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Wear and Friction Studies of Neopentyl Polyol Ester Lubricants

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CONTENTS

ABSTRACT

Wear and friction properties of three representative neopentyl polyol esters, together with the common diester lubricant base, bis(2-ethylhexyl)sebacate, were studied with the four-ball wear machine in the presence and in the absence of tricresyl phosphate. The rubbing surfaces were 440C stainless steel and 52100 steel.

With 52100 low-chromium steel balls, wear rates were largely independent of ester structure and viscosity. Percolated tricresyl phosphate reduced wear moderately at low loads only. Stainless steel 440C gave results significantly different from those with 52100 steel at all loads. Wear was greatly increased at a load of 50 kg. Tricresyl phosphate was ineffective under all conditions. Friction showed little or no correlation with wear or the variables examined.

Experiments with the "as-received" tricresyl phosphate additive failed to confirm the substantial difference between percolated and unpercolated tricresyl phosphate found at the Massachusetts Institute of Technology with a different test method in connection with the Navy gyro bearing program.

PROBLEM STATUS

This is an interim report; work on this and other phases of the problem is continuing.

AUTHORIZATION

NRL Problem C02-03.101
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WEAR AND FRICTION STUDIES OF NEOPENTYL POLYOL ESTER LUBRICANTS

INTRODUCTION

The neopentyl polyol esters show great promise as broad temperature range synthetic lubricants, having excellent thermal and oxidative stability combined with other desirable properties. The major application so far is in high-temperature, gas-turbine aircraft engines. Formulations of these esters are already widely used in military and commercial aircraft, where they have displaced the conventional diester oils, which, under Specification MIL-L-7808, had been used in jet engines since the early 1950's. The polyol ester lubricants are qualified under Specification MIL-L-23699 (1), which is commonly referred to as the "5-centistoke jet engine oil." It was promulgated to anticipate the higher operating temperatures to be encountered in advanced turbine engines for supersonic aircraft. The specification requires test performance at 500°F which the diesters are not able to meet. In current aircraft the change to polyol esters has resulted in cleaner engine operation, longer periods between engine overhauls, longer service as useful lubricants, and higher load-carrying capacities.

Although many esters of neopentyl alcohols have been prepared and their properties studied in relation to structure (2-5), few friction and wear data have been reported. The history of the polyol esters was given by Smith (6). As a class these esters, when pure, resemble the diesters and mineral oils in friction and wear characteristics (7). Critchley and Miles (8) showed incipient seizure load and scar diameter of various polyol esters vs chain length of their acid groups in the four-ball machine. Barnes and Fainman (9) measured static and kinetic friction of a variety of esters in a stick-slip machine. They claimed that esters of straight-chain acids were good boundary lubricants, while those derived from branched-chain acids were poor boundary lubricants. Dukek (10) has discussed the difficulty in finding EP additives for polyol esters.

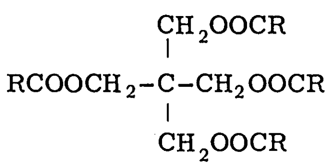
This report will summarize results obtained to date of an investigation of the wear and friction properties of representative polyol esters as measured with the four-ball wear machine. The performance of stainless-steel surfaces lubricated with these compounds was compared with that of 52100 steel. Antiwear effects of tricresyl phosphate (TCP) were studied to provide a base of reference for later work. The purpose of our work is to improve the antiwear or EP performance of polyol esters and to explore for additives free of the objectionable storage properties of TCP (11). TCP is now incorporated in some of the commercial MIL-L-23699 oils. The mechanism of the wear preventive action of TCP is an old controversial topic in the literature. A long accepted theory that TCP reduces wear by phosphide eutectic formation and chemical polishing action has been disproved recently (12-14).

One practical situation for which the present work is pertinent has arisen in connection with the inertial gyro bearing program, in which NRL has been deeply involved for some time. New, rigidly standardized lubricants based on superrefined petroleum oils containing TCP are being developed by Pennsylvania State University and the Kendall Refining Co. and tested by the Instrumentation Laboratory at the Massachusetts Institute of Technology (M.I.T.). Meanwhile, NRL is working on a pentaerythritol ester lubricant for the same purpose. It is possible that some wear-preventing additive will be required for this oil.

