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THE EFFECT OF ANTI-WEAR ADDITIVES ON THE LUBRICATION PROPERTIES OF CORROSION PREVENTIVE OILS

TECHNICAL REPORT

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and
Peter Martin Jr.

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ABSTRACT

Several common extreme pressure and anti-wear additives were investigated to determine their suitability for use in corrosion preventive oils. The lubrication properties of the additives dissolved in a purified base oil were determined and found to be closely related to their adsorption kinetics. Perfluorooctanoic acid and zinc dithiophosphate were the most effective additives examined.

Evaluation of 1.0% by weight zinc dithiophosphate in a proprietary corrosion preventive oil showed that this additive caused a considerable improvement in lubrication properties without being detrimental to the other desired properties of the oil.

The Effect of Anti-Wear Additives on the Lubrication Properties of Corrosion Preventive Oils

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Several common extreme pressure and anti-wear additives were investigated to determine their suitability for use in corrosion preventive oils. The lubrication properties of the additives dissolved in a purified base oil were determined and found to be closely related to their adsorption kinetics. Perfluorooctanoic acid and zinc dithiophosphate were the most effective additives examined.

Evaluation of 1.0% by weight zinc dithiophosphate in a proprietary corrosion preventive oil showed that this additive caused a considerable improvement in lubrication properties without being detrimental to the other desired properties of the oil.

INTRODUCTION

There is extensive use of corrosion preventive oils as lubricants for military applications. Classification of these oils as lubricating fluids was based on the assumption that a good quality mineral oil or synthetic fluid would perform adequately in this regard. This assumption is true if maintenance of a thin hydrodynamic film is sufficient for lubrication. Increasing severity of application in recent years has made it clear that these oils must have good lubrication properties under extreme pressure conditions.

A recent study (*1*) of corrosion preventive oils, qualified under various military specifications, showed that the lubricating ability of these oils under conditions of boundary lubrication is not adequate. The report showed that two oils in particular, VV-L-800 (2) and MIL-L-14107B (3), required considerable improvement as lubricants. It was suggested that extreme pressure (EP) additives be used to enhance the lubrication properties of the oils.

Literature on friction and wear reducing additives and on their mechanisms is abundant. It has been suggested (*4*, *5*), for example, that long-chain polar compounds adsorb on or react with the surface to form an oriented surface film, and that EP and anti-wear additives containing chlorine, phosphorous, and sulfur react with the surface (*6*) to form low shear-strength films of metallic compounds.

Rates of adsorption of lubricant additives are also known (*7*) to be important since single layers of adsorbed films are rapidly worn away and must be readily replaced. Less well known, and of great importance in multi-additive compositions, is the synergistic or antagonistic interaction of anti-wear additives with other additives, such as corrosion inhibitors, anti-oxidants, pour point depressants, etc.

In this investigation, the friction and wear characteristics of several common anti-wear and EP additives dissolved in a purified mineral oil were determined. Surface potential changes of these additives on sand-blasted mild steel specimens were also determined. Two of the additives were selected for extensive tests in both VV-L-800 and MIL-L-14107B specification oils.

MATERIALS

The following additives were used in this investigation: perfluorooctanoic acid, lead naphthenate, zinc dithiophosphate, bis-(β-chloroethyl)vinylphosphonate, 95–99%; oleic acid, purified grade; tricresyl phosphate, technical grade; 1-chlorohexadecane, reagent grade; hexachloro-1,3-butadiene, practical grade; and antimony dialkyldithiocarbamate, a commercial additive. All compounds were used without further purification.

The base oil used was a highly refined mineral oil.

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Prior to use, the oil was slowly percolated through columns containing florisil, fuller's earth, and alumina to remove polar adsorbable impurities. Absence of polar impurities was assumed if drops of the purified oil did not spread on a clean water surface.

APPARATUS

Friction and wear were determined using a Four-Ball Wear Tester equipped with a continuous balance electronic potentiometer capable of indicating temperature and frictional force. Frictional force was measured by a transducer connected to the torque arm of the four-ball cup.

Surface potential changes were followed directly using a vibrating-condenser apparatus as described in a previous article (*8*) with a few modifications. The platinum reference electrode was sprayed with colloidal polytetrafluoroethylene. Conversion of the platinum electrode to a low-energy surface minimized contamination by water and organic vapors. During its use, the electrode developed electrostatic charges on its surface. These charges were removed by using a polonium α particle source mounted near the reference electrode.

