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ADDITIVES FOR HIGH TEMPERATURE LIQUID LUBRICANTS

FINAL REPORT

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ADDITIVES FOR HIGH TEMPERATURE LIQUID LUBRICANTS

I. INTRODUCTION

The purpose of this task was to perform research for the Department of Energy (DOE) on the synthesis and characterization of additives for liquid lubricants which could lead to significant improvements in the major tribological task area of friction and wear reduction at high temperature. To this end JPL surveyed candidate precursor compounds which are soluble in liquid lubricants, synthesized the most promising of these materials, characterized them and submitted these additives to National Institute of Standards and Technology (NIST) for evaluation.

II. BACKGROUND

During boundary lubricating conditions, the frictional heating causes the contacting asperities of the surfaces to fuse and then break apart. The scoring of the surfaces by torn-off particles contribute to breakdown. If a lubricant additive could be found that not only lays down a solid lubricant film, as conventional extreme-pressure additives do, but also reacts with any hot, fresh metal particles torn off of the asperities, the additive should clearly be superior to any additive currently in use. The metal particles would be rendered innocuous, not only preventing the scoring and plowing that these metal particles are known to cause, but also eliminating the contribution of the particles to the catalytic breakdown of the base fluid.

Bearing life could be extended many-fold, and oil and grease changes would be minimized. Moreover, friction would be reduced greatly, resulting in significant energy savings. The approach is based on the premise that aromatic o-dinitriles and related substances will self-condense into planar macromolecules which are capable of strongly chelating metals and forming a lubricating layer on the bearing surfaces. For example, o-phthalonitrile on heating forms phthalocyanine. In the presence of hot metal or metal oxides, the dinitrile forms metal phthalocyanines (PCMe's). Substituted 1,2-butenedinitriles form related tetraazaporphyrins. The reaction of a metal or its compounds with these smaller, precursor molecules to form a larger, more complex one such as these macrocycles (e.g., tetraazaporphyrins), has been called a template reaction (Ref.3). Tetraazaporphyrins such as phthalocyanine are lamellar compounds with interplanar distances identical to that of graphite.

III. PRECURSOR MOLECULES

Ideally, the precursor molecules should be in solution in order to assure that intimate contact occurs under boundary lubricating conditions and that any of the lubricating film is immediately replenished as it is inevitably worn away. Precursor molecules are usually highly polar and are insoluble in the non-polar base fluids.

The solubility parameters of a number of precursor compounds were calculated and are listed in Appendix A.

A suspension of the precursor compound in a representative base fluid could also display some of the effects of the additive in increasing wear life of bearings. Thus, the feasibility of the concept could be demonstrated with suspensions and could prove to provide superior lubricating properties than conventional lubricants. It was found that o-phthalonitrile (PCN) and tetrafluoro-o-phthalonitrile (TFPCN) did display some solubility in bis(diethylhexyl)sebacate (DEHS). Experiments were conducted using both suspensions and solutions in an early study (See Table 2 A-O and J-L). The results were encouraging and formed the basis for a more extensive program.

A. LITERATURE SURVEY

The literature was surveyed with the intent of finding suitable precursor compounds.

Interest in the properties of liquid crystals has led many researchers to study the structure of phthalocyanines.

Structures for films of metallophthalocyanines (PcM) with peripheral hydrocarbon chains include a discotic mesophase (C. Piechoki, et al, JACS 1982 104, 5245) which is defined as a flat aromatic core surrounded by several flexible hydrocarbon chains and stacked in columns which form a hexagonal array. This proposed structure (with C12 substituents) includes the untitled, parallel stacking of molecules.

A series of studies at the Naval Research Laboratory (A. Snow & N. Jarvis, JACS 1984, 106, 4706; W. Barger et al, Thin Solid Films, 1985, 133, 197; D. Dilella, et al, Thin Solid Films, 1985. 133, 207) uses cumylphenoxy groups as the peripheral substituents. The PcM's formed were soluble enough to prepare Langmuir-Blodgett monomolecular layers. The conclusions based on these films was that the PcM's formed densely packed stable stacks with cofacial orientation (about 8-10 PcM rings per stack) and with the axis of the stack not parallel to the plane of the film. However, when these films are applied to a surface, such as gold, the stack axis is oriented so that only the bottom PcM rings of each stack are in contact with (and parallel to) the surface. Other studies (G. Kovacs, et al, Can. J.

