a numerical method as follows. For the present case, the series in Equation [2], due to its rapid convergence, can be truncated to only one term.

$$C(x,y) = 1.385 (C_o - C_1) \psi\left(\frac{y}{\xi}\right) \exp\left(\frac{-3.719 Dx}{\xi^2 u_o}\right) + C_1 \qquad [3]$$

TABLE XLIX

NOMENCLATURE

a = Minor diameter of wear scar on ball, cm

a_o = Hertz diameter, cm

b = Major diameter of wear scar on ball, cm

B_n = A constant in Equation [2]

C = Concentration, gm/gm, a function of x, y

C_o = Initial concentration, gm/gm

C_a = Concentration at the exit of contact region, gm/gm, $C(a,y)$

C_1 = Concentration at the wear surface, gm/gm, $C(x, \xi)$

D = Mass diffusivity, cm^2/sec

D_b = Diameter of the ball, cm

D_c = Diameter of the cylinder, cm

L = Relative compliance

m = Number of moles Fe to react with 1 mole of O_2

n = A constant

s = Wear distance, cm

t = Time, sec

u = Flow velocity, cm/sec

u_o = Sliding speed, cm/sec

V = Wear volume, cc

x, y, z = Coordinates

X = Dimensionless group, $\dfrac{D\,x}{\xi^z\,u_o}$

Y = Dimensionless y, y/ξ

β_n = Eigenvalue

θ = Dimensionless concentrations, $\dfrac{C - C_1}{C_o - C_1}$

ξ = Average clearance between two sliding surfaces, cm

ρ = Density of liquids, gm/cc

ρ_{Fe} = Density of steel, gm/cc

ψ_n = Eigenfunction, a function of X, Y

(A) SLIDING CONTACT FOR BALL ON CYLINDER
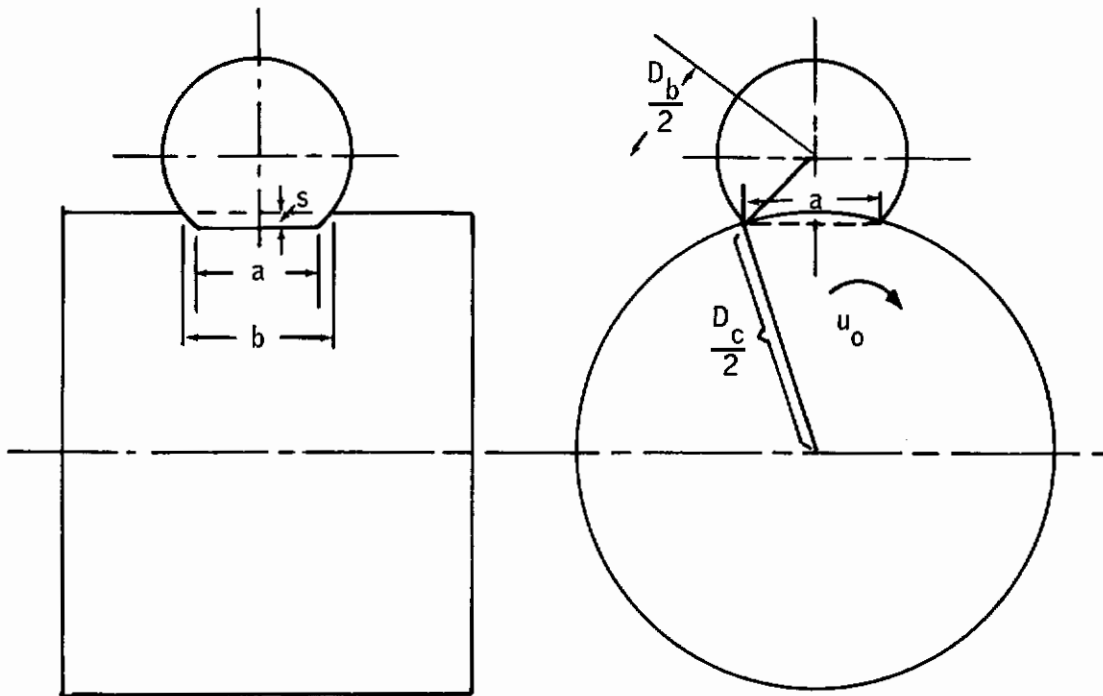
(B) APPROXIMATION FOR DIFFUSION ANALYSIS
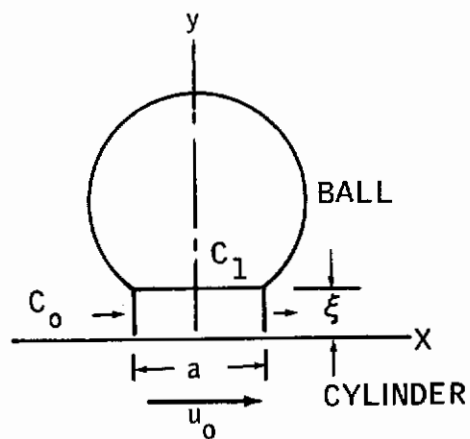
FIGURE 40 - SKETCH FOR BALL-ON-CYLINDER SYSTEM
(A) Sliding Contact for Ball-On-Cylinder
(B) Approximation for Diffusion Analysis

Since it is assumed that the wear is caused by removing the atmospheric corrosion product instantaneously and that the oxygen is entirely consumed at the wear surface ($C_1 = 0$), the wear rate at any instant is a function of the size of the wear scar and the total amount of oxygen diffused to the wear surface, so that:

$$\frac{dV}{dt} = \frac{\rho_f \ \bar{u} \ (\zeta b) \ (C_o - \bar{C}_a) \ (mM_{Fe})}{\rho_{Fe} M_g} \qquad [4]$$

The value for $\bar{C}_a$, the mean oxygen concentration at the exit, can be obtained from Equation [3]. Based on the geometry of the contact surfaces, it is found (see Appendix B) that:

$$t\zeta = \frac{1}{1.64 \ C_o u_o \rho_f} \int_{a_o}^{a} \frac{a^2 da}{1 - 1.08 \ \exp \frac{-3.719 \ Da}{\zeta^2 u_o}} \qquad [5]$$

Equation [5] predicts the wear scar size at various times using the mass diffusivity, average clearance, sliding speed, and initial concentration of the dissolved oxygen as parameters.