PROCEDURE

Each additive was evaluated at an arbitrarily selected concentration in mineral oil. The acidity of each solution was determined by a thermometric method previously described (9). In addition, two of the additives, zinc dithiophosphate and perfluorooctanoic acid, were tested in qualified samples of VV-L-800 and MIL-L-14107B oils.

Friction and wear of the solutions were determined with the four-ball wear tester operated at 75C and 1200 rpm for one hr at loads of 15, 35, and 60 kg. These loads correspond to calculated initial bearing pressures ranging from 238,900 psi at 15 kg to 379,200 psi at 60 kg.

The balls used were 52100 composition steel. Prior to use, they were degreased by several rinses in reagent grade benzene. Four new balls were used for each test. Before each experiment, all parts of the test cup were degreased with petroleum solvent. Wear scar diameters were measured with the wear lines both normal and parallel to the vertical axis of the microscope.

In all surface potential experiments, the mild steel specimens were prepared by sandblasting with clean, white, dry sand, free from organic matter. They were then placed in a desiccator until used.

To determine the surface potential changes of the oil solutions, an initial potential measurement was made of the bare steel surface. Approximately 0.2 ml of the oil solution was then placed on the steel surface. The specimen was immediately placed in the vibrating-condenser apparatus. The lower electrode was raised until the film-covered specimen was within 0.5 mm of the reference electrode. The potential changes (ΔV) due to adsorption were periodically measured for one hour.

Vibrations of the reference electrode were stopped when measurements were not being taken because the close proximity of the vibrating electrode caused an unnatural thinning of the oil film. All measurements were made at 25 ± 1C and 40 ± 10% relative humidity.

RESULTS AND DISCUSSION

The physical properties and wear test results for the additive solutions are shown in Table I. Some of the additives, because of their reactivity as compared with the base oil, caused considerable increase in scar diameter at the lower loads. Results at 60 kg indicate that all of the additives but four caused some reduction in wear at this load. However, only two of the additives, zinc dithiophosphate (ZnDTP) and perfluorooctanoic acid (PFOA) showed significant wear reduction at all loads.

The coefficient of friction (f) was calculated for each solution at all applied loads. Since the variation of f with reciprocal load was linear for all solutions used, only values obtained at 60 kg are listed in Table I.

Surface potential changes with respect to time for the oil solutions are shown in Fig. 1a and 1b. The ΔV values measured were positive with respect to the metal-air potential (bare steel) with the exception of perfluorooctanoic acid. The positive values mean that the potential change was due to the rearrangement of the dipoles present in the oil and that the positive end of the dipole was oriented upward. ΔV becomes larger as the orientation of the dipole to the vertical increases, and as the dipoles become more tightly packed. The negative ΔV observed for perfluorooctanoic acid is analogous to results obtained by Fox (*10*) for a series of perfluorinated fatty acids at the air-water interface.

All of the curves reached an asymptote within one hour, with the exception of the base oil and tricresyl phosphate (TCP). The rapid increase of ΔV with time for the base oil and TCP probably indicates permeation of the adsorbed film by water.

Since adsorption is an important part of the formation and orientation of a surface film on a metal, the surface potential changes with time are an indication of the progress of the adsorption process. These curves were interpreted to be a relative indication of the tendency of the additives to adsorb. Previous authors (*11–12*) have also interpreted these surface potential changes with time as rates of adsorption.

The tendency to adsorb, as indicated by the time required for an equilibrium potential to be reached, are listed below in order of decreasing rate:

ZnDTP > PFOA ≅ bis(β-chloroethyl)vinylphosphonate > oleic acid > oleic acid + TCP > antimony dialkyldithiocarbamate ≅ 1-chlorohexadecane > hexachloro-1,3-butadiene > lead naphthenate > TCP > base oil.