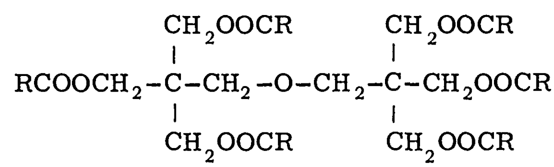
While TCP is a common wear-prevention additive in conventional petroleum lubricants and was often used in diester-type gas-turbine lubricants, inadequate data exist on its use with polyol esters or with stainless steel. Since 440C stainless steel is replacing the standard 52100 steel in miniature ball-bearing manufacture, a need for such data exists.

APPARATUS AND MATERIALS

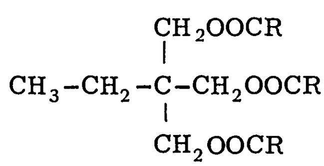
Commercial lubricants based on the polyol esters are formulations containing one or more of the pentaerythritol, dipentaerythritol, and trimethylolpropane esters:



pentaerythritol ester



dipentaerythritol ester



trimethylolpropane ester

The acyl groups are from monobasic, aliphatic acids having chain lengths from C_5 to C_{10}. The superior thermal stability of these esters is ascribed to their unique neopentyl carbon structure (6). When, as in this case, there are no hydrogens on the beta carbon in the alcohol group, the usual low-energy breakdown path of esters via a cyclic intermediate cannot take place. A representative ester from each class was selected for testing along with a conventional diester, bis(2-ethylhexyl)sebacate, for comparison. The composition and properties of these four test fluids are shown in Table 1 (15,16). These are base stocks obtainable from commercial sources for formulating finished lubricants. The diester was obtained from Rohm and Haas as Plexol P-201 and then vacuum distilled. All test samples were purified by percolation through an adsorption column containing equal layers of Florisil and activated alumina. This treatment removed any polar impurities which might have acted as antiwear agents and thus confused the results. An oxidation inhibitor, phenyl α-naphthylamine (PANA), was added to all samples in the amount of 1%. The inhibitor was obtained from Union Carbide Corp. as Ucar brand additive PN-1. TCP was obtained from Fisher Scientific Co. as a technical-grade, 80/20 para/meta isomer mixture. It was percolated as above, and the purified product was used except where otherwise noted. A 1% concentration of TCP was employed except for a few tests at 3%. All experimental fluids were prepared and stored in acid-cleaned, dry, Pyrex bottles. Precautions against contamination were observed in their use.

The four-ball wear machine used here was the Brown-G.E. modification (17,18) built by Roxana Machine Works, St. Louis, Mo., which is an advanced version of the usual Shell four-ball wear machine made by Precision Scientific Co. It embodies a pneumatic loading system, automatic feedback motor speed control, timed automatic shutoff, and conventional Honeywell recorder that records temperature and friction every 30 sec each and controls temperature. Friction torque was measured with a direct-current strain gage system using a Statham unbonded wire strain gage mounted on an adjustable arm and a battery-powered control box. Calibration was checked with dead weights by

Table 1
List of Test Lubricants and Properties

Sample*	Parent Polyol	No. of Acyl Groups	Predominant Acid Groups	Average Acid Chain Length	Mol. Wt.	Viscosity (cs)	
						100°F	210°F
DPE 6.3	90% DPE	6	$C_{5\text{-}8\text{-}10}$	6.3	832	56.1	8.9
PE 6.1	99% PE	4	$C_{5\text{-}6\text{-}7\text{-}8\text{-}9}$	6.1	532	20.4	4.6
TMP 8.8	TMP	3	C_9	8.8	587	23.5	-
Sebacate	-	1	-	-	426	12.6	3.3

*PE = pentaerythritol; DPE = dipentaerythritol; TMP = trimethylolpropane.

means of a string and pulley before and after each test. This model was further improved by providing a better clock and a modern continuous strip-chart recorder with fast response time (Esterline-Angus Speed-Servo) for the friction channel. The latter greatly improved the observation of friction, especially transient phenomena. The load was controlled to ±0.1 kg, the temperature to ±3°F, and the speed to less than ±50 rpm.