If the oxygen is totally consumed at the wear surface, $C_1 = 0$, and the value of $\left(\frac{\beta_n^2 \ Da}{\zeta^2 \ u_o}\right)$ is so great that the exponential term is negligibly small; this represents a case of total diffusion. Under this condition:

$$C(a,y) = 0$$

$$t\zeta = \frac{1}{4.92 \ C_o \bar{u} \ \rho_f} (a^3 - a_o^3) \qquad [6]$$

This proposed model assumed the contact surfaces to be parallel plates so as to facilitate the mathematical derivation. The elliptical scar, as observed in a ball-on-cylinder system, was approximated as a rectangular surface. Due to this approximation, an error is introduced but this was estimated to be less than 10% in evaluation of "a".

The Correlation Between Wear Rate and Oxygen Diffusion

Figure 41 is a plot of wear versus time in dry and humid air. To correlate wear rate with atmospheric diffusion, the average clearance, ζ, was first evaluated from Equation [5] by neglecting the exponential term and substituting a wear scar diameter from a run of a certain time duration. Based on the experimental data from a 64-minute run in humid air, ζ was determined to be 6.7 microinches. For a surface finish of about 10 micro-inches CLA, this computed value is quite reasonable and lends confidence to the mathematical model used in the analysis. A comparison of this computed value of clearance with the other theoretical prediction will be further discussed in the subsequent section. This value was then substituted into Equation [5] to give a generalized equation for wear-time relationships as:
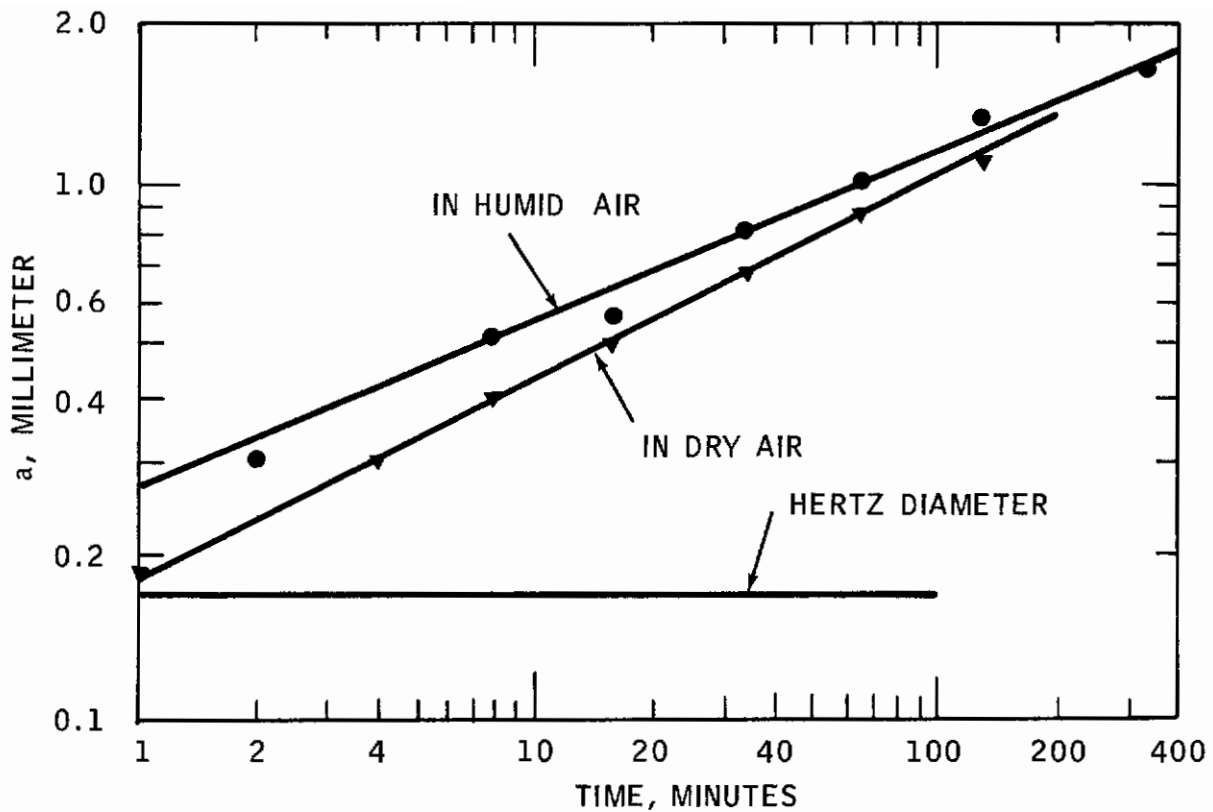
FIGURE 41 - WEAR VS TIME FOR LUBRICATED SYSTEM IN AIR,
1000g LOAD AND 56 cm/sec SLIDING SPEED

$$4.17 \times 10^{-6} \, t \;=\; \int_{a_o}^{a} \frac{a^2 da}{1 - 1.08 \, \exp \, (-2.38 \times 10^8 \, Da)} \qquad [7]$$

For the case of total diffusion, the exponential term is negligible. Equation [7] becomes

$$a^3 - a_o^3 \;=\; 1.26 \times 10^{-5} \, t \qquad [8]$$

Equation [8] forms a straight line with a slope of 1/3 in a log-log plot which fits the experimental data very well as shown in Fig. 42. This shows that corrosive wear is quantitatively correlated with the oxygen consumption in the contact regions, and constitutes a second verification for the corrosive wear.