Physics 1985 63, 346; J. Fryer, et al, Nature (London) 1985 313, 382) using films of PcM with t-butyl substituents indicate that the PcM rings are tilted to the plane of the surface by 52°.

It is possible that the oxygen-containing PcM used at the Naval Research Laboratory may influence structure. The oxygen molecules may be favorably attracted to the surface, forcing the macromolecule into a parallel orientation. Also, the greater bulk of the cumylphenoxy groups compared to t-butyl may greatly influence the packing arrangement.

B. SYNTHESIS OF PRECURSOR COMPOUNDS

It was then decided to synthesize oxygen-containing phthalonitriles, i.e., ethers with long hydrocarbon chains to take advantage of their solubility in the base fluids and the high probability of forming films in which the macromolecules are parallel to the metal surfaces.

The synthesis of precursor molecules containing oxygen molecules was accomplished in a four step process (S. Pamowski and M. Hanack, Synthesis, 1980, 287-289). It begins with the nuclear bromination of o-xylene to 1,2-dibromo-4,5-dimethylbenzene, using bromine and methylene chloride as solvent. Side-chain bromination using N-bromosuccinimide in carbon tetrachloride

produces 4,5-bis(bromomethyl)-1,2-dibromobenzene. The reaction of this compound with the appropriate sodium alkoxide in the corresponding alcohol gives the bis(alkoxymethyl) derivative. The o-dinitrile is formed by reacting this compound with a small excess of cuprous cyanide in dry dimethylformamide.

IV. FRICTION STUDIES

The apparatus used to measure wear life was a JPL-built rider and disk device used for measuring friction and wear life of solid lubricants according to ASTM D-2716. In this apparatus, a hemispherical rider is allowed to rest on a rotating steel disk. The rider is made of Type 440 stainless-steel HRC 55 and the disk is 17-4PH. The speed of rotation is controlled, as is the distance of the rider from the center, so sliding speeds are known. Variable loads can be placed on the rider to obtain the unit loads (and Hertzian stresses) while a strain gauge is used to measure the force due to friction resisting the movement of this rider over the disk. Breakdown is assumed when the frictional forces become so high that the disk and rider start to grab, run erratically, vibrate and stop. Experiments were conducted with both high and low speeds and with increasing loads.

A. FRICTION TESTING

Tables 1 and 2 list the data obtained from friction studies at JPL.

1) Pathfinder Tests

The first tests were performed with the following lubricants:

1. Diethyl Hexyl Sebacate (DEHS).
2. DEHS with 1.0% Tetrafluorophthalonitrile (TFOPN).
3. DEHS with 1.0% phthalonitriles (OPN).

A total of five tests were conducted at 5.6 Kg load with these lubricants. Data are shown in Table I (1-5).

The highest breakout friction of .21 was obtained with the DEHS alone. Running friction data were collected after approximately one hour of running time during which the friction decreased and then stabilized. The Tetrafluorophthalonitrile solution gave the lowest running friction data with values of 0.05 and 0.06.

2) Tests with Varied Loads

The next set of tests varied the load, but other conditions were constant.

Results are shown in Table I (6-11). The breakout friction was higher with the 2.0kg load than with either the 3.5 or 5.6kg loads.

The running friction values also tended to be lower with 3.5 and 5.6kg loads as compared with those of samples with the 2.0kg load.

The difference between the 2.0kg load tests and the other loads is not readily apparent.

3) Tests with Lighter Load and Slower Speeds

Tests were then conducted with low loads, 0.65, 1.1 and 2.0 Kg. The surface speed was also maintained as slow as the equipment could sustain a constant velocity without stalling (0.07 m/s). The lubricants were diethyhexyl sebacate (DEHS) and a one percent solution of phthalonitrile in

DEHS. The running friction tests were conducted for periods of four to five hours.

The data are shown in Table I (12-15). The data implies that the breakout friction decreases with decreasing load. It is questionable whether the differences between the two lubricants is valid at the 2.0kg load level.