The 52100 chrome steel balls used were Atlas grade 25 (SKF Industries, Inc.). Balls of 52100 chrome steel are normally used in the four-ball apparatus and in ball bearings. The stainless-steel balls were AISI 440C alloy, grade 10 AFBMA, obtained from Industrial Tectonics, Inc., Ann Arbor, Michigan. The 440C alloy (17% chromium, no nickel) is of interest, because it is becoming widely used in ball-bearing manufacture. Both types were through-hardened. In addition, the stainless-steel balls were surface-treated in manufacture by passivation in 10% nitric acid. Hardness was checked with a Tukon Tester. The 52100 and stainless-steel balls gave Diamond Pyramid Hardness numbers of 902 and 760, respectively, or Rockwell numbers R_c 67 and 63. The makers' values were R_c 63 to 66 for 52100 and R_c 58 to 64 for 440C. The maker's value of compressive strength for 440C steel was 400,000 psi. The maximum Hertz pressure reached in the study was 356,000 psi at a 50-kg load. The balls were cleaned thoroughly by treating them with boiling benzene (analytical grade) in a Soxhlet extractor and were stored under benzene until used.

PROCEDURE

All tests were run 60 min at 266°F bulk-oil temperature and at a speed of 600 rpm in room air. The loads used were 5, 10, 20, and 50 kg. Following each test the oil was poured out of the sample cup and examined for any change in appearance or odor and for the presence of metal wear particles. The cup, balls, ball retainer, and clamping ring and the chuck for the rotating ball were cleaned by repeated rinsing in pure toluene followed by acetone. The cup and retainer were replaced in the apparatus and given a bakeout, whereby the temperature was raised quickly to 400°F and then allowed to cool. This precaution was intended to remove any trapped solvent. It also served to eliminate possible low-boiling polar contaminants, whether from outside or from thermal breakdown of the preceding sample. Balls were used twice by rotating them to new positions when reinserting them in the sample cup. Wear scars on the three fixed balls were located under a medium-power microscope and then measured with a 76-power microscope having a filar-graduated eyepiece and a calibrated movable stage. The maximum dimensions of each wear scar, both parallel and perpendicular to the direction of sliding, were measured and averaged. The dimensions of the scars on the three balls were then averaged. The width of the wear track on the rotating ball was measured at four points 90 degrees apart and averaged. Shapes of wear scars were noted and recorded.

RESULTS AND DISCUSSION

Wear and Friction of 52100 Steel Balls with Polyol Esters

Wear test data on the 52100 steel balls are shown in Table 2 and Figs. 1 to 3. The results are of interest per se and as a basis for comparison with the data that will follow. Figures 1 and 2 show the effect of load and of ester type on wear. In Fig. 2, 1% TCP was present. The Hertz line shows the initial diameter of the contact area between balls due to elastic deformation under each applied load. The corresponding contact stresses varied from 165,000 psi at a 5-kg load to 356,000 psi at a 50-kg load as shown in Table 3. (Stresses applied in gyro bearing technology correspond to less than a 10-kg load.) The wear results fall on straight lines in the log-log plots. Hence, the relation between wear and load is in the form of a power function. For example, the equations for TMP 8.8 in Figs. 1 and 2 are $d = 0.22\ L^{0.28}$ and $d = 0.090\ L^{0.51}$, respectively, where d is the wear-scar diameter in millimeters and L is the load in kilograms. Furthermore, the plots tend to parallel the Hertz line (in the absence of TCP).

Table 2
Summary of Wear-Scar Data With 52100 Steel Balls

Sample	Diameter of Wear Scar at Various Loads (mm)			
	5 kg	10 kg	20 kg	50 kg
Sebacate	0.381	0.433	0.620	0.872
Sebacate + 1% TCP	0.236	0.387	0.590	0.953
DPE 6.3	0.353	0.495	0.640	0.785
DPE 6.3 + 1% TCP	0.279	0.427	0.520	0.825
TMP 8.8	0.345	0.426	0.525	0.641
TMP 8.8 + 1% TCP	0.204	0.286	0.487	0.653
PE 6.1	0.434	0.586	0.656	0.819
PE 6.1 + 1% TCP	0.272	0.360	0.635	0.915