Equation [7] shows that wear is a function of the mass diffusivity for a given time. For 32-minute runs, Equation [7] was solved by trial and error to give a relationship between "a" and D as shown in Fig. 43. It indicates a lower limit and an upper limit for mass diffusivity: below the lower limit the wear is negligible because diffusion is too low; above the upper limit the wear becomes asymtotic due to the total diffusion. Between these two limits, the wear is controlled by the mass diffusivity. Within this region, the theoretical concentration distributions at the exit of the contact region for several cases are illustrated in Fig. 44. For the oil used in this work, the mass diffusivity for oxygen was estimated from Wilke and Chang's expression to be 3.12×10^{-5} cm^2/sec which was far beyond the upper limit. It should therefore be a case of total diffusion.

It is obvious that there is no simple answer as to whether the diffusion would restrict the oxygen moving toward the metal surface. For other cases in lubrication the limits of mass diffusivities given in Fig. 43 may be used as an approximate guide in considering the possible effect of oxygen diffusion.

One interesting point stems from the fact that, as estimated by either of the two current theories--hydrodynamic and Eyring, mass diffusivity is inversely proportional to the viscosity of the oil. This means that a higher viscosity lubricant may contribute somewhat to the reduction of the corrosive wear due to the lowering of mass diffusivity in addition to its normal function of carrying the load.

Additional experimental data were obtained for an unlubricated system at 240 gram load in humid air. In this case, a stream of humid air, instead of the liquid lubricant, was considered to flow through the clearance of the contact surfaces. The diffusion in the gas is much faster than that in the liquid. Here there is no doubt that the oxygen is totally diffused. The average clearance was determined to be 3.3 micro-inches which was in the same order of magnitude as that of the lubricated system (13 micro-inches). The theoretical relationship for wear versus time was found to be

