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THE OXIDATIVE STABILITY
OF
DEUTERATED LUBRICANTS

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THE U.S. NAVAL RESEARCH LABORATORY
AND
THE OFFICE OF NAVAL RESEARCH
UNDER CONTRACT NUMBERS
N00173-80-C-0419
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PREPARED BY
GEO-CENTERS, INC.
381 ELLIOT STREET
NEWTON UPPER FALLS, MASSACHUSETTS 02164

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1. INTRODUCTION

The demand for lubricants exhibiting superior performance characteristics has increased dramatically since World War II. Recently developed civilian and military systems require lubricants which perform over greater temperature ranges, maintain viscosity, and pose no fire hazard. In addition, many critical precision applications, e.g., guidance systems, require lifetime lubricants to minimize maintenance, inventory, and capital costs, as well as to ensure mission reliability. A new class of synthetic lubricants, in which the hydrogen atoms have been replaced with deuterium, is considered to be an excellent candidate to meet these requirements.

These deuterated lubricants, when employed as a base stock for a grease formulation, were shown by the Naval Air Development Center (NADC) at Warminster, Pennsylvania, to increase bearing life in the laboratory by a factor of five.(1,2,3) Further, deuterated lubricants exhibited an increased resistance to oxidation compared with their non-deuterated counterparts. The research performed by NADC revealed that the increased lifetime of the bearing containing the deuterated hydrocarbon was to be a strong nonlinear function of the percentage of deuterated atoms in the lubricant. At the level of 97 percent deuteration, a five-fold improvement in bearing lifetime was observed. Additionally, when the resistance to oxidation was studied, it was found that the induction period to the onset of auto-oxidation for the deuterated lubricants was four times greater than for their hydrogen analogs.

To further explore the potential of deuterated lubricants, this early research was expanded in the following areas:

1. Elucidate the mechanisms that enhance stability and increase lifetime through the determination of the rate of oxidation and pyrolytic decomposition.
2. Confirm and extend the laboratory bearing tests originally performed by NADC.
3. Initiate an evaluation of economic feasibility and identify applications of deuterated lubricants.

The results of each of these tasks are discussed separately in this report.

2. DETERMINATION OF OXIDATIVE STABILITY

2.1 BACKGROUND

Until World War II, petroleum-based fluids, with but minor exceptions, provided most of the lubricants required by the technology of that period. They served admirably, both with regard to availability and performance, although for certain limited applications, natural products such as sperm whale oil and vegetable oils were employed. Since that period, however, the increase in performance and reliability required of postwar power plants and instruments in both civilian and military applications revealed those traditional lubricants to be inadequate, particularly with regard to high-temperature stability and certain physical properties. To a large extent, these deficiencies were met with the introduction of the diester fluids in the early 1950s(4,5,6) and, more importantly, the neopentylpolyol esters in the 1960s.(7) When properly formulated, the latter fluids are relatively resistant to oxidative degradation at 200°C, and pyrolytically stable at 275°C. In addition, they have excellent viscosity-temperature characteristics, low pour and freeze points (<55°C), and are relatively nonvolatile. For a variety of lubricant applications, ranging from miniature precision instrument bearings(8) to aircraft turbine engines, this combination of heat stability and physical properties of the esters has resulted in their widespread use. Recent advances in power transmission technology and instrumentation are such as to require even further improvement in some lubricant properties, particularly oxidative stability.

The auto-oxidation of esters follows the same general reaction path ascribed to hydrocarbons:

$$
\begin{array}{lll}
RH \xrightarrow[\nabla]{O_2} ROOH & & \\
ROOH \longrightarrow RO\cdot + HO\cdot & & \text{Initiation}
\end{array}
$$

$$
\begin{array}{lll}
RO\cdot + RH \longrightarrow R\cdot & & \\
R\cdot + O_2 \longrightarrow ROO\cdot & & \text{Propagation} \\
ROO\cdot + RH \longrightarrow R\cdot + ROOH & &
\end{array}
$$

$$RO\cdot + ROO\cdot + ROOH \xrightarrow[\nabla]{O_2} \text{Products Termination,}$$

where R represents a hydrocarbon moiety.

In the sequence shown, the oxidation rate is seen to be a function of the ease of cleavage of the carbon-hydrogen bond. When hydrogen is replaced by deuterium, the energy required to cleave the bond is larger because of the kinetic isotope effect.(2)

Figure 1 is a diagram of the vibrational levels in a molecule containing C-H(D) bonds undergoing chemical reactions. If it is assumed that this potential surface is virtually the same for both the normal and deuterated materials and that the vibrations approximate harmonic oscillation (Hooke's law), then the vibrational frequency of a species is simply dependent on the mass of the vibrating atoms:

$$\nu_H/\nu_D \sim \sqrt{m_D/m_H} = \sqrt{2}$$

For low or moderate temperatures, the vibrational energy is

$$E = 1/2\ h\nu$$

where h is Planck's constant.

This is the so-called zero point energy. If the rate determining step in a molecular reaction is attack on the C-H or C-D bond, then absolute rate theory predicts that the reaction rate ratio K_H/K_D is dependent on the difference between the activation energies E_H-E_D. At temperatures below 525°C, the rate factor K_H/K_D ranges from ~2-10, the lower the temperature the greater the factor.

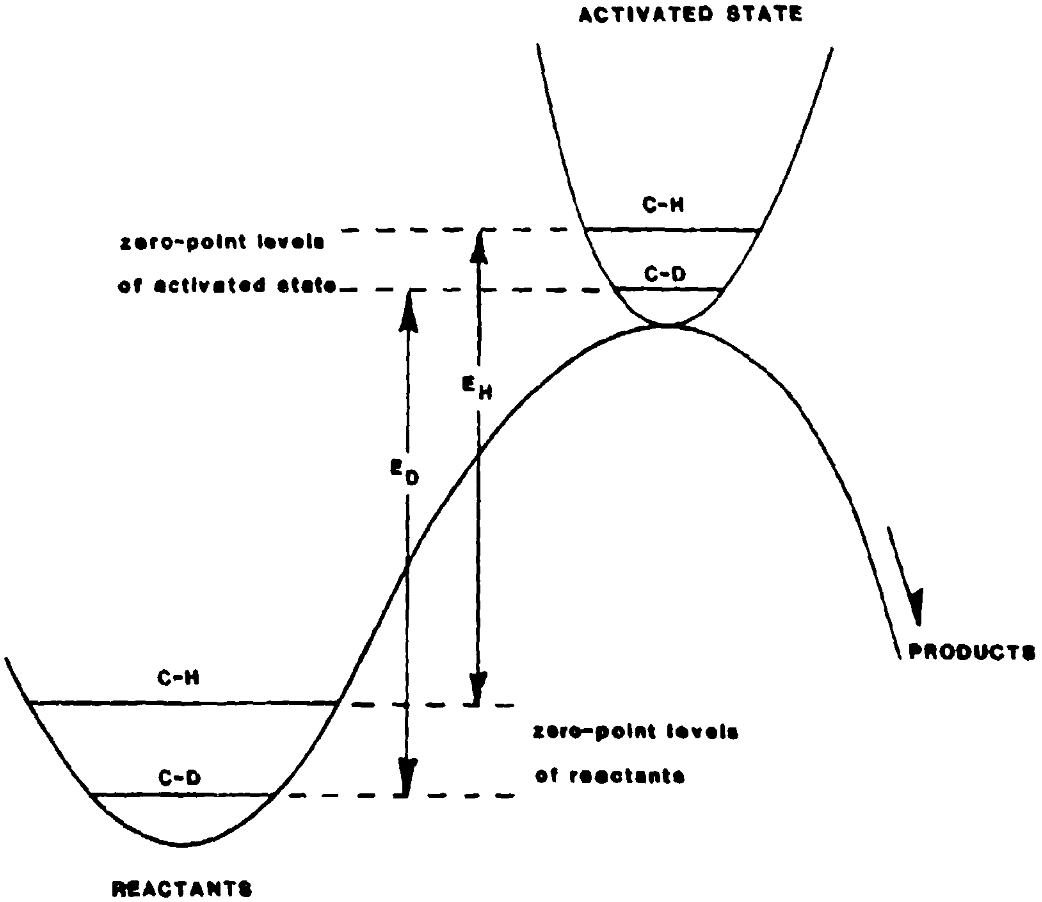

Figure 1. Isotope effect in biomolecular abstraction reaction: $X + Y - H \rightarrow Y \cdots H \cdots X \rightarrow Y + X - H$
$X + Y - D \rightarrow Y \cdots H \cdots X \rightarrow Y + X - D$
(Always $E_D > E_H$)