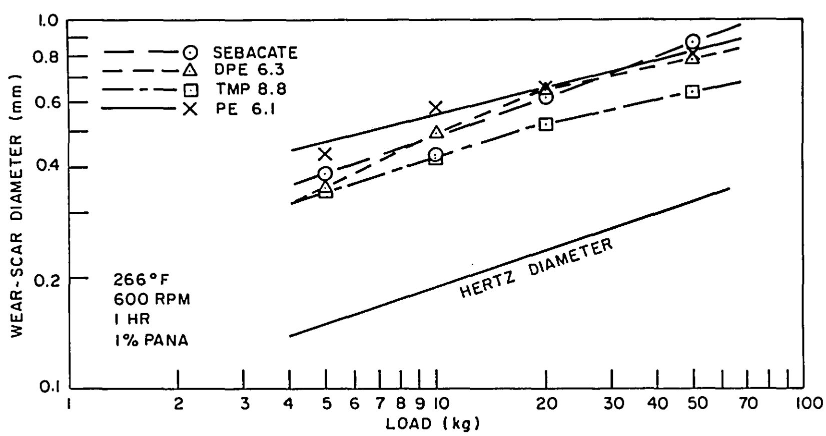


Fig. 1 - Results of four-ball wear tests on neopentyl polyol esters and a diester with no TCP present using 52100 steel balls

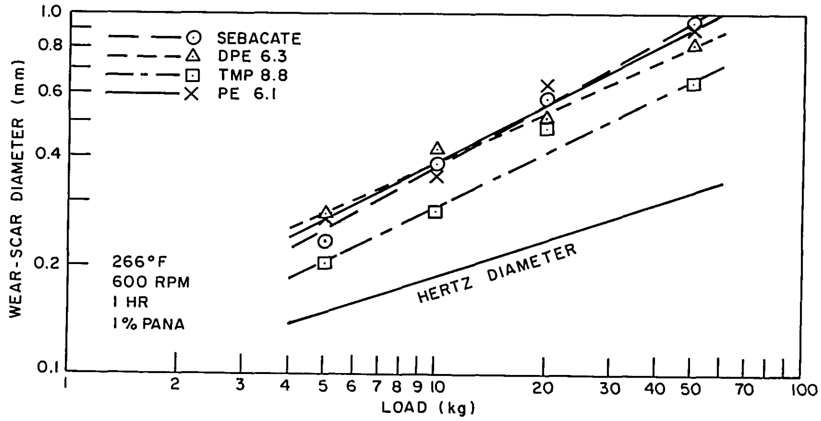


Fig. 2 - Results of four-ball wear tests on neopentyl polyol esters and a diester with 1% percolated TCP added using 52100 steel balls

Wear differences between esters were relatively small and not significant with the possible exception of TMP 8.8, the trimethylolpropane ester. This ester gave somewhat less wear than the others, but the difference may not be significant. This means that ester structure had little or no effect on wear in these tests and that there was no viscosity effect. If there were a viscosity effect, at low load at least, the more viscous DPE 6.3 should show the least wear and sebacate the most. Such was not the case. The absence of a viscosity effect is not inconsistent with Clinton's results (19) in view of the difference in load ranges. Additional tests were conducted which might reveal the presence of a hydrodynamic component of friction or wear. The speed was varied between 50 and 1500 rpm using low and high load. A reduction in the friction coefficient at low load or high speed would have pointed to a hydrodynamic effect. Instead, friction was independent of speed and load.

In Fig. 3, the above wear-scar data are replotted to show directly the effect of the percolated TCP. Table 4 shows the averaged results in tabular form. It is apparent that TCP reduced the wear somewhat at low loads but was ineffective at high loads. There was a crossover point at loads of about 35 kg. This effect is in accord with general experience with conventional lubricants (19,20). Klaus distinguished between this kind of antiwear effect by TCP and the corresponding wear curves for conventional EP agents on the one hand and mild EP agents on the other hand. The lack of any wear reduction at 50 kg has been explained previously as a desorption of TCP or its reaction products due to the increased temperature at asperity contacts. Or perhaps TCP forms a protective film of some sort on the metal, but at high loads the greater wear rate destroys it as fast as it forms.