$$a^3 - a_o^3 \;=\; 1.92 \times 10^{-5} \, t \qquad [9]$$

Equation [9] is also in good agreement with the experimental results as shown in Fig. 42. This further confirms that the corrosive wear was controlled by the reaction between the metal surface and the surrounding atmosphere.
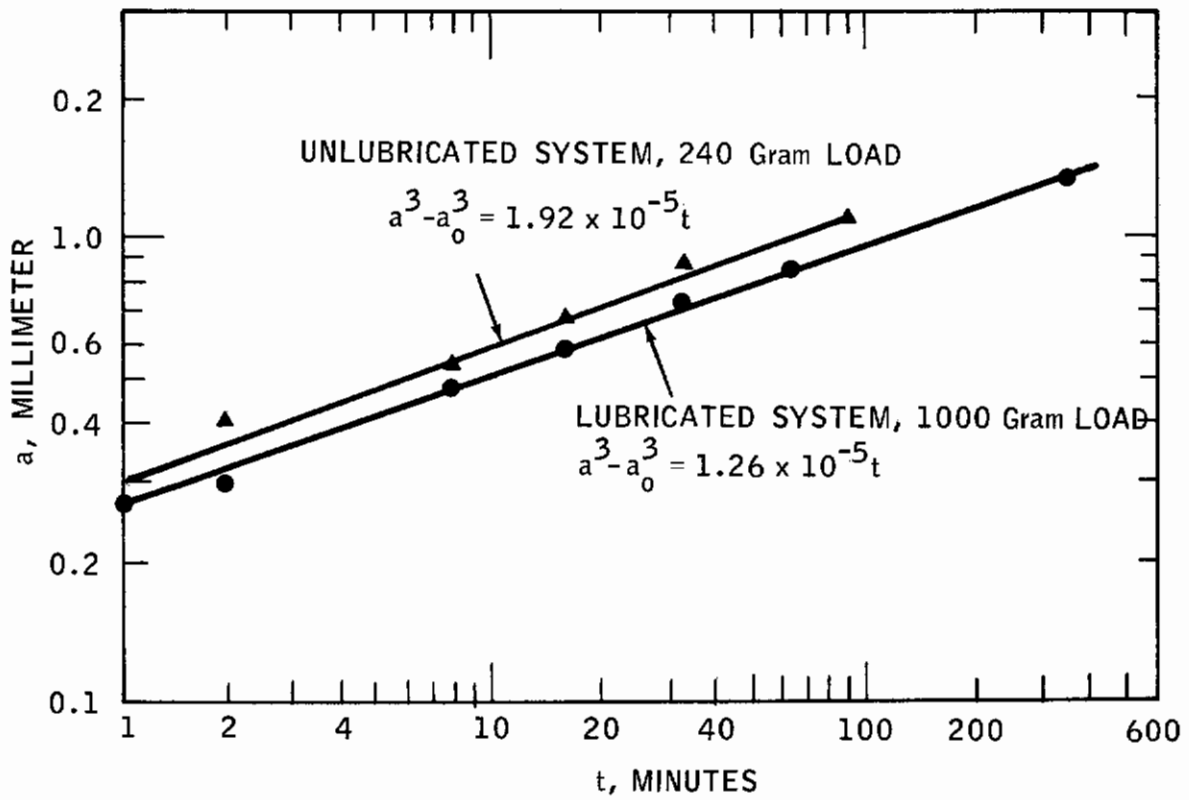
FIGURE 42 - WEAR VS TIME IN HUMID AIR FOR LUBRICATED AND
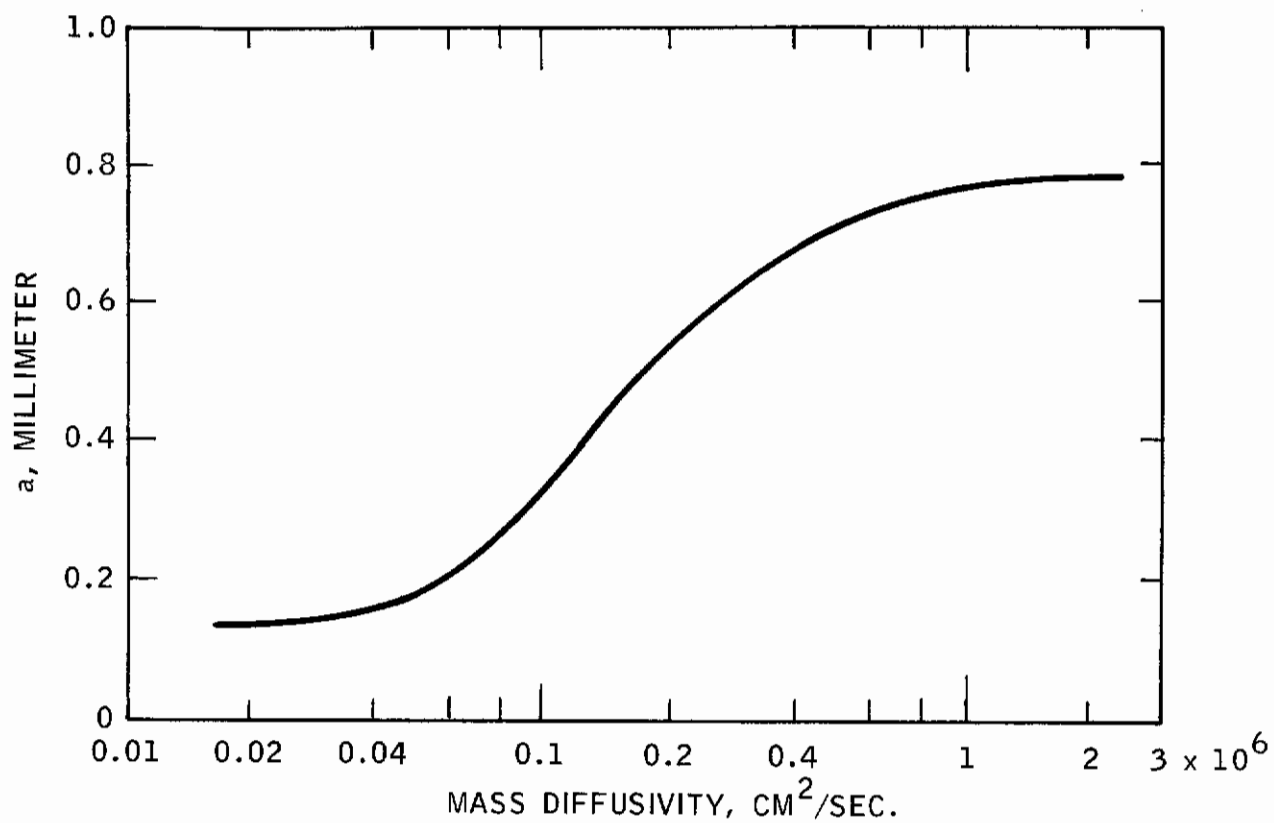UNLUBRICATED SYSTEMS--EXPERIMENTAL VS THEORETICAL