The deuterium isotope effect on lubricant stability and performance was initially investigated by Rebuck et al.(1) They compared the performance life of bearings lubricated with formulated greases based on both a synthetic hydrocarbon derived from polymerized olefins and an analog deuterated in various amounts ranging from 50 to 97%. These results are comprehensively summarized in Figure 2. They found bearing life was increased approximately five-fold when the 97% deuterated material was employed. Other experiments strongly suggested that this enhanced performance was due to the increased oxidation stability of the deuterated base stock. This increase was in the range predicted by the kinetic isotope effect theory.

Based on these promising results, we have commenced investigation of the effect of deuteration on the high-temperature oxidation stability of neopentylpolyol esters. The results reported here represent the first phase of the investigation.

2.2 EXPERIMENTAL WORK

2.2.1 General Method

Historically, the oxidative stability of a lubricant has been determined by either passing air or oxygen through the fluid at some elevated temperature and following the increase of viscosity, acidity, or peroxide concentration with time, or monitoring the decrease in antioxidant concentration or oxygen pressure (in a bomb apparatus). The former procedure requires that periodic samples be taken from the oxidation cell for analysis. This is tedious, labor intensive, and wasteful of the lubricant sample. The bomb apparatus requires large samples, is awkward to use, and does not permit periodic analysis of the contents. To obviate these problems, a new technique for monitoring lubricant stability has been developed. It was observed that the oxidative breakdown of lubricants was accompanied by the evolution of low molecular weight gases and vapors. Monitoring of these with a low cost, solid state metal oxide semiconductor gas sensor (sensitive to combustible hydrocarbons) provided a simple, continuous indication of the lubricant conditions. A block diagram of the experimental apparatus is shown in Figure 3. The response of the detector (i.e., output voltage) as a function of time exhibits a characteristic peak at the beginning of an oxidation experiment, which results from lower molecular

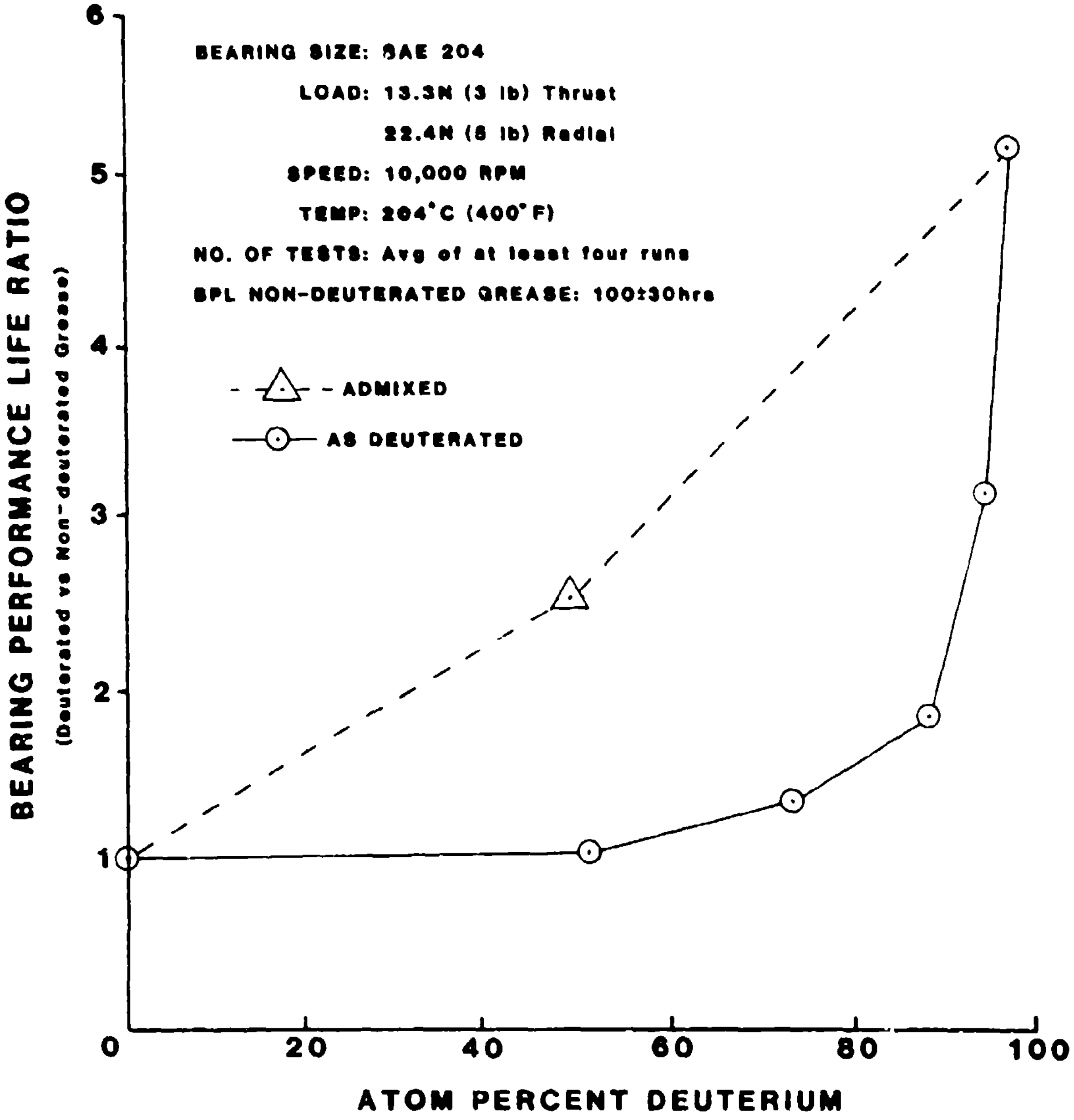

Figure 2. Antifriction bearing performance life ratios of deuterated lubricants. (NADC Results, 1977)(1,2)

weight impurities evaporating from the lubricant base stock. The sensor then provides a small, steady signal until the lubricant has reached the end of its induction period (useful life), at which time large amounts of gas are evolved and a correspondingly high sensor response is generated.