In general, those additives which adsorb rapidly to

TABLE I—PROPERTIES OF ADDITIVES IN A PURIFIED MINERAL OIL

Additive	Concentration (% by Wt)	Total Acid No. (Mg$_{KOH}$ gm^{-1})	Kinematic Viscosity @ 100F (cSt)	Wear Scar Diameter[a] (mm) Load 15 kg	35 kg	60 kg	Coefficient of Friction[b]
None	—	0	11.75	0.56	0.82	1.60	0.098
Oleic acid	2.0	4.40	10.36	0.54	0.60	1.61	0.083
Perfluorooctanoic acid	0.05	0	10.32	0.53	0.62	0.72	0.086
Lead napthenate	1.0	1.13	10.44	0.48	0.77	1.59	0.091
Zinc dithiophosphate	2.0	1.98	10.54	0.22	0.44	0.89	0.101
Antimony dialkyl-dithiocarbamate	2.0	1.25	10.69	0.47	0.73	1.11	0.105
1-chlorohexadecane	2.0	0	10.07	0.56	0.91	1.50	0.102
Hexachloro-1, 3-butadiene	2.0	0	9.93	0.55	0.92	1.02	0.084
Tricresyl phosphate	1.5	0.62	10.19	0.38	0.65	1.62	0.089
Bis-(β-chloroethyl)-vinylphosphonate	1.0	0.48	10.95	0.64	0.85	1.02	0.081
Tricresyl phosphate and oleic acid	Both 1.5	3.55	10.24	0.23	0.41	1.60	0.083

[a] All tests conducted at 1200 rpm, 75C for 1 hr.
[b] Calculated from frictional force at 60 kg load.

form monolayers may be expected to be effective in reducing wear. The main function of the lubricant film is to reduce the number of metallic contacts by interposing monolayers which reduce penetration, while maintaining easy shear between them. Rapid adsorption of the monolayer will, therefore, result in a decrease of metallic adhesion.

Wear results in Table I are in good agreement with the adsorption studies since the most effective additives also exhibited the most rapid rates of adsorption. This indicates that the rate at which a molecule is adsorbed on a surface, as well as its orientation, is important for effective lubrication. These results were used as a basis for selecting ZnDTP and PFOA for evaluation in the VV-L-800 and MIL-L-14107B oils.

VV-L-800 is a mineral oil containing various additives; wear properties similar to those exhibited by the additive-base oil solutions were expected. MIL-L-14107B, however, is a tetraalkylsilicate ester and is much less viscous than VV-L-800. The effect of ZnDTP and PFOA on the wear properties of these oils is shown in Figs. 2 and 3. The broken Hertz line shown in both figures gives the diameter of the calculated elastic deformation of the steel balls for the corresponding applied loads.

The wear scar diameter at 60 kg for ZnDTP in the

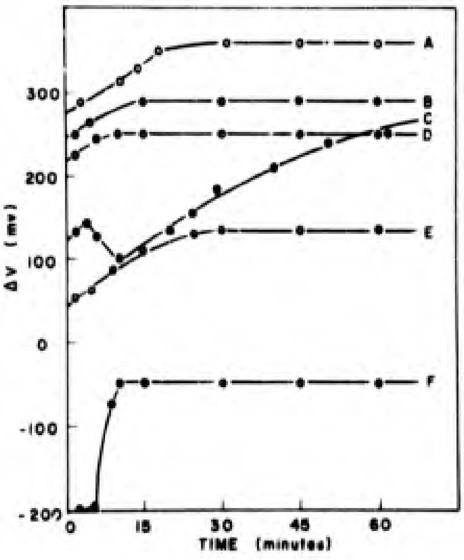

Fig. 1a—Surface potential changes on mild steel.
- A. Antimony dialkyldithiocarbamate
- B. Oleic acid—tricresyl phosphate
- C. Base oil
- D. Oleic acid
- E. 1-Chlorohexadecane
- F. Perfluorooctanoic acid

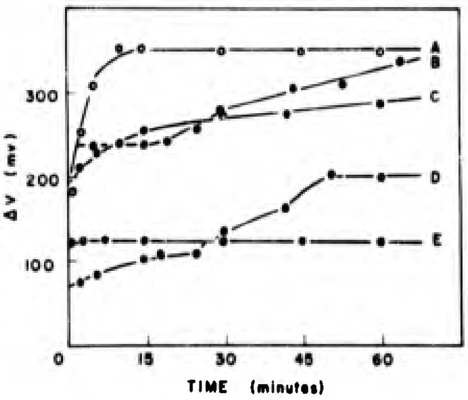

Fig. 1b—Surface potential changes on mild steel.
- A. Bis-(β-chloroethyl)vinylphosphonate
- B. Tricresyl phosphate
- C. Lead naphthenate
- D. Hexachloro-1,3-butadiene
- E. Zinc dithiophosphate