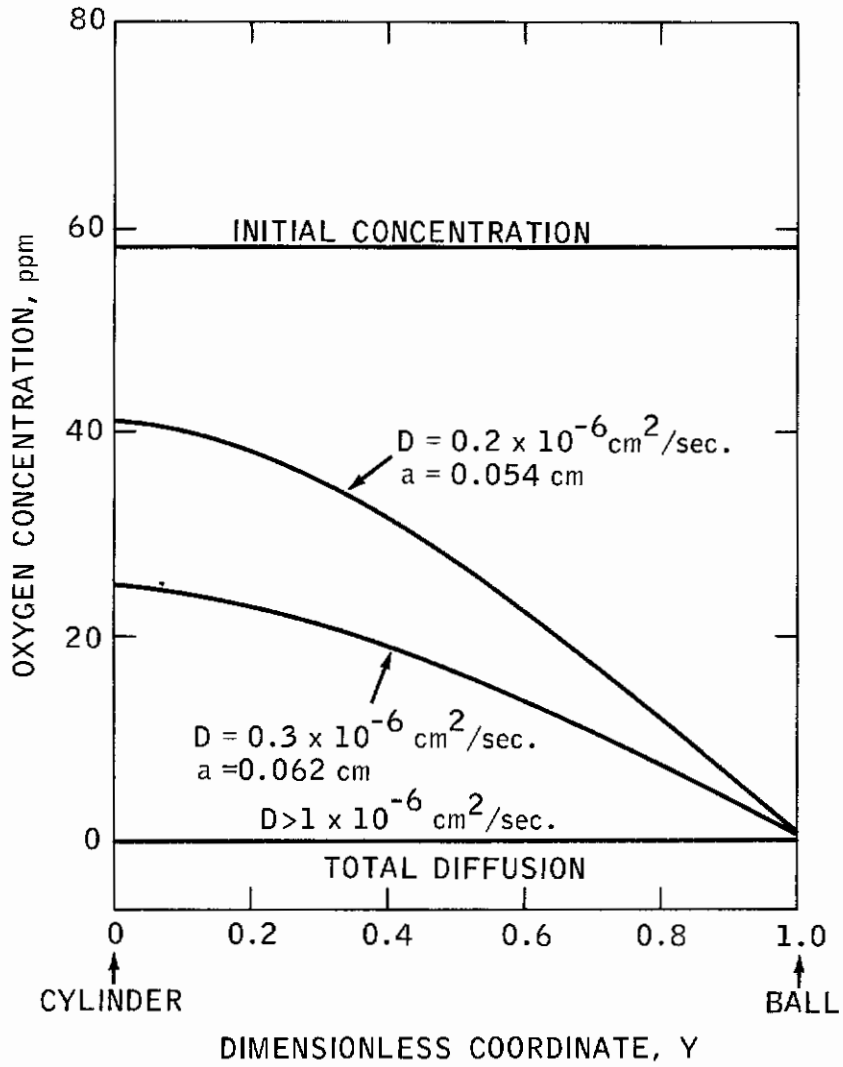FIGURE 43 - THE EFFECT OF MASS DIFFUSIVITY ON WEAR
--A THEORETICAL PREDICTION

FIGURE 44 - OXYGEN CONCENTRATION DISTRIBUTION AT THE EXIT OF
CONTACT SURFACES--A THEORETICAL PREDICTION

The Effect of Oxygen Concentration

The amount of oxygen in the contact region should, of course, depend upon its solubility in the lubricant. The dissolved oxygen in a lubricant is proportional to its partial pressure of the oxygen in the atmosphere by following Henry's law. This has been verified by analyzing the oxygen content in the liquid and gas phases with an oxygen analyzer and a gas chromatograph technique. In this study the effect of the oxygen concentration was experimentally investigated in the ball-on-cylinder device under controlled atmospheres containing various percents of oxygen by properly proportioning dry air and argon.

For a run of 32 minutes duration the wear scar is related to the initial oxygen concentration from Equation [5] as,

$$a^3 - a_o^3 = 6.8 \ C_o \qquad\qquad [10]$$

Equation [10] is shown in Fig. 45 together with the experimental data. The increase of wear due to the increase of oxygen concentration from the experimental measurements is slightly lower than that predicted from Equation [10]. This discrepancy is believed attributable to the fact that the oxygen is not quantitatively and instantaneously consumed at the wear surface, which was one of the original assumptions. That is, the formation of iron oxide is not linear with oxygen concentration, but somewhat less than linear. Had the oxygen been consumed instantaneously, the wear scar might not have been so regular as observed experimentally due to the depletion of oxygen through the contact. Another possibility is that all of the oxide film is not removed from the surface instantaneously, but rather that the fraction removed is an inverse function of the amount formed, or it can not be removed until a certain thickness of oxide film is formed. These points are worthy of consideration in refining the theoretical analysis for corrosive wear.

The Effect of Sliding Speed and Load

Two other important factors influencing wear are sliding speeds and load. The sliding speeds control the flow rate of the lubricant through the clearance. It not only affects the rate of oxygen supply, but also the length of time available for diffusion of oxygen to the surface as shown in Equation [5]. The effect of the sliding speed was investigated experimentally in ball-on-cylinder tests at cylinder speeds from 120 rpm to 600 rpm. For the case of 32-minute runs in air Equation [6] becomes

$$a^3 - a_o^3 = 7.2 \times 10^{-6} \ u_o \qquad\qquad [11]$$

That is, the wear scar diameter increases as the 1/3 power of sliding speed.

Figure 46 is a plot of wear vs. sliding speed which shows the close agreement between the experimental data and theoretical prediction as derived from Equation [11].