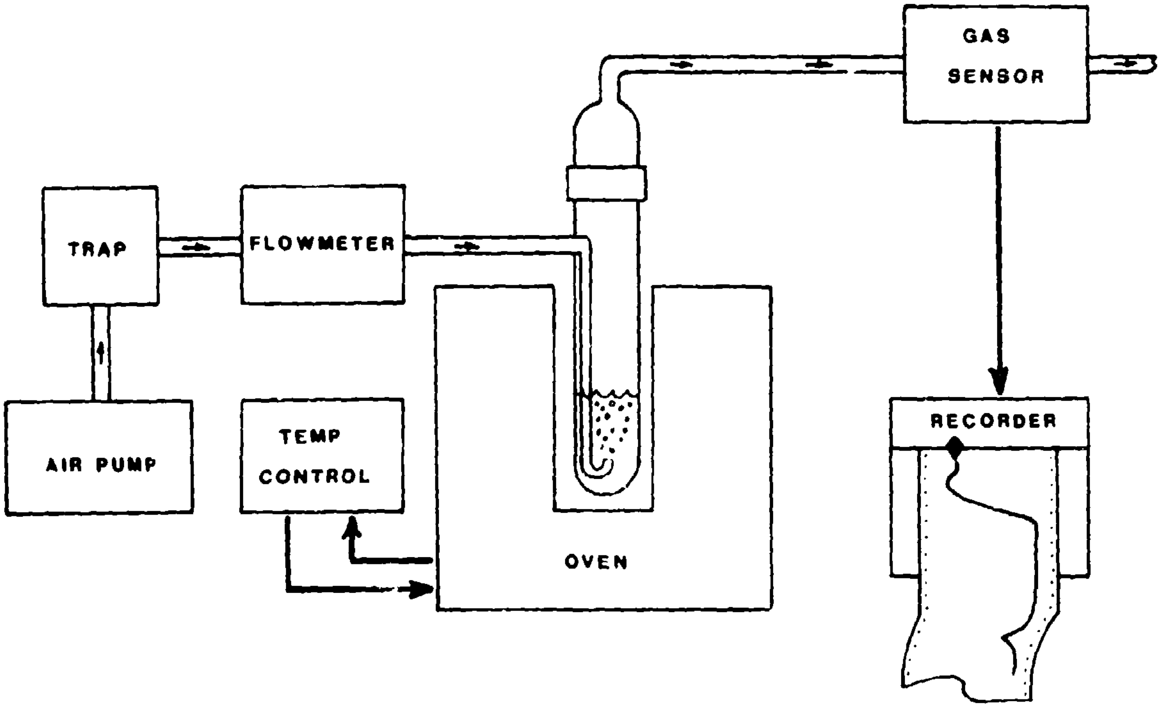

Figure 3. Oxidation test apparatus.

Oxidation of the lubricant samples was carried out in glass cells through which dry, filtered air was bubbled. The glass cells were heated in a temperature-controlled oven whose long-term stability was better than ±0.5°C. Prior to use, the cells were cleaned in a hot nitric/sulfuric acid bath, rinsed repeatedly with distilled water, and baked overnight in an oven. All samples contained a lubricant base stock and an antioxidant. Samples were typically 1 to 2 milliliters in volume.

2.2.2 Correlation of Gas Evolution with Classical Indicators of Lubricant Lifetime

Experiments were conducted to verify that gas evolution was indeed a valid indicator of lubricant lifetime. For this purpose, a commercial pentaerythritol tetrahexanoate ester lubricant base stock containing an antioxidant was oxidized and periodic samples taken. The antioxidant was an alkylated phenyl-alpha-napthylamine (Geigy IRGANOX LO-6) whose volatility at the 200°C oxidation temperature was determined to be small. An antioxidant concentration of 0.50% (by weight) was employed. The oxidized samples were analyzed for changes in viscosity (using a Cannon-Fenske type viscometer), antioxidant concentration (using liquid chromatography with UV detection), and acidity (by base titration). The gas evolution rate of the lubricant was measured continuously with the gas sensor and displayed on a stripchart recorder.

The results of this evaluation, shown in Figure 4, indicate a very close correlation between gas evolution and some classically accepted indicators of lubricant stability. Heating the lubricant at 200°C, while bubbling air through it, resulted in the steady depletion of the antioxidant. As the antioxidant concentration approached zero, a rapid increase in the viscosity, acidity, and gas evolution signaled the onset of lubricant oxidative breakdown. The close correlation of these events provides conclusive evidence that monitoring gas evolution is an effective method of determining lubricant life.

2.2.3 Deuterated Lubricant Evaluations

The relative oxidation stabilities of three lubricant base stocks, each in both deuterated and non-deuterated versions, were determined. Stabilities were determined by measuring the time required for significant gas evolution to occur. The intersection of the extrapolated gas evolution rate curve segments with the pre-evolution baselines established a precise induction time. Oxidation tests were performed on the fluids (approximately 2 ml) at a fixed temperature (200°C for two base stocks and 220°C for the ester) and air flow rate (25 ml per minute). Typically, six oxidation tests were conducted for each lubricant system so that the statistical precision (i.e., standard deviation) of the measurements could be determined.

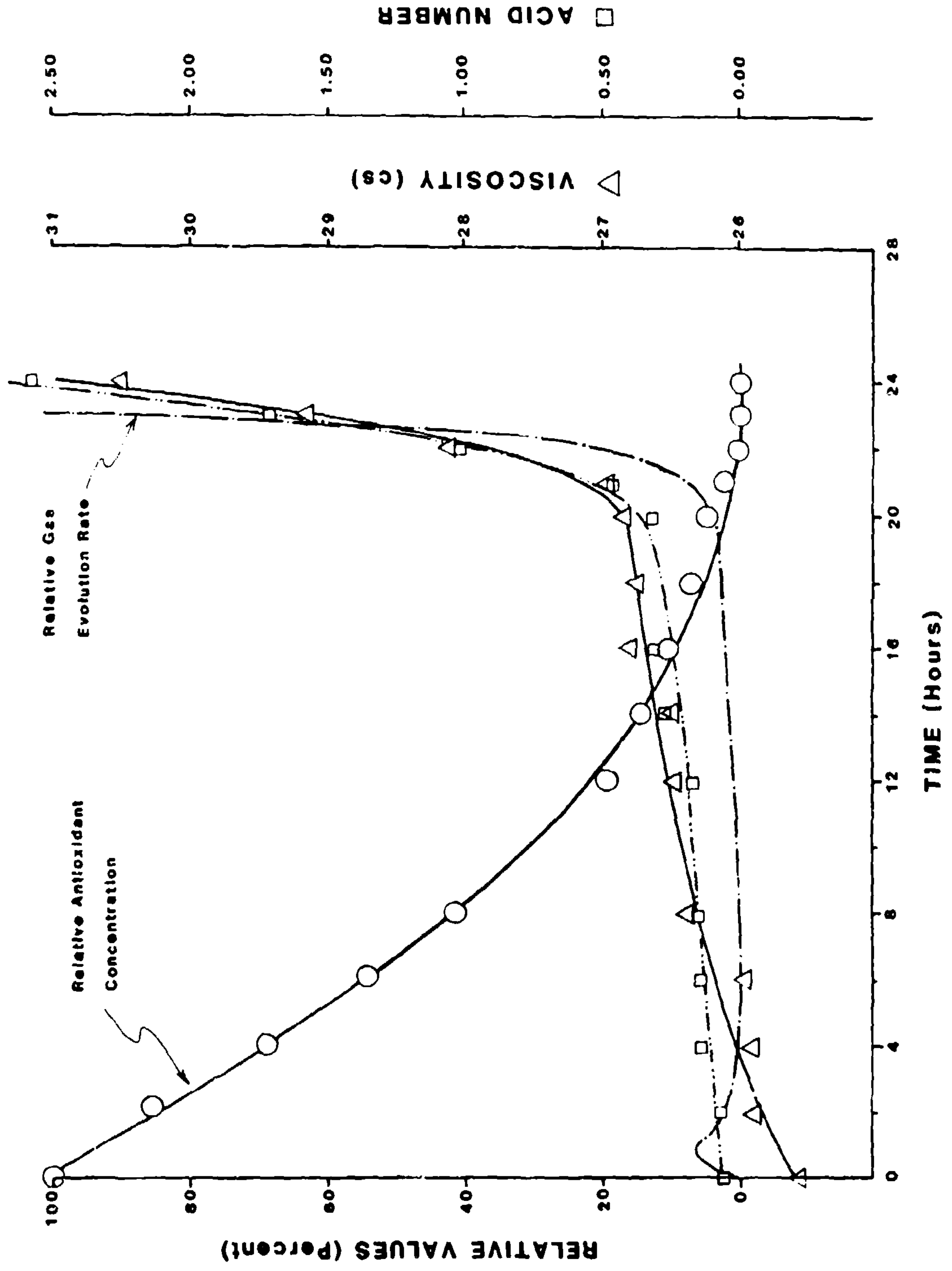

Figure 4. Correlation of oxidative breakdown indicators.