The data show then that wear rates with polyol esters were about the same as with conventional lubricants, such as diesters and mineral oils. Thus, the type of wear mechanism, under the conditions studied, must have been the same in all cases. Where comparison with the literature was possible, agreement was good (6). Reproducibility of the wear data averaged ±5%.

Friction measurement has been considered less satisfactory than wear measurement with the four-ball machine. Indeed, friction measurements here showed somewhat more variability and less reproducibility than the wear data. Nevertheless, with the enhanced sensitivity and the dynamic observation achieved in this study, the friction results merit attention. They afford valuable clues to the mechanism of wear, because as a group the

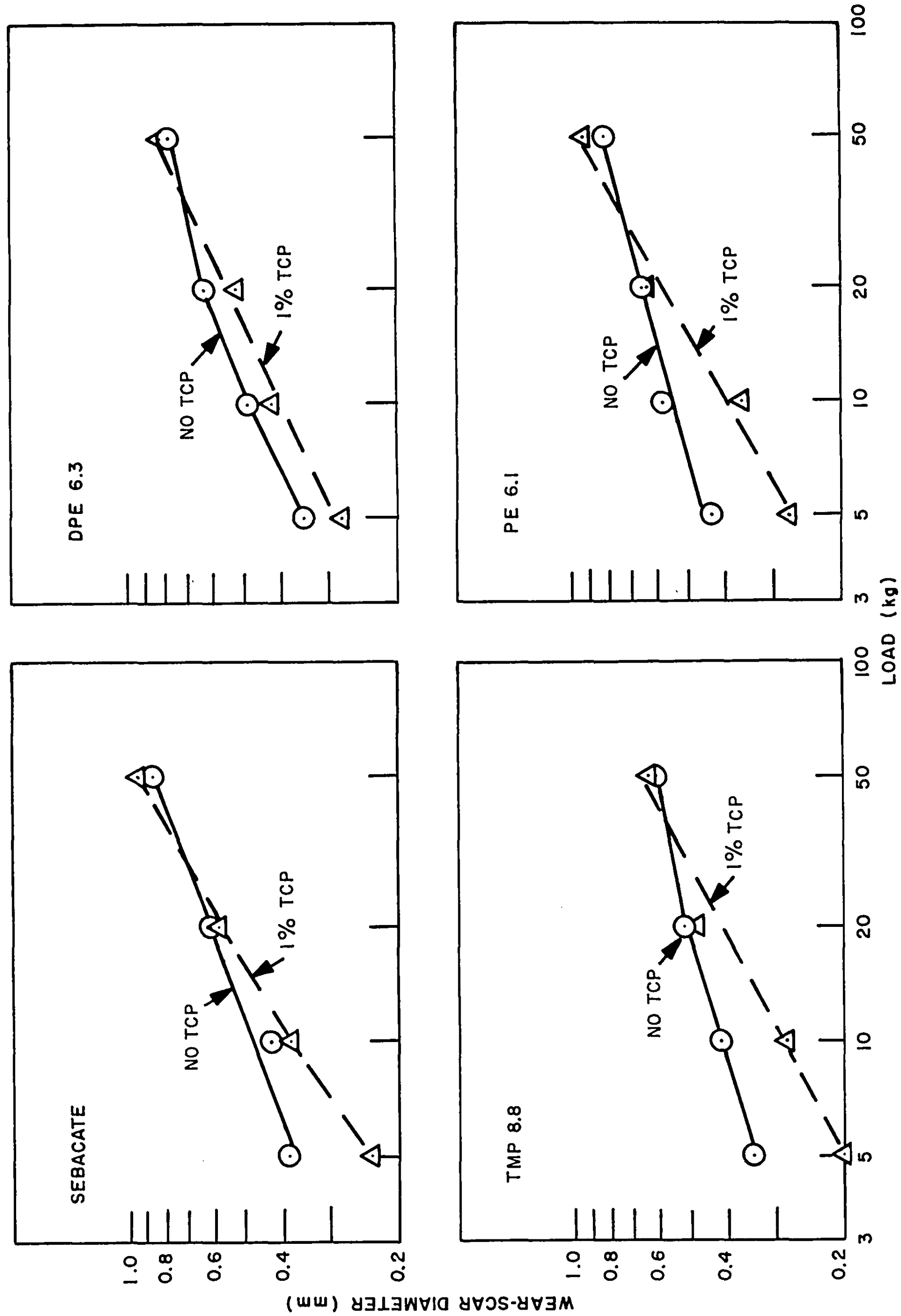


Fig. 3 - Comparison between wear rates with and without 1% TCP using 52100 steel balls. The test conditions are 266°F, 600 rpm for 1 hr, using 1% PANA.