The load factor was not considered in the analysis for diffusion in the contact region, but showed its effect on wear as shown in Table L. Atmospheric corrosive wear involves at least two steps, the oxidation of the metal and the removal of the oxide by rubbing. The diffusion of oxygen to the metal should, of course, be the major factor for oxide formation, but the load must play a significant part in removal of the oxides from the surface. In this analysis, a first approximation was that the oxide was removed as soon as it formed. In actual sliding, the two surfaces are not smooth and the true area of contact is propor-
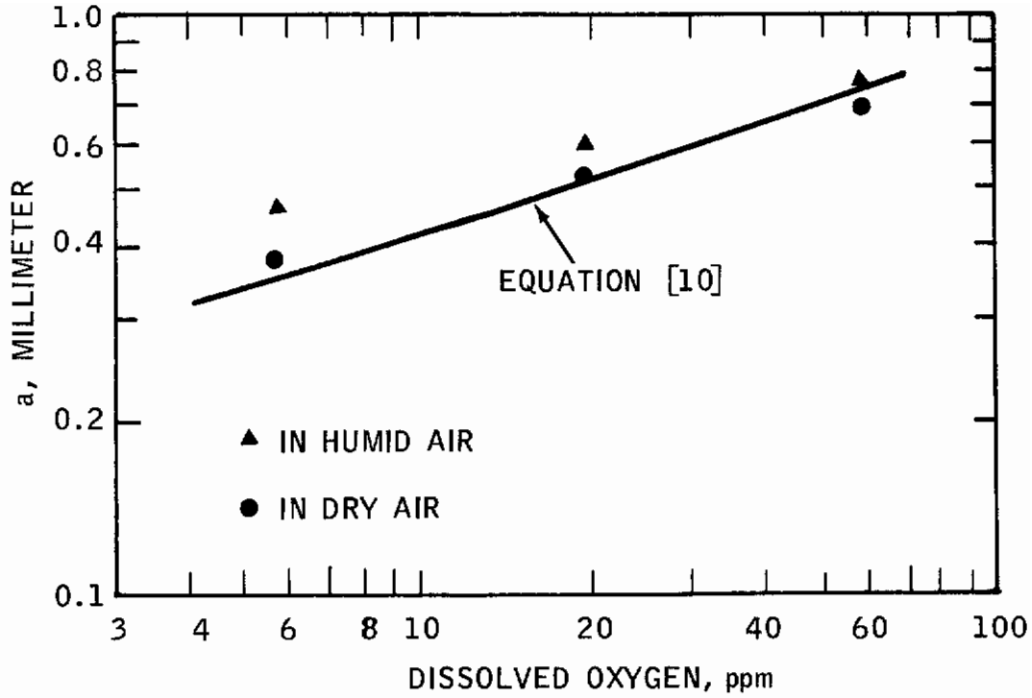
FIGURE 45 - THE EFFECT OF DISSOLVED OXYGEN ON WEAR
--EXPERIMENTAL VS THEORETICAL
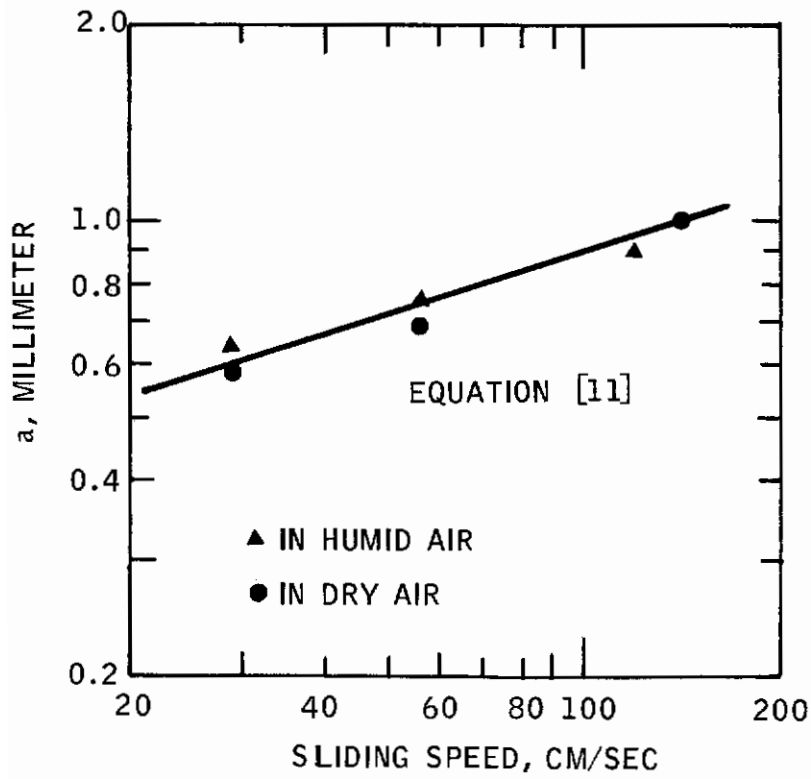
FIGURE 46 - THE EFFECT OF SLIDING SPEED ON WEAR
--EXPERIMENTAL VS THEORETICAL

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TABLE L

THE EFFECT OF LOAD ON WEAR
(LUBRICATED CASES, 240rpm, 32min)

Load g	Wear Scar Diameter in Dry Air, mm			Wear Scar Diameter in Humid Air, mm		
	a	b	Mean	a	b	Mean
240	0.55	0.63	0.59	0.67	0.75	0.71
1000	0.68	0.78	0.73	0.75	0.87	0.81

tional to load. Hence, oxide removal will be faster at higher loads. The calculated clearance can only be regarded as an average separation between the two contact surfaces. For the present case, the CLA of the cylinder was about 10 microinches and the maximum height of the asperities was 15 microinches by surface finish measurements. (No significant change after tests.) Based on these values, the average clearance was in the order of 11 microinches for 240 gram load and 9 microinches for 1000 gram load. The computed average clearance from Equation [6] was 13 microinches for 1000 gram load and 10 microinches for 240 gram load. It is impossible that the clearance decreases at a lower load, and this discrepancy is believed due to the incorrectness of the assumption that the scraping of the oxide film is instantaneous and independent of load. In studying the asperity distribution of metallic surfaces, Ling showed a relationship between the load and the "compliance" which is a measure of the penetration for asperities of various probable distributions. Using his experimental results, the relative compliance, (1), defined as the ratio of the compliance at a certain load to that at 1000 gram load, is plotted against the experimental measurements of wear from ball-on-cylinder tests as shown in Fig. 47. The slope for the dry air case is noted to be steeper than that for the humid air case. This again indicates that the removal of the material in wet corrosion is easier than that in dry corrosion and therefore is less dependent upon the asperities penetration. For the case of the humid air, $a \propto L^{0.2}$. If the probability of scraping off the oxides or wear is assumed to be proportional to the relative compliance, the equation [6] may be corrected to,

$$\int t = \frac{1}{4.92\ C_o \bar{u}\ \rho_f} \left(\frac{a^3}{L^{0.6}} - a_o^3 \right) \qquad [12]$$

The average clearance at 240 gram load was then computed to be 16 microinches. This is only a tentative suggestion to incorporate the load effect into the diffusion and wear relationship.

CONCLUSIONS

The observed corrosive wear in air can be quantitatively correlated with the consumption of oxygen from a mathematical analysis considering the oxygen diffusion to the rubbing surface. The analysis indicates two limits of mass diffusivity, a lower limit (about 3×10^{-8} cm^2/sec) below which corrosive wear is negligible because diffusion is negligible; and an upper limit ($1 \times 10^{-6}cm^2$/sec) above which the corrosive wear becomes asymptotic because diffusion is complete. Within these two limits, the wear is dependent upon the mass diffusivity. These limits, although derived for a specific case, may serve as an approximate guide in considering the possible effect of oxygen diffusion in boundary lubrication. The average clearance between two sliding surfaces predicted from this analysis is of the reasonable order of magnitude to assure the feasibility of the mathematical model.