The first lubricant investigated was a synthetic hydrocarbon containing a proprietary antioxidant additive. This formulation had been investigated in an earlier study.(2) The deuterated synthetic hydrocarbon was enriched to 97 atom percent. Both deuterated and non-deuterated samples contained identical concentrations of antioxidant.

The second lubricant system was pentaerythritol tetrahexanoate containing 0.50% of alkylated phenyl-alpha-napthylamine antioxidant (Geigy IRGANOX LO-6). The deuterated and non-deuterated forms of this tetraester were custom-synthesized by KOR Isotopes, Inc., Cambridge, Massachusetts. Purity of both base stocks was better than 98% as determined by NMR, IR, and titration. NMR analysis of the deuterium-enriched ester (pentaerythritol perdeutero tetrahexanoate) indicated a 97 atom percent enrichment. One to two milliliter aliquots of the tetraester lubricants were evaluated under the same conditions (except for temperature) as the synthetic hydrocarbons.

The third lubricant system was bis(2-ethylhexyl) azelate and a deuterated version bis (2d-2-ethylhexyl) azelate in which the beta hydrogen of the alcohol was replaced with deuterium. These compounds were synthesized by EMERY Industries, Inc., Cincinnati, Ohio, and supplied to NRL by the Naval Air Development Center, Warminster, Pennsylvania. The deuterated azelate ester was enriched to 90 atom percent deuterium at the beta hydrogen position. Alkylated phenyl-alpha-napthylamine antioxidant (0.50% by weight) was added to the esters prior to evaluation.

2.3 RESULTS AND DISCUSSION

The lubricant lifetimes for the systems studied are presented in Tables 1 and 2 and Figures 5 and 6. Variously summarized are (a) the superior lifetime characteristics of deuterated versus non-deuterated materials, and (b) the temperature effects on lifetime characteristics of deuterated and non-deuterated esters. It is clear that in all cases, deuterium enrichment of the lubricant base stocks resulted in a significant improvement of oxidation stability. The results for the synthetic hydrocarbon evaluation are in good agreement with the previous study(9) which investigated bearings lubricated with grease formulated from the same deuterated and undeuterated synthetic hydrocarbons. Bomb oxidation tests of the base stocks verified the increased stability of the deuterated fluid.

Table 1. Lifetime of lubricants.

Lubricant	Anti-Oxidant	Oxid. Temp. (°C).	Non-Deuterated Average Time (Hours)	Deuterated Average Time (Hours)	Relative Increase
Synthetic Hydrocarbon	Proprietary	200	3.6 ± 0.5	15.2 ± 1.2	4.2
Pentaerythritol Tetrahexanoate	0.50% Alkylated Pan	220	7.3 ± 1.7	102.4 ± 15.1	14.0
Bis(2-Ethylhexyl) Azelate	0.50% Alkylated Pan	200	0.9 ± 0.15	1.7 ± 0.4	1.9

Table 2. Oxidative stability test results as a function of temperature.

Temperature (°C)	Induction Time (Hours)		Relative Increase
	Non-Deuterated Ester	Deuterated Ester	
200	42.4	850.0	20
220	7.4	102.4	14
235	0.9	17.2	19

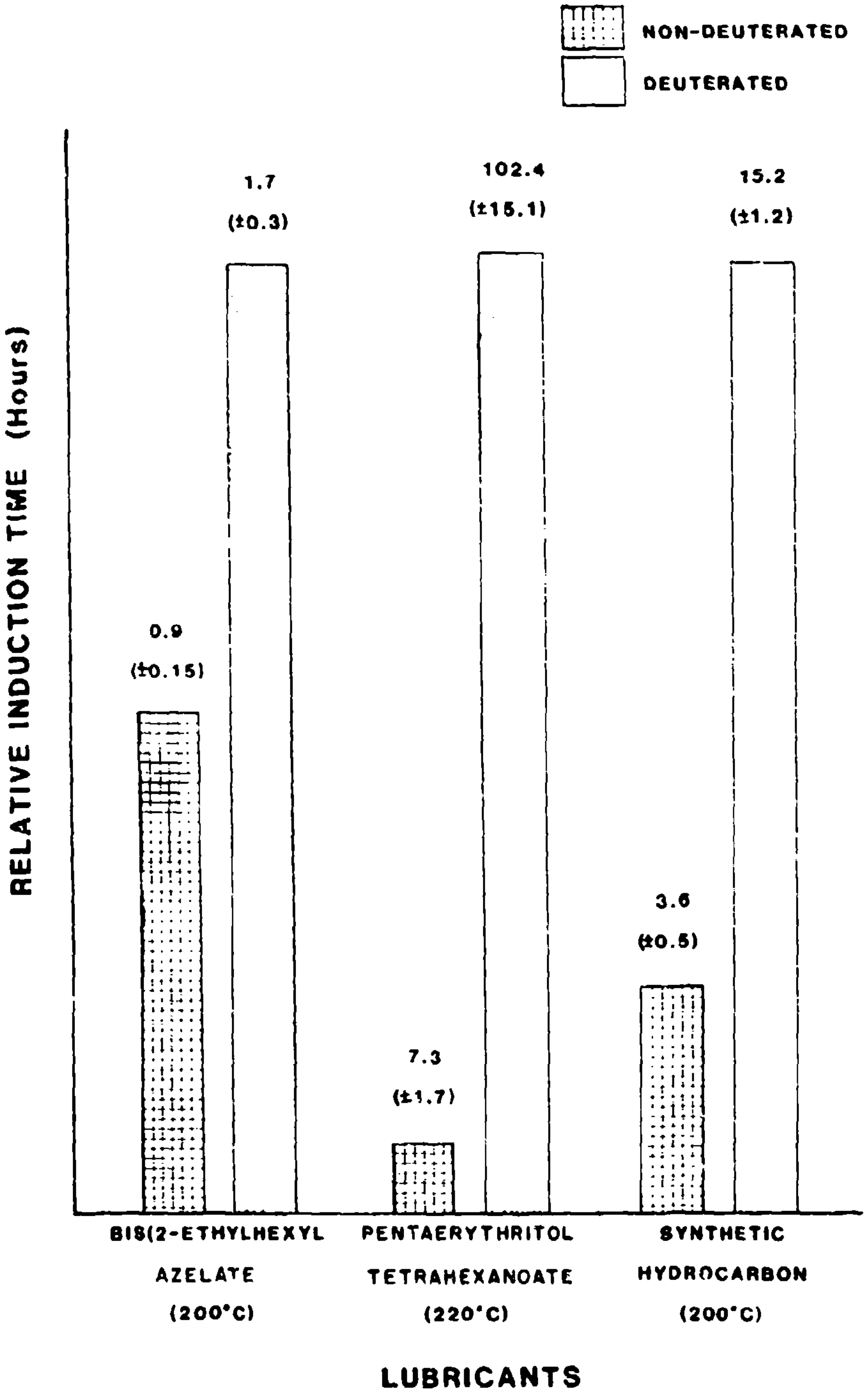

Figure 5. Relative induction time for array of deuterated materials and their non-deuterated counterparts. Lifetime improvements vary by factors of 2, 4, and 15.