The running friction does not vary significantly with either load or lubricant. Again the 2.0 Kg load level value with the one percent phthalonitrile solution is not significantly lower than the value for DEHS alone.

4) Tests with BMPN

A new compound, bis butoxymethyl phthalonitrile (BMPN), was tested at a wide range of loads (1.1 - 5.6 Kg). The duration of each test was 4-5 hours. The data does not indicate that the additive had any significant effect. (Table 1, 16-23)

Measurement of wear indicated that addition of BMPN generally resulted in less wear on the pins. However, there was very little wear on any of the discs ($<4 \mu\text{m}$).

5) Tests with OMPN

Another new compound, bis octoxy methyl phthalonitrile (OMPEN), was similarly tested. The data is in Table I (24-31).

The breakout friction data does not indicate that the additive OMPEN has any significant effect.

Similarly, the running friction values which represent values at the end of four hours do not show any significant effect from the additive. However, the amount of wear on the riders was generally less with additive when compared with the data from 100% mineral oil. It follows that the compressive load is higher when the wear is lower. The profilometer charts of the wear patterns on the discs showed no wear with the 1.1 and 2.0Kg nominal loads. There was $10\mu\text{m}$ and $12.5\mu\text{m}$ of wear with 3.5 and 5.6 Kg.

6) Tests with TBPB

Friction tests with mineral oil alone and with 1.0% additive of t-butyl phthalonitrile were conducted at 0.13 m/s for four hours. The nominal loads were 1.1, 2.0, 3.5 and 5.6kg. The friction data shown in Table I (32-34) indicates that the additive did not have a discernable effect as the load was increased. The wear data are so variable that no specific trend is evident.

7) Original Tests

It was decided to rerun the friction tests originally reported in Reference 1 and which formed the rationale for this program. The results of the original tests are shown in Table 2 (A-C, J-L).

The results at that time showed that the additives

did offer a significant reduction in wear of bearings during sliding friction and under high load.

It is also significant that both an aromatic and aliphatic precursor compound was effective, indicating that there may be families of compounds that could be useful as lubricant additives based on the postulated concept.

The sebacate ester proved to be a more effective lubricant than mineral oil and required more drastic conditions to achieve breakdown. The solutions increased the bearing life by a factor 255 percent with the 0.5% solution of o-phthalonitrile, and the tetrafluoro-o-phthalonitrile increased the life by 370%. The suspensions in mineral oil did much better, but these experiments were conducted under a much lighter load and lower sliding speed.

8) Repeat of Original Tests

A study was then conducted in order to verify reproducibility of the data. The conditions were mostly the same as in the original study.

The mineral oil solutions contained 1.0% orthophthalonitrile (OPN) and 1.0% metal free phthalocyanine (PC) by weight. The diethylhexyl sebacate solution contained 1.0% of tetrafluoro-orthophthalonitrile by weight.

The surface speed with the mineral oil tests was

0.13 m/s while the surface speed with the diethylhexyl sebacate tests was 0.26 m/s. The nominal loads were 1.1 and 5.6 Kg for mineral oil and diethylhexyl sebacate tests, respectively. The suspensions in mineral oil were sonicated for 15 minutes.

All of the tests were run for three hours. The later procedure differed from the original by setting the zero point on the chart recorder without any weight on the arm. The weight was then added and adjusted in position so that the recorder was again set to zero without any change in recorder settings.

The data from the later tests are shown in Table 2 (D-I, J-P). The data from mineral oil tests had consistently lower breakout and running friction (.05 to .10 vs. .04 to .15) values during the later tests shown in Table I. The data with mineral oil alone and with additives OPN and metal free PC did not indicate any significant trends. The wear diameters on the pins after three hours of rotation at a surface speed of 0.13 m/s did not exhibit any significant trends with the presence of additives.

The second run with diethylhexyl sebacate without any additive had higher breakout and running frictions than expected. The wear diameter was also exceptionally high (0.100 inches).