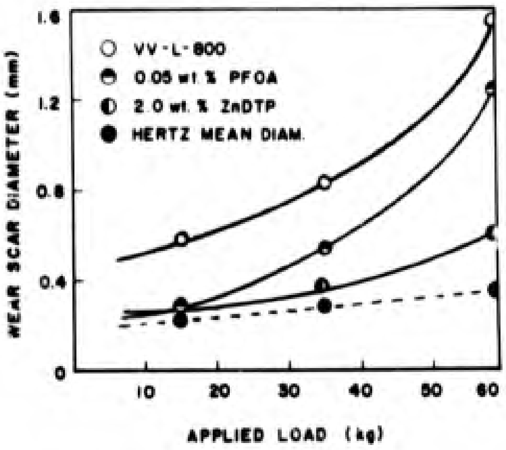

Fig. 2—Effect of additives on wear properties of VV-L-800 oil.

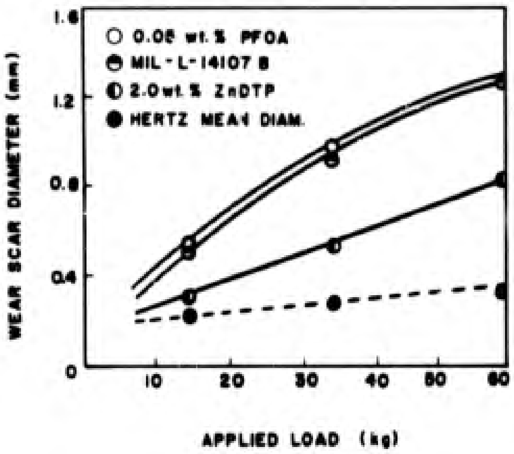

Fig. 3—The effect of additives on the wear properties of MIL-L-14107B oil.

base oil was 0.89 mm. When the same concentration of ZnDTP was used in VV-L-800 oil the scar was reduced to 0.59 mm as shown in Fig. 2. Evidently there is a synergistic interaction of the additives present in the oil with ZnDTP.

PFOA exhibited a wear scar at 60 kg of 0.72 mm in the base oil but rose to a value of 1.23 mm in the VV-L-800 oil. This reduction in lubricating ability may be explained by results obtained by Zisman (*13*). He showed that retracted monolayers of perfluorinated acids have low values of f and good film durability; loss of film durability resulted when conditions were such as to permit formation of a mixed monolayer. In our experiments, it is probable that a single-component film of the PFOA was adsorbed from the base oil. The outermost terminal group (—CF_3) of the adsorbed molecules comprised a surface of very low surface free energy. This results in very low adhesion between adsorbed films and decreased metallic adhesion. When PFOA was dissolved in the VV-L-800 oil, competitive adsorption of the various additives present took place which resulted in reduced lubricating efficiency of the perfluorinated compound.

Both VV-L-800 and MIL-L-14107B oils contain several additives, e.g. corrosion inhibitors, pour point depressants, antioxidants, and water-displacing agents. The exact compositions of these oils is proprietary; however, both oils usually contain 3-5% of a sulfonate-type inhibitor. These compounds have been shown (*14*) to adsorb rapidly at the metal-oil interface. The sulfonates have the same adsorption rates as PFOA, which could result in competitive adsorption at the metal surface. ZnDTP adsorbed at a much faster rate than the sulfonates.

Results shown in Fig. 3 indicate that PFOA has no anti-wear properties in MIL-L-14107B oil. ZnDTP, however, did show a considerable reduction in the amount of wear at all applied loads.

Specification tests were run on both VV-L-800 and MIL-L-14107B oils containing 2.0% by weight ZnDTP. Results of the VV-L-800 specification tests shown in Table II indicate that ZnDTP has caused a change in two important properties of the oil. Both the viscosity at −65F and the corrosiveness and oxidation stability tests failed to meet requirements. In the latter test, there was a large reaction with the copper specimen and the viscosity of the oil increased 28.8%.

Several different concentrations of ZnDTP in VV-L-800 oil were then tested at 60 kg in the four-ball tester. Figure 4 shows that 1.0% by weight of ZnDTP is sufficient to give the same lubrication results obtained at the 2.0% concentration. The viscosity at −65F and the corrosion and oxidation stability tests were rerun at the 1.0% concentration and, as shown in Table II, passed the requirements.