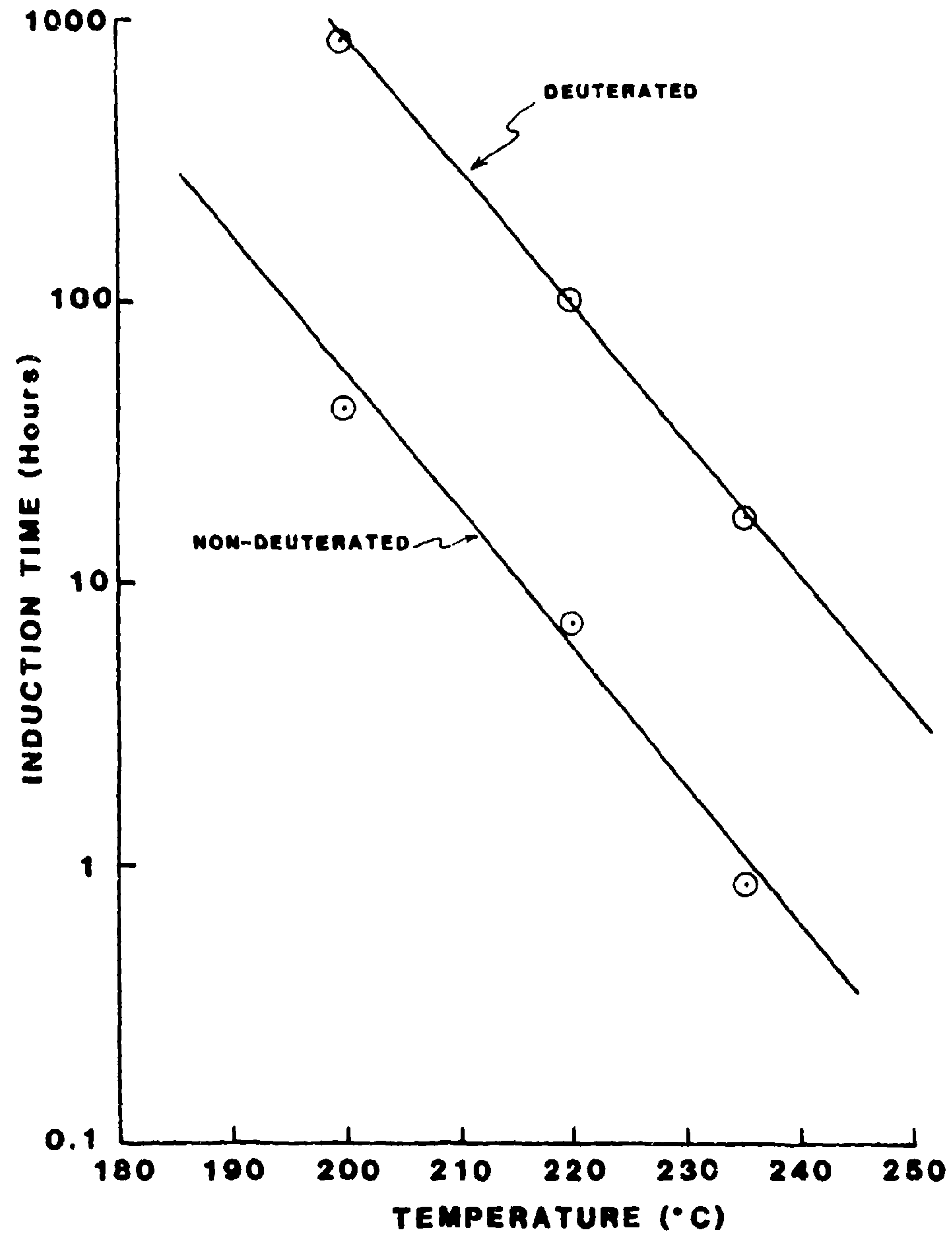

Figure 6. Induction time as a function of temperature for both a deuterated and non-deuterated ester (pentaerythritol tetrahexanoate) with 0.5% alkylated pan anti-oxidant additive. (For a given temperature, deuterated material exhibits lifetime improvement by a factor of 15 over the non-deuterated version. For a given lifetime, deuterated material performs at an elevated temperature of 25°C above that of its non-deuterated counterpart.)

Perhaps the most exciting results were obtained from the pentaerythritol ester. The factor of 15 improvement produced by deuteration of only the acid component of the compound exceeded the improvement predicted by the kinetic isotope effect alone. Preliminary evaluations of antioxidant depletion from the deuterated pentaerythritol tetraester also revealed another unusual facet – the original antioxidant appears to be almost completely consumed within the first quarter of the lubricant lifetime, yet oxidative breakdown is not observed at that point. This phenomenon will be further investigated in future work.

Also encouraging were the results from the azelate diester evaluation. A nearly 100% improvement in stability was obtained with the substitution of deuterium at only two sites in the molecule. Clearly, this offers considerable promise for the future. The substitution of relatively small amounts of deuterium at the most reactive sites in a particular lubricant molecule could result in a very significant improvement in performance with only a reasonable increase in cost.

Finally, the performance of the gas sensor apparatus in determining lubricant oxidation induction times was most gratifying. The technique permitted analyses to be made of samples as small as 1 cc, which greatly reduced the cost of investigating these research materials. Furthermore, the automatic, continuous monitoring afforded by the technique permitted a significant reduction in the labor required to obtain the data. Numerous evaluations of the technique with viscosity, acidity, and additive depletion measurements always provided very close correlations.

3. LABORATORY BEARING TESTS

3.1 BACKGROUND

As previously discussed, the first significant work in the testing of the performance of deuterated lubricants was conducted by Rebuck et al.(1) of the Naval Air Development Center (NADC). Using a deuterated and non-deuterated hydrocarbon grease (MIL-G-81322) time-to-failure tests were conducted at a fixed temperature of 400°F (≈190°C). Grease formulations consisted of 51, 72, 88, 94, and 97 atom percent deuterium content and a 50/50 admixture of non-deuterated and 97% deuterated material. The results from these are summarized as follows:

1. Bearing performance life ratio increased monotonically as a function of atom percent deuteration (Figure 2).
2. The increase is most dramatic as percent deuteration exceeds 70% and approaches 100%.
3. The 50/50 admixture was superior (by at least a factor of 2) over the 50% atomic mixture.

These results were both qualitatively and quantitatively significant and set the stage for further testing. Accordingly, laboratory bearing tests designed to duplicate and extend the NADC tests were considered to be an essential part of this research. The following discussion summarizes the basic testing configuration and the results of these tests. A complete discussion is presented in a separate report.(10)

3.2 OPERATING BEARING EVALUATION

The operating bearing evaluation was designed to compare the life of standard off-the-shelf bearings running under controlled conditions when lubricated with a hydrogenated and a 97% deuterated version of the same synthetic hydrocarbon. The comparisons were to be made at each of three temperatures by measuring the running time to failure (defined as that point at which the bearing package torque doubles) of six sets of bearings with each lubricant (H = hydrogenated, D = 97% deuterated lubricant). (See Table 3.) The bearings were to be run in air at 12,000 r/min at a preload of 5 to 7 lbs (Hertz-stress range of 108,000 to 152,000 lb/in.^{2}) and no externally applied load.

Standard R-4 size bearings, purchased from KuBar Bearings, Inc., Cambridge, Massachusetts, were received dry from the manufacturer and without the shields assembled. Before running in bearing cartridges (Figure 7), in which the preload could be set by suitable manipulation of the lengths of the preload spacers, bearings were processed as follows:

1. Ultrasonically cleaned in successive baths of toluene, Freon, and methanol, vacuum dried between each bath, and finally dipped in a 50/50 mixture of methanol and acetone.
2. Weighed with shields and snap-rings.
3. Lubricated by immersion in a 50/1 mixture of hexane and SRG-60.
4. Calibrated.
5. Approximately 35 mgm of grease was applied to each side of each bearing before shields and snap-rings were installed. Each bearing rotated under no load to distribute lubricant.

Fixtures were built that could mount six bearing cartridges and maintain them at the test temperature, while the shafts were rotated at 12,000 r/min with dc permanent magnet motors whose armature current was measured to determine running torque (of motor plus test bearings). The torque constants of the motors were 2.27 $\frac{\text{oz-in.}}{\text{amp}}$ (±3%).