Therefore, this test is suspect. The first run had a breakout friction which was similar to the two runs with the tetrafluoro-PN additive (.12 vs. .10 and .12). The running frictions at 0.26 m/s runs number 1 with and without additive were the same (0.9 to .10). However, the second run with the additive had a wider spread after three hours (.03 to .09). The data in shows that the mean running friction during the previous test was .02. Refinements in the test procedures would indicate that the results from the current tests are more reliable than those obtained from earlier tests. The tests with mineral oil and diethyhexyl sebacate whether with or without additives did not exhibit significant differences in breakout and running friction values.

B. CHANGES IN PROCEDURE

During the course of JPL's friction studies, a number of refinements were made in the disc and rider apparatus. 1) Efforts were made to eliminate contamination by having all of the discs and riders cleaned with acetone and Freon TF. 2) A lubricant retainer (tape) was wrapped around the periphery of each disc. 3) The breakout friction was obtained by rotating the disc manually and as slowly as possible. 4) The zero point for each test was set on the chart with only the weight of the arm (0.2Kg). The weight was then placed on the arm and the position of the

weight on the arm adjusted so that the chart would record the same zero point.

The result of all these refinements was that the data was somewhat more consistent, but the improvements in the coefficients of friction were minimized.

C. FORMATION OF WEAR TRACKS

The experiments to study wear tracks were performed with discs and riders machined from 17-4 PH and 440C, respectively. The lubricant was one percent phthalonitrile in diethylhexyl sebacate. Tests were conducted at ambient conditions and at 24rpm which gave a surface speed of 0.06 m/s. This was the lowest rate which could be sustained with the DC motor. The loads were 2, 3.5, and 5.6kg for approximately five continuous hours of running time. Efforts were made to eliminate the possibility of silicone contamination by having all of the discs and riders cleaned with acetone and Freon TF. The items were assembled with care so that no fingerprints would appear on any surface. A tape lubricant retainer was wrapped around the periphery of each disc. Five drops of lubricant were added at the start. A separate disc and rider were used for each load. The breakout friction was obtained by rotating the disc manually and as slowly as possible. This procedure and reduction of surface speed was an effort to bracket the inception of "sticktion", i.e. oscillation in the coefficient of friction. There were two runs conducted at each of the load levels. Results are shown in Table I (6-11). The breakout friction was higher with the 2kg load than with either the 3.5 or 5.6kg loads. There was no phenomenon of sticktion. The running friction values also tended to be lower with 3.5 and 5.6kg loads as

compared with those of samples with the four pound load. The sticktion phenomenon was present in all of the running friction tests. The implication is that the oscillation in the coefficient of friction occurs somewhere below the 0.06 m/s surface speed. It would probably be valid to take the mean of the oscillations as the coefficient of friction value.

1) Examination of Wear Tracks

The wear tracks were examined by Fourier Transform Infrared (FTIR) microscopy. This was to determine if any metal phthalocyanine was formed on the wear surface. The FTIR microscope was used to allow small regions to be examined with precise location. The microscope works by reflecting the FTIR spectrometer beam off the sample surface. The measurement is difficult on the wear tracks because of their rough, scattering surface. This required long spectrometer scans to achieve the suitable signal to noise ratio. The Digilab instrument used has a narrow band MCT, liquid nitrogen cooled detector which was operated in the 4000 to 700 wavenumber spectral range. The sample disks with the wear tracks were rinsed with HPLC grade Freon TF to remove all, but the bound insoluble wear residue. A location off the wear track was used as a blank. A 200mm spot size was used as a sampling diameter. The rinsed disks

in the off track (blank) locations were virtually free of any peaks in the mid-infrared region. The diethylhexyl sebacate and the phthalonitrile were effectively rinsed off by the Freon.

The wear tracks have peaks in the mid-infrared region which indicates the presence of a bound insoluble material on the track surface. There were large, broad peaks in the low frequency range (800cm⁻¹ and below) which are likely from metal oxides. There was also hydrocarbon peaks (possible aromatic, C-O) and weak peaks in the 1100-1600 cm⁻¹ range on the wear tracks. It is difficult to definitively assign these peaks to metal phthalocyanine compounds. This is because the levels of the hydrocarbon peaks are near the detection limit and there is no specific marker peak for the porphyrin ring in this spectral region. No carbonyl (ester, organic acids, organic acid salts) was found on the wear track surface. Carbonyl compounds may be expected from the sebacate ester degradation. The FTIR technique is not sufficiently sensitive to identify the composition of the film in the wear tracks. However, the residual film was found only in the wear tracks and not elsewhere on the metal surfaces.