A MIL-L-14107B containing 2.0 wt % ZnDTP failed to meet specification requirements. The viscosity at −65F and the hydrolytic stability tests failed. In the latter test, the used oil was a resinous mass and it was impossible to conduct further tests. Evidently some type of polymerization of the ester had taken place. No further tests were conducted on MIL-L-14107B oil.

SUMMARY

This investigation has shown that anti-wear effectiveness of a number of common additives is closely related to their adsorption kinetics.

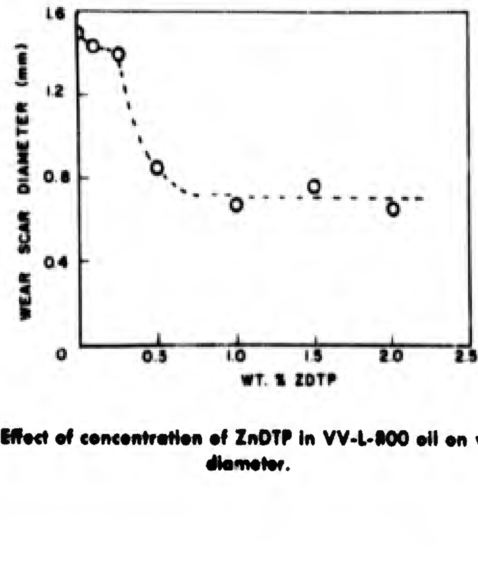

Fig. 4—Effect of concentration of ZnDTP in VV-L-800 oil on wear scar diameter.

Table II—RESULTS OF SPECIFICATION TESTS FOR 2.0 WT% ZnDTP IN VV-L-800 OIL

Test	Sample		Requirement
Flash point, °F, min.	295		275
Pour point, °F	−75		−70 or lower
Viscosity:			
@ 100F, cSt, min.	12.4	1.0 wt %	12
@ −40F, cSt, max.	4,160	ZnDTP	7,000
@ −65F, cSt, max.	64,007	54,831	60,000
Precipitation number	Trace		Shall not be more than 0.05 ml
Copper-strip corrosion	1a		Any corrosion evident shall be less than No. 3 of the ASTM scale
Corrosiveness and Oxidation stability:			
Max. wt change per specimen	Cu: 11.31 Others: None	Cu: 0.2 Others: None	±0.2 mg/cm²
Appearance of specimens after test	Heavy black corrosion on Cu. Others OK	OK	No pitting, etching, or visible corrosion at 20x magnification
Max. viscosity change, cSt	+28.8	+1.8	−5 to +20%
Max. neutralization No. increase	−0.57	−0.73	0.20
Separation or gumming	None	None	None
Corrosion protection:			
Humidity cabinet, days, min.	OK		8
Corrosivity	OK		The fluid shall prevent the formation of rust on steel discs, covered with a brass clip, after exposure at 80F and 50% relative humidity.
Water displacement and Water stability:			
As received	OK		Shall satisfactorily displace water
After storage in contact with water	OK		
Removal	OK		Removable with naphtha cleaning solvent
Cloud intensity at low temperature	OK		The fluid shall not gel, crystallize, solidify, nor show evidence of separation of insoluble material after 72 hours at −65F. Turbidity shall not be greater than the standard.
Film characteristics	OK		No gumminess, tackiness, or hardening.
Color, ASTM, max.	3		No. 7
Workmanship	OK		No suspended matter, grit, water, etc.

Specification tests on two corrosion preventive oils containing ZnDTP indicate the need for basic studies on additive interaction. Such information will be necessary before reliable predictions can be made about the effectiveness of anti-wear additives in proprietary oils. The comparison of the adsorption rates of the sulfonates, PFOA, and ZnDTP indicates that surface potential changes may be useful in predicting competitive adsorption of other additive combinations from oil solutions.

A concentration of 1.0% by weight ZnDTP in VV-L-800 oil has been found effective in greatly increasing the lubrication properties without being detrimental to other required properties of the oil. It is anticipated that these results will accelerate research on anti-wear additives compatible with corrosion preventive oil and result in more stringent wear requirements in government specifications.

ACKNOWLEDGEMENT

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The opinions or assertions contained herein are not to be construed as official nor do they reflect the views of the Department of the Army or the Department of Defense.

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13. ABSTRACT

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