The experimental observations, in agreement with the theoretical prediction, shows that corrosive wear increases with the increase of oxygen concentration and sliding speed. Further refinement of the theoretical analysis should consider the load effect and the residual oxygen at the boundary of the wear surface.
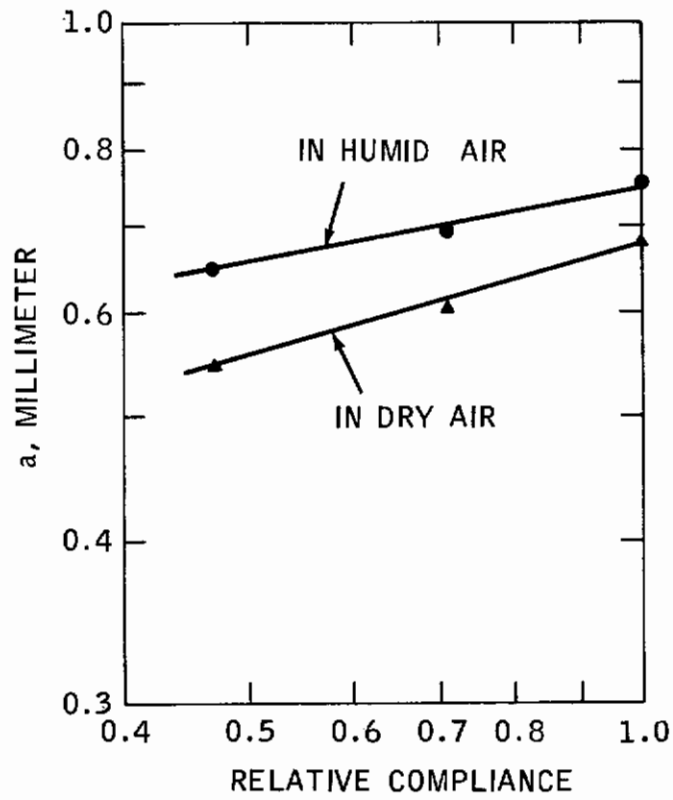
FIGURE 47 - THE EFFECT OF COMPLIANCE ON WEAR

APPENDIX

A. The Numerical Solution of Diffusion Equation

The diffusion equation [1] can be transformed into a dimensionless form as

$$\frac{\partial \theta}{\partial Y^2} = (1 - Y) \frac{\partial \theta}{\partial X} \qquad [13]$$

with boundary conditions

$$\theta\,(0, Y) = 1, \quad 0 \leqslant Y \leqslant 1$$

$$\theta\,(X, 1) = 0, \quad X > 0$$

$$\frac{\delta \theta}{\delta Y}\,(X, 0) = 0, \quad X \geqslant 0$$

By means of the separation of variables, the solution of Equation [13] becomes an eigen value and eigen function problem as follows.

$$\theta = \sum_{n=o}^{\infty} B_n \, \psi_n\,(Y)\, \exp(-\beta_n^2 X) \qquad [14]$$

where

$$\psi_n{}'' + \beta_n^2\,(1 - Y)\,\psi_n = 0 \qquad [15]$$

with boundary conditions

$$\psi_n\,(1) = 0$$

$$\psi_n\,(0) = 1$$

$$\psi_n{}'\,(0) = 0$$

and

$$B_n = \frac{\int_o^1 (1 - Y)\, Y\, \psi_n\,(Y)\, d\,Y}{\int_o^1 (1 - Y)\, Y\, \psi_n^2\,(Y)\, d\,Y} \qquad [16]$$

Equation [15] is solved numerically by Numerov's method with the following iteration.

$$\Psi_{n,i+1} = [2 - \beta_n^2 (\Delta Y)^2 (1 - Y_i)] \Psi_{n,i} - \Psi_{n,i-1} \qquad [17]$$

where $i = 1, 2, 3 \ldots k$, and $0 < (Y_i = i\Delta Y) < 1$.

The initial values for iteration are obtained from the boundary conditions that

$$\Psi_n = 1, \quad \Psi_{n,1} = -\frac{\beta_n^2 \Delta Y^2}{2} + 1$$

A trial value of β_n^2 is assumed and the value of $\Psi_{n,k+1}$ corresponding to $\Psi_n(1)$, is obtained from Equation [17] by iteration. The true value of β_n^2 is thus attained by many trials until $\psi_{n,k+1}$ becomes less than a designated limit to approximate zero. The false position method was applied to reach the final convergence for this iteration. The values of the first eigen value and eigen functions ($n = 1$) are given below:

$\beta_1^2 = 3.719$					$\beta_1 = 1.385$					
Y	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$\Psi_1^{(Y)}$	1	0.982	0.934	0.859	0.764	0.653	0.531	0.402	0.269	0.135	0

For the present case, the series in Equation [14], due to its rapid convergence, can be trancated to only one term so that

$$\theta = 1.385 \, \Psi_1 (Y) \exp(-3.719 \, X) \qquad [18]$$

or

$$C(x, y) = 1.385 \, (C_o - C_1) \Psi\left(\frac{y}{\xi}\right) \exp\left(\frac{-3.719 \, D x}{\xi^2 \, u_o}\right) + C_1 \qquad [19]$$