V. REVISED MECHANISM OF O-DINITRILE LUBRICATION

Results obtained at JPL on the pin and disk apparatus together with NIST results (See Appendix B) prompted a closer look at the older data.

The absence of any lowering of the coefficient of friction, C_f , in the results reported by NIST and the similar results reported by JPL at lighter loads, prompted a review of our earliest results (Reference 1). These were run at a 1.1kg load at 0.13 m/s, using suspensions in mineral oil (Table 2, A-C). In every case the presence of the additive increased the lifetime of the bearing 5 to 10 times. Subsequent experiments in diethylhexyl sebacate solution did provide a significant lowering of C_f (from 0.10 for the reference fluid to 0.03 and 0.02 with the additives). In these cases, there was a 5.6kg load and the sliding speed was 0.13 m/s. (Table 2, J-K).

At the time, the differences were attributed to the change of solvent, but it should be noted that the wear life was improved by a factor of 2.5 to almost 4.

These results suggest that the protective effect of the additives is not necessarily coupled to a reduction of C_f . If the uncoupling of the C_f reduction and wear reduction is real, then the answer may lie in the frictional heating necessary to initiate the template reaction. However, the data at present are too scattered and the tests too uncontrolled to do much more than offer a working hypothesis.

We have demonstrated that at a load of 1.1kg (Hertzian

stress = 1.05 GPa) excellent results were obtained with various o-dinitriles suspended in mineral oil (Table 2, A-C)). Higher loads (5.6 kg, Hertzian stress = 1.75 GPa) were used with two aromatic o-dinitriles in diethylhexyl sebacate (DEHS). The higher load of 5.6kg was intended to produce faster wear in order to facilitate comparisons among the additives. Excellent lubricity was observed (Table 2, J-L). At lighter loads with DEHS at JPL (Table 1, 12-15) and in a polyol ether (trimethylolpropane tripelargonate) at NIST (Appendix B) have shown no effect of the additives relative to the base fluid. Only at the higher loads did any effect of the dinitrile manifest itself.

There was no intent to compare loads between the 4-ball tester and the rider-on-disc apparatus. However, a general trend was observed even though the operations are different. A hypothesis to explain these data may reside in the effect of the solvent on the mechanism of the reaction. The formation of phthalocyanine from o-phthalonitrile is commonly called a "template reaction" (Ref. 3). That is, four nitrile groups must coalesce around a single metal atom to form the planar macrocycle. Since it is extremely improbable that four dinitrile molecules would react simultaneously with a central metal atom, the reaction almost certainly is sequential. There is a question whether the metal is even necessary since molten o-dinitriles react in the absence of metal to form the phthalocyanine (Ref. 4). However, phthalocyanine can form at lower temperatures in the presence of metals so the central atom may enter into

the reaction (Ref. 5).

A major difference in the studies (vis-a-vis JPL and NIST) to date has been the base fluid. The fluids have lower solubility parameters than the solutes, therefore the solutes will compete more favorable for the surface of the metal substrate. Metals have solubility parameters in the hundreds (Ref. 6). Even though the concentration of the solute may be 1% or even 0.5%, the solute is more polar. However, as polyester and polyether replace hydrocarbon solvents, the additive may not compete as well for the surface.

Of course, it has not definitely been demonstrated that the reaction occurs on the surface of the metal. That is, one o-dinitrile reacts with a metal, forming a reactive intermediate which then reacts sequentially with other o-dinitriles as they come in contact, until the macrocycle is closed. Alternatively, the metal may be pulled off the surface and the reaction occurs in solution. This is less likely to occur when dramatic reductions of C_f 's are observed, since it would be expected that a lubricating additive film is anchored to the surface. In this case, the reacting molecules may be anchored to the surface by a combination of higher pressure and faster reaction due to the higher temperatures from friction.