Prior to installing the bearing cartridges in the running fixture, the motors were run for a short time with the fixture at test temperature in order to determine the running torque of the motors alone. The bearing cartridges were then installed and the test was begun.

Table 3. Lubricant test matrix (showing number of tests for different lubricants as a function of temperature).

Temperature (°F)	Lubricant			
	Grease		Oil	
	H	D	H	D
400	6	6		
350	6	6	6	6
250	6	6		

Note: (H = hydrogenated, D = 97% deuterated lubricant)

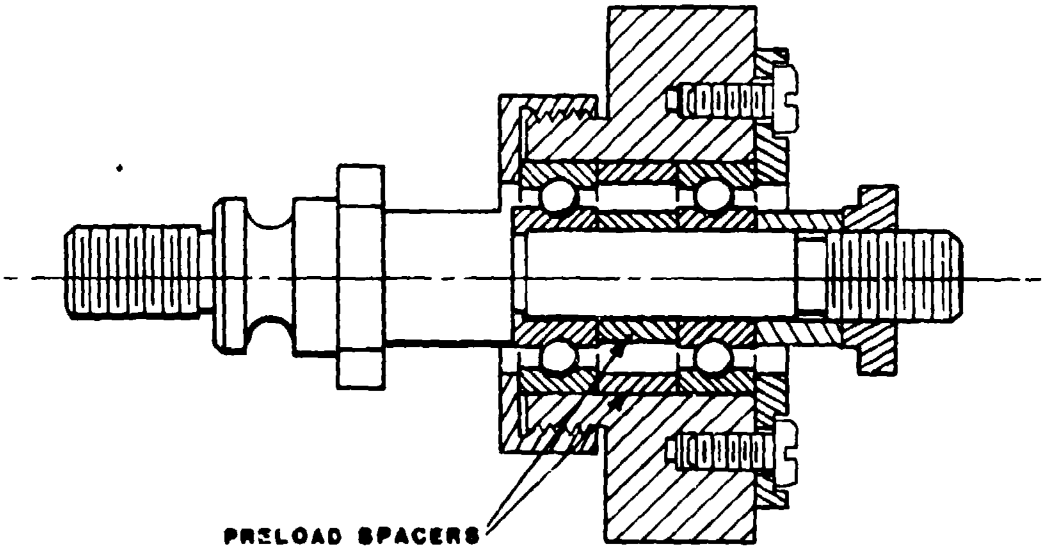

Figure 7. Bearing cartridge.

A compilation of the test results is shown in Table 4; the average times to failure with standard deviations are shown in Table 5 and Figure 8. Many of the test sets did not show a smooth monotonic torque increase (hash and/or average level) to failure. This introduces some uncertainty into interpretation of the results but does not change the basic conclusion that the deuterated grease produced increased time-to-failure of the deuterated lubricants ranging from 0.5 to 3. In all cases the deuterated lubricants performed better than the hydrogenated with the greater improvements at the lower temperatures. These results correlate with those reported in the oxidative stability tests.

3.3 RESULTS AND DISCUSSION

The results reported by NADC were duplicated in these tests. Additionally, tests were run at various temperatures and in different operating conditions. The results of the operating bearing evaluation showed remarkable improvement with deuterated lubricants at all temperatures. As expected, the greatest improvements were at the lower temperatures.

Table 4. Time-to-failure test results (raw data).

Lubricant/Temperature (°F)	Date Started	Failure Times (Hours)
Hydrogenated grease/400	11/19/80	All 6 sets failed in 2-12 hours (no recording).
Hydrogenated grease/400 (second set)	6/23/81	12.7(a), 4.9(a), 18.1(a), 22.2(b), 13.2(a), 15.2(a).
Deuterated grease/400	12/11/80	<3.0, 30.3(b), 29.0(b), 32.3(a), 31.0(b), <1.0.
Hydrogenated grease/350	1/16/81	46.2(b), 48.2(b), 42.2(a), 36.2(b), 50.8(a), 39.0(b).
Deuterated grease/350	1/29/81	53.3(a), 82.6(a), 144.6(a), 86.0(a), 102.6(a), 28.3(b).
Hydrogenated grease/250	2/12/81	8.5(b), 116.1(b), 217.2(b), 437.4(a), 252.3(a), 645.8.
Deuterated grease/250	3/23/81	492.2(b), 908.5(b), 813.9(a), 210.2(b), 1356(b), 1853.8 (and still running when stopped).

Notes: (a) Essentially monotonic torque increase to failure.
(b) Other (i.e., erratic).

Table 5. Average time-to-failure test results (GEO-CENTERS/NRL results, 1981).

Temperature (°F)	Non-Deuterated Average Time (Hours)	Deuterated Average Time (Hours)	Relative Increase (%)
400	14.4 ± 5.8	21.1 ± 14.8 (30.7*) ± (1.4)*	50
350	43.8 ± 5.6	82.9 ± 40.2	90
250	279.6 ± 229.7	939.2* ± 593.0**	240

* Excluding two immediate failures.
**One set still running without signs of failure when test was terminated at 1853.8 hours.