B. Corrosive Wear Rates

It is assumed that the contact surfaces are parallel plates as shown in Figure 40, with a length of a, a width of b and an average clearance of d. The ratio of b to a is assumed to be 1.14 which is the ratio of major and minor diameter of the elliptical scar on the ball sliding against a cylinder as determined geometrically as shown in Fig. 40A. If the wear is assumed due to the reaction,

$$2 \text{ Fe} + O_2 \longrightarrow 2 \text{ FeO}$$

or

$$2 \text{ Fe} + O_2 + 2 H_2O \longrightarrow 2 \text{ Fe (OH)}_2$$
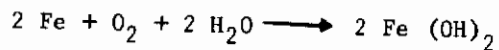
the volume wear rate is therefore,

$$\frac{dV}{dt} = \frac{\rho_f \ \bar{u}(\xi b) \ (C_1 - \bar{C}_a) \ \left[2 \ (55.85)\right]}{(32) \ \rho_{Fe}} \qquad [20]$$

From geometry

$$s = \frac{D_B}{2} - \sqrt{\frac{D_B^2}{4} - \frac{a^2}{4}} = \frac{1}{2}\left(D_B - \sqrt{D_B^2 - a^2}\right)$$

$$\frac{ds}{dt} = \frac{a}{2\sqrt{D_B^2 - a^2}} \ \frac{da}{dt}$$

Since

$$a^2 \ll D_B^2$$

$$\frac{ds}{dt} = \frac{a}{2D_B} \ \frac{da}{dt} \qquad [21]$$

and

$$\frac{dV}{dt} = \frac{\pi a^3}{8D_B} \ \frac{da}{dt}$$

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The mean concentration at a is,

$$\bar{C}_a = 2 \int_0^1 (1 - Y) \, C\,(a, Y) \, dY + C_1 \qquad [22]$$

Substituting Equation [19] into Equation [22]

$$\bar{C}a = 2.77 \, (C_o - C_1) \exp\left(\frac{-3.719 \, Da}{\xi^2 \, u_o}\right) \int_0^1 (1-Y) \, \psi_1 \, (Y) \, dY + C_1 \quad [23]$$

The integral in Equation [23] is evaluated numerically by Simpson's rule from the known values of the eigen function, i.e.

$$\int_0^1 (1 - Y) \, \psi_1 \, (Y) \, dY = 0.39$$

Equation [23] thus becomes

$$\bar{C}_a = 1.08 \, (C_o - C_1) \exp\left(\frac{-3.719 \, Da}{\xi^2 \, u_o}\right) + C_1 \qquad [24]$$

Combine Equations [20], [21], and [24] to give,

$$1.64 \;\; \bar{u} \; \xi \, \rho_f \int_0^t dt = \int_{a_o}^a \frac{a^2 \, da}{(C_o - C_1)\,[(1 - 1.08 \, \exp\,(\frac{-3.719 \, Da}{\xi^2 \, u_o})]} \quad [25]$$

or

$$t\,\xi = \frac{1}{(C_o - C_1)(1.64 \; \bar{u} \; \rho_f)} \int_{a_o}^a \frac{a^2 \, da}{1 - 1.08 \, \exp\,(\frac{-3.719 \, Da}{\xi^2 \, u_o})} \quad [26]$$

XI

PUBLICATIONS

Two papers for publication have been written on work performed under this contract:

(1) "Lubricity of Jet Fuels" by J. K. Appeldoorn and W. G. Dukek. This was presented at the SAE National Aeronautics and Space Engineering and Manufacturing meeting in Los Angeles, October 3-7, 1966.

(2) "The Role of Diffusion in Corrosive Wear" by F. F. Tao. To be presented at the ASLE-ASME Joint Conference, Chicago, October 17-19, 1967.

XII
FUTURE WORK

The research to date has shown a complicated interaction among a number of variables. However, a general pattern is emerging. Two kinds of wear are involved: corrosive wear, which requires a corrodible metal and is enhanced by the availability of oxygen and water, and scuffing which is more severe with hard or stainless surfaces, high loads, and dry, inert atmospheres. Hydrocarbon type and additives also differ, some tending to prevent corrosive wear, others to prevent scuffing.

To complete the picture, several more interactions will be studied: (1) The effectiveness of various additives in preventing scuffing. The work so far has been largely limited to their ability to prevent corrosive wear. (2) The effectiveness of additives at higher temperatures. The present data are badly confused by the fuel oxidation products formed. (3) The influence of other metallurgies, particularly 440 stainless and 304 stainless steels, tool steels and tungsten carbide.

In addition, the effect of dissolved water will be studied over the range from bone-dry to saturated fuel. Finally, it is hoped that an explanation will be found for the anti-wear effect of heavy aromatics and the behavior of additives at various temperatures.

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13. ABSTRACT The study of the lubricity of jet fuels has been expanded to examine several new variables: hydrocarbon type, dissolved oxygen, dissolved water, higher temperatures, and metallurgy. Several important interactions have been found among these variables.

The compounds most responsible for good lubricity are heavy aromatics. Removal of these materials during refining is the major cause of poor lubricity fuels. The heavy aromatics by themselves show unusual friction and wear behavior, giving low wear in air and scuffing in dry, inert atmospheres.

Dissolved oxygen and water increase wear and friction by a corrosion process. Corrosive wear appears to be the most serious cause of friction and wear problems of jet fuels. Nitrogen blanketing can eliminate wear completely in vane pump tests. Certain additives are effective only when water and air are present. A literature survey has been made of the effect of oxygen and water on lubrication. A mathematical model of corrosive wear has been constructed and shows good agreement with experimental data.

Higher temperatures give more wear and friction especially in air. However, oxidation of the fuel will form polar compounds that act as lubricity agents. This reaction tends to mask the effect of temperature. Certain lubricity additives become much less effective at higher temperatures.

Metals that resist corrosive wear, such as stainless steel, are better than chrome steel at low loads, but scuff more easily at higher loads.

Future work will concentrate on higher temperatures and different metallurgies and the interaction of these variables with atmosphere and additive action.

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