In one case only an effect with the tetrafluoro-o-dinitrile was observed in NIST. The more weakly basic nitrile could form much more acidic metal-free phthalocyanines. This might support a solution rather than a surface reaction

since the more acidic chelate would react more readily with the metal. However, we do not know the nature of any reacting intermediate which could have an acidic hydrogen. These arguments suggest that the additives that are soluble in hydrocarbons would be most effective in providing lubricity. It also suggests that the more polar the base fluid, the less effective the additive will be on metals. Ceramics may behave differently depending on their surface character and history. With metals, the hypothesis could be best demonstrated by using a dinitrile that is soluble in both a hydrocarbon base fluid and a more polar fluid such as the polyesters.

The above arguments must be considered tentative in view of the limited data currently available, however it does offer some explanation for some of the results. For example, at lower pressures, we could observe no phthalocyanine film on either the pin or the disk. At the high loads it may have been removed shortly after formation. This implies the template reaction does not occur as rapidly as thought. By contrast, the films of the blue phthalocyanine were readily observable with the naked eye when metal-free phthalocyanine was tested by Battelle in the '50s (Ref. 8). To reiterate, the above reasoning is hypothesis, since no phthalocyanine have been observed in our studies.

IV. CONCLUSIONS

Refinements in the test procedures would indicate that the results from the later friction tests are more reliable than those obtained from earlier tests. The latest tests exhibited no significant improvements in breakout and running friction values due to additives. The concept of forming lubricating films by reaction with metal surfaces unfortunately has been neither proved nor disproved by this study.

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APPENDIX A

SOLUBILITY PARAMETERS

Calculations have been made to estimate the Hildebrand solubility parameters for candidate precursor compounds. The preliminary data is listed in Table A-1. The initial listing was confined to dinitriles which can form chelates with metals or their compounds. The goal to find soluble additives that can react in situ with the bearing surface to form an adherent lubricating film. Although none of the compounds listed match the solubility parameters of liquid lubricants, the lowest solubility parameters were calculated for dialkyl substituted compounds. In this case, there is probably sufficient solubility to provide adequate amounts of reactants on the metal surfaces.

Additional calculations have been made of the relationship expressed by the product of the molar volume of the additive and the square of the difference between the solubility parameters of the additive and the vehicle (see Table A-2). The smaller the numerical value of this relationship, the greater the solubility.

TABLE 1

Solubility Parameters

Phthalonitrile	14.1
<u>Monosubstituted</u>	
n- Butyl	12.2
n - Dodecyl	10.8
Heptafluorobutyl	10.9
<u>Disubstituted</u>	
n - Butyl	11.4
iso- Hexyl	10.7
n - Octyl	10.4
Butenedinitriles	
<u>Disubstituted</u>	
n - Butylthio	11.6
iso - Butylthio	11.5
<u>Lubricants</u>	
Paraffin Oil	7.5
Aromatic Oil	8.0

TABLE A-2

<u>Solubility Parameter (σ)</u>		<u>X_{1,RT}</u> <u>Aliphatic Oil</u>	<u>X_{1,RT}</u> <u>Aromatic Oil</u>
Phthalonitrile	14.1	4370	3740
-perfluoro	14.7	5930	5135
-dioctyl	10.4	1756	1522
-diperfluoro-	7.1	102	515
dodecyl			
-monoperfluoro-	10.9	2323	1575
Butenedinitriles			
-dioctylthio	10.5	3190	2210
-diperfluoro-	7.7	39	62
dodecylthio			

$$X_{1,RT} = V_A (\sigma_A - \sigma_{OIL})^2$$

X_1 = Solubility Ratio

V_A = Molar Volume of Additive

σ = Solubility Parameter

APPENDIX B

Friction tests were at NIST using precursor molecular provided by JPL. This Appendix is a synopsis of reports supplied to JPL by Richard S. Gates of the Ceramics Division of NIST (Reports dated 22 May 1992, 23 September 1992 and 7 September 1993)

Three chemical compounds were sent to NIST for wear test evaluation. These compounds are shown below with their additive code assignments supplied by NIST.