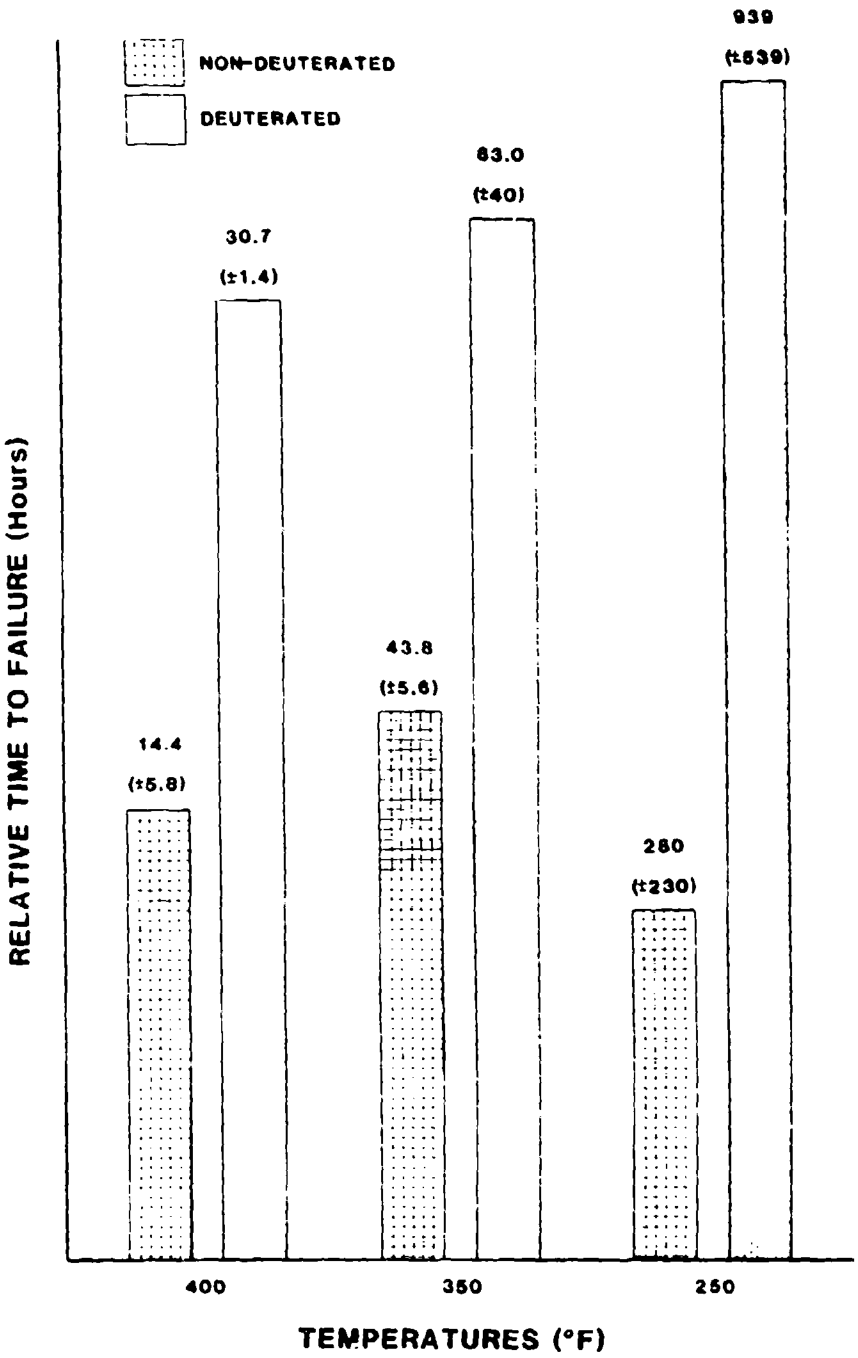

Figure 8. Relative time to failure for lubricated bearings using deuterated and non-deuterated grease at 400, 350, and 250°F. (Relative improvement factor is between 2 and 3.3.)

4. ECONOMIC STUDIES

4.1 BACKGROUND

In addition to evaluating the physical and chemical characteristics of deuterated lubricants, it was deemed necessary to look at potential applications of such lubricants and to initiate an investigation of the economic feasibility of their use. It has been clearly established that there are significant savings such as reduced capital expenditures, lower maintenance and replacement costs, inventory reduction, costs of unexpected failures, manpower costs, and lower energy consumption to be gained from tribological improvement. A report published by Great Britain's Department of Education and Science in 1966 estimated the potential savings to be derived from tribological improvements in Great Britain alone to be in excess of £500,000,000 (U.S. $1,236,000,000).(11) In 1975, H. Peter Jost estimated that emphasis on tribology could result in more than $12 billion in savings (1974 dollars) in the United States.(12)

Table 6 gives the breakdown of potential savings to be derived from tribological improvements in Great Britain as of 1965 and their corresponding dollar amounts. Table 7 compares the Gross Domestic Product for the United States and Great Britain in 1971 and estimated savings in 1974 currency.(12) Finally, it was estimated in 1977 that investments in tribological research and development could effect a $16 billion savings in energy reduction alone in the United States.(13) (See Table 8.)

Table 9 shows the equipment maintenance costs for thirty-five separate U.S. companies in 1979. It is not known what percentage of these costs can be attributed to the failure of rotating parts, nor which of these failures were caused by lubricant degradation. However, it can be safely estimated that

Table 6. Estimated savings through tribology.[a]

	£ Million[b]	$ Million
Reduction in Energy Consumption through Lower Friction	28	67
Reduction in Manpower	10	24
Savings in Lubricant Costs	10	24
Savings in Maintenance and Replacement Costs	230	552
Savings of Losses Consequential on Breakdowns	115	276
Savings in Investments Due to Higher Utilization and Greater Mechanical Efficiency of Machinery	22	53
Savings in Investment through Increased Life of Machinery	100	240
1965 Totals (as published in 1966)	£ 515	$1,236

Notes: (a) Data from Great Britain extracted from Reference 11.
(b) 1£ = $2.40.

Table 7. Potential savings comparison United Kingdom – United States.[a]

	1971 Gross Domestic Product (million dollars)	1974 Estimated Savings on their Tribology (million dollars)
United Kingdom	134,838	2,040
United States	1,045,753	12,000 to 16,000

Note: (a) See Reference 12.

Table 8. Potential energy savings in U.S. economy as a function of tribological R&D costs.[a]

Area	Potential Energy Savings (billions of dollars per year)	Total Estimated R&D Costs (millions of dollars)
Road Transportation	$11.00	$12.60
Power Generation	0.30	2.10
Turbo Machinery	0.75	5.20
Industrial Machinery and Processors	4.20	3.70
TOTAL	$16.25	$23.60

Note: (a) See Reference 13.

Table 9. Corporate maintenance costs.

Chemical Companies	Maintenance Costs (million dollars) 1979	Percentage of Sales (%)	Percentage of Net Income (%)
DuPont	$ 724.5	5.8	77.2
Union Carbide	616.3	6.7	110.8
Dow Chemical	536.7	5.8	68.5
Monsanto Company	405.4	6.4	122.5
Allied Chemical	238.1	5.5	---
PPG Industries	224.5	7.3	102.6
Celanese Corporation	157.0	5.0	111.3
American Cyanamid	155.1	4.9	9.2
Herculese, Inc.	107.0	4.6	62.0
Diamond Shamrock	106.2	4.5	59.6
Stauffer Chemical	83.9	5.5	61.7
Rohm and Haas	77.1	4.8	75.0
Air Products & Chemicals	76.0	6.2	77.9
Ethyl Corporation	75.1	4.5	77.0
Akzona Inc.	58.1	3.7	226.5
Pennwalt Corporation	37.4	3.5	74.8
Reichhold Chemicals	30.4	3.5	248.6
Morton-Norwich	28.6	3.9	31.5
Witco Chemical	21.2	2.2	49.6
Lubrizol	20.8	2.8	22.9
Exxon	1,509.8	1.9	35.1
Mobil	800.5	1.8	39.9
Goodyear	451.4	5.5	308.8
Eastman Kodak	428.4	5.3	42.8
Georgia-Pacific	300.0	5.8	91.7
Ownes-Illinois	247.0	7.0	185.1
International Paper	246.0	5.4	46.8
FMC Corporation	150.2	4.5	90.1
Koopers	97.1	5.3	112.3
Pfizer	84.5	3.1	35.5
Vulcan Materials	71.5	9.6	112.0
Dart Industries	69.8	3.4	40.6
Cabot Corporation	49.0	4.4	69.6
Upjohn	28.4	2.5	25.7
Sherwin-Williams	26.9	2.2	149.2
TOTAL	$8,339.9		

Source: Form 10-K filed annually by public corporation with S.E.C.

these costs could be reduced significantly through the use of superior lubricant systems and improved bearing design. The total maintenance costs for these thirty-five companies in one year alone are $8,339.9 million. An example of maintenance costs directly related to bearing failure comes from a company rolling aluminum sheet. The cost to replace the bearings in one medium-sized mill would be $40,000, plus the costs of lost production from downtime.(14) While the cost of substituting a deuterated lubricant in this instance would be prohibitive, this does provide an indication of the potential savings from improved lubricants and longer lasting bearings.

Much has been written in recent years expressing concern over attitudes regarding specification of bearings and lubricants in new systems. The prevailing theme is that too often performance criteria are inadequate, and selections are made based on lowest cost rather than appropriate quality. The result is that inferior bearings or lubricants are placed in critical systems and cause low reliability and extremely high maintenance costs. The loss of a bearing, possibly caused by lubrication degradation, in the avionics of a $50,000,000 aircraft can mean the loss of a mission or even the aircraft itself.

The opportunity for cost savings from the development of superior lubricants is great and includes savings from reduced maintenance requirements, inventory costs, lower capital costs, and less downtime. The preceding provides a view of the overall need for tribological improvements; the following more specifically addresses the value of deuterated lubricants.

4.2 TASK DEFINITION

The efforts reported here involved two basic tasks:

1. Determination of need for a superior lubricant along with identification of some particular application; and
2. A preliminary investigation of the cost effectiveness of the use of deuterated lubricants.

It was found that the specific data regarding maintenance costs, maintenance schedules, losses from downtime, etc., attributable to lubricant failure, were either proprietary or non-existent in the private sector. Whether or not sufficient data to permit a complete cost-benefit analysis are available within the government remains unclear; it is, however, believed that this information can be derived from available data. In this report, whenever specific comparisons are made or when applications for deuterated lubricants are identified, a general improvement in overall performance of the lubricant system is assumed. Further development of deuterated lubricant systems is essential to permit valid and complete analyses of the specific substitution of deuterated lubricants for those currently in use.