AD6269	tetrafluorophthalonitrile
AD6270	O-phthalonitrile
AD6288	2,3-bis(methylthio)butenedinitrile

Samples of each of the additives were dissolved in a polyol ester (AD6320 - trimethylolpropane tripelargonate) at a concentration of 1.0% (w) for subsequent wear testing. The fluorinated phthalonitrile was barely soluble in the ester at 1% at room temperature.

Wear tests were conducted, using 12.7mm (0.5") diameter 52100 steel ball specimens, and conditions of 0.23 m/s (600rpm), 30 minutes, and 6 μ l lubricant. In addition to the 1% JPL additives, tests were also conducted on the neat ester as a baseline comparison. Additional tests were conducted using known antiwear additives (ZDP's) at 1% (w) in the same ester to show the ability of the test sequence to measure an antiwear effect. Initially tests were conducted at 60kg load.

In general, load capacity plots result in wear test data that roughly parallel the Herzian contact diameter line. The closer to the line, the more effective the antiwear capability of the lubricant. As an example, the neat ester roughly parallels the Hertz line, and is relatively distant from this line. This indicates relatively poor antiwear capability for the neat ester. The ester with 1% alkyl ZDP parallels the Hertz line much more closely at low loads, indicating a significant antiwear effect.

At higher loads, the ZDP loses its effectiveness, and wear increases back to the level of the neat ester. This is a typical load/wear behavior for antiwear compounds such as ZDP.

The three experimental compounds did not exhibit a much of a deviation from the neat ester case, with two minor exceptions.

The tetrafluorophthalonitrile (AD6269) did indicate a slight antiwear effect at 20kg load. The

2,3bis(methylthio)butenedinitrile gave slightly higher wear than the neat ester at 10kg load.

Discussions with JPL indicated that 52100 steel may not be best suited for evaluation of these additives since it has a relatively low maximum operating temperature of 150°C. It is far easier to form chromium or molybdenum phthalocyanine. 52100 steel contains no molybdenum, and only a small amount of chromium (1.3-1.6%). Another bearing steel (M50) has a higher temperature capability (425°C), and contains both molybdenum and chromium. With higher concentrations of chromium (3.75% minimum) and molybdenum (4% minimum) this material would appear to be better suited for lubrication by metal-phthalocyanine precursor compounds. Tests were run on M50 balls (same conditions, same lubricants as for 52100 steel). The results indicate that TMP by itself seems to lubricate at low load, and ZDP provides additional antiwear protection. The three JPL experimental additives have no antiwear effect at low loads, but seem to have a small effect at intermediate loads. The load capacity is pushed back from 35 kg (neat polyol ester) to 45 kg (polyol ester +

additives). Actually, the butenedinitrile (AD6288) was somewhat corrosive at low loads and pushed the wear transition to 55 kg. None of the surfaces had visible films on the surface after the test, as had been described in the patent for lubrication by phthalocyanines. For all of the tests the friction coefficient was between 0.07 and 0.1, with one of the lowest values for neat TMP.

Later, three additional precursor compounds were sent to NIST:

AD6358	4,5-bis(butoxymethyl)-o-phthalonitrile
AD6359	4,5-bis(octoxymethyl)-o-phthalonitrile
AD6360	4,5-butyl-o-phthalonitrile

Test lubricants were made from these compounds by blending to 1% (w) in a polyolester. NIST conducted micro-sample four-ball tests on M50 steel and compared the data to the results of the previous compounds, the base fluid, and ZDP.

According to the wear data, AD6359 and AD6360 are indistinguishable from the polyol base fluid itself and show no effect. AD6358 seems to have a small, but measurable effect on the load capacity when compared to the neat polyol ester. None of the compounds performed as well as the reference ZDP compound. A supply of 0.5" grade 25, 440C stainless steel balls was procured to allow four-ball testing using this material. Samples of the three new JPL additives were tested using the same set of operating conditions previous used, and the new 440C steel material. The data show that none of the additives (including ZDP) were effective.