4.3 DETERMINATION OF NEED

The first area of investigation involved establishing the fact that a need exists for a superior, i.e., deuterated, lubricant. In 1979 more than 109 million complete bearings less than 30 mm OD were shipped by bearing manufacturers. (See Table 10.) (The current cost of deuterated lubricants dictates that the primary application will be that which requires only minute quantities of fluid; thus, only bearings less than 30 mm OD were considered.) A large percentage of these bearings were likely destined for installation where accessibility is limited; where the lifetime of the system is closely related to the lifetime of the bearing; where the effect of a "down" system is intolerable, because of either criticality or cost; or where success of a mission, or even human lives, are dependent on the reliability of the bearing. In instances where accessibility is limited, for example, the replacement of a critical bearing demands the grounding of an aircraft, the shutdown of a nuclear plant, or the temporary lack of use of a ship. It is clear that the value of a lubricant rises significantly as it functions to increase bearing life. The authors are aware of a particular bearing used in an Amplidyne Generator which the Navy uses in the rod drive systems of its nuclear reactor plants. The shelf life of this bearing is less than three years and is specifically limited by lubricant failure. Failure of this bearing results in a costly shutdown of the plant. Large inventories of these bearings ($500-$1,000 each) are maintained, yet the bearings are often unusable when needed.

Table 11 lists a number of applications which have been identified as viable candidates for a superior lubricant. The first group consists of critical applications where a failed bearing or a "down" system are extremely costly or disastrous. The second group are consumer-oriented applications in which only minute quantities of lubricant are necessary and where failure is frequently attributed to bearing lubricant failure.

Table 10. Shipments of antifriction ball and roller bearings: 1979 and 1978. (Quantity in thousands of units; value in thousands of dollars.)

	Number of Companies	Quantity of Shipments (1979)	Value (1979)	Quantity of Shipments (1978)	Value (1978)
Ball Bearings, Complete Ground or Precision Single Row Conrad					
9 mm OD through 30 mm OD (ABEC 1 and 3)	17	77,881	80,032	66,550	72,994
9 mm OD through 30 mm OD (ABEC 5 and up)	8	5,137	18,324	4,454	16,532
Integral Shaft Ball Bearings	15	26,463	125,971	22,858	87,739
Cylindrical Roller Bearings					
Precision (ABEC 5 and up)	8	289	36,907	255	27,025
TOTAL		109,770	261,234	94,117	204,290

Table 11. Potential applications.

Group	Applications
Group 1.	**Critical Applications**
	Nuclear Plant Components
	Control Rod Driver
	Navigational and Guidance Systems
	Remote Handling Devices
	Computers
	Shipboard Instrumentation
	Weapons Control Systems
	Drilling Rigs
	Process Equipment
Group 2.	**Consumer-Oriented Applications**
	Copying Equipment
	Fans
	Elevators
	Lathes
	Blenders
	Refrigerators
	Air Conditioners
	Lens Grinders
	Machine Tools
	Simulators
	Sealed Motors
	Watches

4.4 COST EFFECTIVENESS

Deuterated lubricants are currently synthesized in small quantities and cost approximately $12,000 per kilogram or $4,090 per gallon. The ultimate cost of these lubricants will be affected by a number of factors which can be quantified further along in the research. Generally, however, some factors to be considered include:

1. Research and development costs
2. Capital expenditures
3. Raw material
4. Production costs.

Based on the results of the research to date and the projections of future research, we can estimate time-to-failure of three to twenty times greater with deuterated lubricants than with non-deuterated lubricants. Assuming that these ratios stand with continued research and testing, the potential reduction in maintenance costs alone should justify the costs of the research effort, and, later, the costs of implementation. Five areas in which benefits should derive from the use of deuterated lubricants are:

1. Reduction in maintenance costs resulting from unexpected failures.
2. Reduction in scheduled maintenance costs.
3. Reduction in inventory costs.
4. Reduction in capital costs.
5. Increased reliability.

A preliminary effort to quantify the economic feasibility of deuterated lubricants was made. Although the initial cost of deuterated lubricants may appear exorbitant based on current quotations, Table 12 demonstrates that the potential increase in operating life will almost void the additional cost of the lubricant. The Total Expected Operating Life is that of a typical aircraft navigational system with existing procedures (approximately 300 hours) and with varying lifetimes expected with deuterated lubricants.

A specific application, that of a G-200 gyro bearing, was identified as an application of deuterated lubricants on which an initial cost comparison could be performed. This bearing is widely used in navigational equipment, both civilian and military. A specific service facility was identified where maintenance records were maintained and complete for a period of one year, June 1, 1978 to May 31, 1979. Table 13 indicates that a savings of $1 to $2 million can be obtained through use of deuterated lubricants in one type of bearing coming through one service facility.

Table 12. Cost per usage hour for applications requiring 1 cc of lubricant.

Lubricant	Lubricant Cost per Application	Total Expected Operating Life (Hours)	Cost per Usage Hour
Deuterated Hydrocarbon or Ester	$0.13	300	$0.00043
	$1.08	600	$0.00180
	$1.08	900	$0.00120
	$1.08	1200	$0.00090
	$1.08	1500	$0.00072
	$1.08	1800	$0.00060
	$1.08	3000	$0.00036
	$1.08	6000	$0.00018

Table 13. Analysis of deuterated lubricants in G-200 gyro bearing.

Number of Systems in Survey	6500
Number of Systems Serviced Annually	1065
Repair Cost per Unit	$2208

Lubricant	SRG-160	Deuterated
Quantity per Application	1 cc	1 cc
Cost per Application	$ 0.13	$ 1.08
Cost per Kilogram	$500.00	$4090.00
Cost to Lubricate all Units (6500 units)	$845.00	$7020.00
Annual Service Cost (1979 dollars)	$2.3 million	----
Annual Service Cost Lifetime Increased Two Times		$1.2 million
Annual Service Cost Lifetime Increased Five Times		$0.5 million
Annual Service Cost Lifetime Increased Ten Times		$0.2 million
Potential Cost Savings		$1.1 to $2.1 million

5. CONCLUSIONS AND RECOMMENDATIONS

The extremely positive results of the three areas of investigation — bearing tests, determination of oxidative stability, and economic studies — emphasize the value of continued research into deuterated lubricants. The bearing tests not only confirmed results previously reported by NADC, but, since the tests were run over a wider range of temperatures and under more stringent specifications, show even more impressive promise for deuterated lubricants. The stability measurements demonstrated a factor of three to twenty improvement of deuterated compounds over their hydrogenated counterparts, and the economic analysis indicates that, even at current prices for compounds, the potential benefits in a number of applications are great.

Oxidative stability tests were performed on deuterated and non-deuterated synthetic hydrocarbons containing a proprietary antioxidant additive, tetraesters containing antioxidants, and azelate esters. The substitution of deuterium for hydrogen in these lubricant systems has resulted in a significant improvement in their oxidative stability. The 14-fold improvement observed when 98% deuterated hexanoic acid was used to prepare pentaerythritol tetrahexanoate cannot be explained by a simple kinetic isotope effect alone. The deuterated compound outlasted its non-deuterated counterpart even though the original antioxidant had been almost completely consumed within the first quarter of the evaluation. This phenomenon should be investigated in further research; and theoretical models must be developed and tested in the laboratory.

While the results of the bearing laboratory tests were all positive, the time-to-failure testing is inherently limited; frequently the performance of the lubricant is not separable from the quality of the bearing. Future work should make use of selected bearings in an effort to isolate effects. Further, the use of superior deuterated lubricants may necessitate the development or selection of superior bearings to take full advantage of extended lifetime performance.

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