TABLE 1 FRICTION TESTS

TEST	COEFFICIENT OF BREAKOUT	FRICTION RUNNING	LOAD (kg)	SPEED (m/s)	HERTZIAN STRESS (GPa)
1	0.21	0.10	5.6	0.13	1.80
2	0.16	0.08	5.6	0.13	1.80
3	0.15	0.08	5.6	0.13	1.80
4	0.14	0.06	5.6	0.13	1.80
5	0.10	0.05	5.6	0.13	1.80
6	0.11-0.10	0.08-0.12	2.0	0.06	1.25
7	0.12-0.10	0.07-0.08	2.0	0.06	1.25
8	0.04-0.05	0.006-0.05	3.5	0.06	1.55
9	0.04-0.07	0.006-0.07	3.5	0.06	1.55
10	0.05-0.06	0.014-0.04	5.6	0.06	1.80
11	0.05-0.07	0.01-0.04	5.6	0.06	1.80
12	0.15	0.09-0.10	2.0	0.07	1.25
13	0.10	0.08-0.10	0.65	0.07	0.88
14	0.14	0.08-0.10	1.1	0.07	1.05
15	0.23	0.05-0.06	2.0	0.07	1.25
16	0.10	0.07-0.10	1.1	0.07	1.05
17	0.10	0.04-0.10	2.0	0.07	1.25
18	0.15	0.08-0.11	3.5	0.07	1.55
19	0.15	0.10-0.12	5.6	0.07	1.80
20	0.06	0.05-0.11	1.1	0.07	1.05
21	0.10	0.07-0.10	2.0	0.07	1.25
22	0.11	0.08-0.11	3.5	0.07	1.55
23	0.09	0.07-0.09	5.6	0.07	1.80

TEST	COEFFICIENT OF FRICTION		LOAD (kg)	SPEED (m/s)	HERTZIAN STRESS (GPa)	
	BREAKOUT	RUNNING				
24	MINERAL OIL	0.10	0.10-0.07	1.1	0.07	1.05
25	"	0.10	0.04-0.01	2.0	0.07	1.25
26	"	0.15	0.08-0.11	3.5	0.07	1.55
27	"	0.15	0.10-0.12	5.6	0.07	1.80
28	" +0.25% OMPN	0.13	0.06-0.11	1.1	0.07	1.05
29	"	0.12	0.08-0.11	2.0	0.07	1.25
30	"	0.13	0.12-0.14	3.5	0.07	1.55
31	"	0.16	0.09-0.12	5.6	0.07	1.80
32	MINERAL OIL	0.10	0.03-0.07	1.1	0.13	1.05
31	"	0.13	0.07-0.10	2.0	0.13	1.25
33	"	0.11	0.07-0.09	3.5	0.13	1.55
34	"	0.12	0.07-0.08	5.6	0.13	1.80
36	" + 1% TBPN	0.09	0.06-0.07	2.0	0.13	1.05
37	"	0.07	0.06-0.07	2.0	0.13	1.25
38	"	0.13	0.07-0.09	3.5	0.13	1.55
39	"	0.16	0.05-0.08	5.6	0.13	1.80

TABLE 2 FRICTION TESTS

TEST	COEFFICIENT OF BREAKOUT	FRICTION RUNNING	LOAD (kg)	SPEED (m/s)	HERTZIAN STRESS (GPa)
A	0.15	0.12-0.13	1.1	0.13	1.05
B	0.15	0.10-0.15	1.1	0.13	1.05
C	0.12	0.1-0.13	1.1	0.13	1.05
D	0.12	0.05-0.09	1.1	0.13	1.05
E	0.08	0.05-0.09	1.1	0.13	1.05
F	0.09	0.07-0.10	1.1	0.13	1.05
G	0.10	0.06-0.09	1.1	0.13	1.05
H	0.10	0.05-0.10	1.1	0.13	1.05
I	0.10	0.05-0.09	1.1	0.13	1.05
J	0.20	0.10	5.6	0.26	1.80
K	0.15	0.03	5.6	0.26	1.80
L	0.15	0.02	5.6	0.26	1.80
M	0.12	0.09-0.10	5.6	0.26	1.80
N	0.16	0.10-0.13	5.6	0.26	1.80
O	0.12	0.09-0.10	5.6	0.26	1.80
P	0.10	0.03-0.09	5.6	0.26	1.80
Q	0.23	0.12-0.19	3.5	0.07	1.55
R	0.22	0.15-0.24	3.5	0.07	1.55