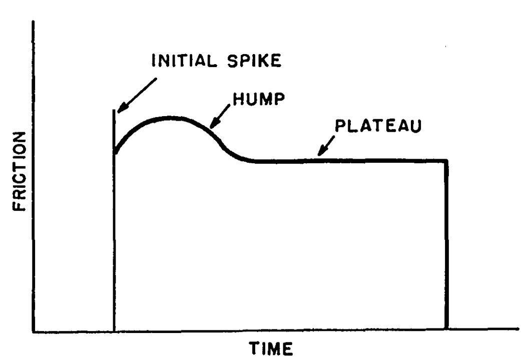
Table 3
Hertz Diameters and Pressures for
1/2-in.-Diameter Steel Balls

Load (kg)	Hertz Diameter (mm)	Hertz Stress	
		Kg/cm^2	Psi
5	0.150	11,600	165,000
10	0.189	14,600	208,000
20	0.238	18,500	262,000
50	0.323	25,100	356,000

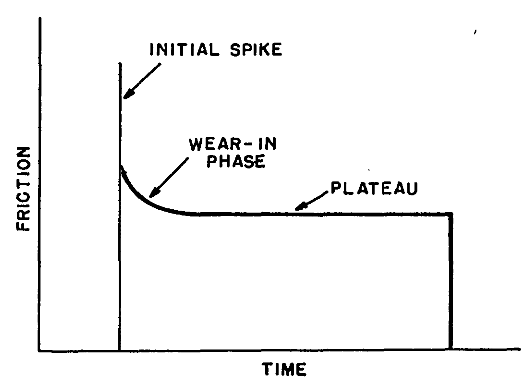
Table 4
Effect of 1% TCP with 52100 Steel Balls

Load (kg)	Average Reduction in Wear-Scar Diameter (%)
5	34
10	22
20	9
50	7 (increase)

friction data fell into a definite pattern. The general features of typical friction-vs-time traces are represented in Fig. 4a. The traces were usually divisible into three periods: a starting period extending to 30 seconds or less, the "hump" or "wear-in" period comprising the rest of the first 15 to 20 min of the run, and the "plateau" phase (20 to 60 min), where friction was essentially constant and at a lower level than the hump. The initial spike was not always present. The start and wear-in phases showed more variability than the plateau phase. The distinctive wear-in phase is noteworthy. It indicates that the metal surface film and the mechanism of wear underwent progressive changes before stabilizing. Wear-scar-diameter-vs-time curves, on the other hand, showed no similar wear-in effect (Fig. 5). However, the effect would be more difficult to observe in this case, because the plotted points represent integrated rather than instantaneous values. Occasional spikes or other irregularities or fine structure in the friction traces suggested further insights into the wear process.



(a) 52100 steel



(b) 440C stainless steel

Fig. 4 - Typical friction-vs-time curves showing only general features

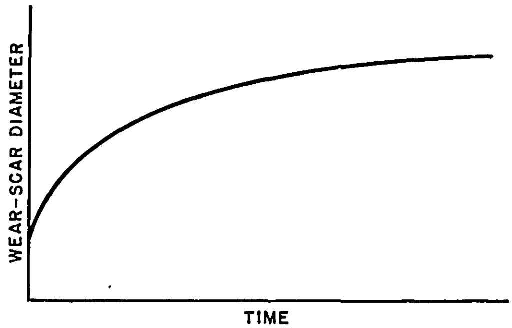


Fig. 5 - Typical plot of wear-scar diameter vs time (rectangular coordinates). (The corresponding log-log plot is a straight line.)

Friction coefficients are shown in Table 5 and Figs. 6 and 7. Average plateau values are suitable for comparative purposes. Due to the greater variability of the start and wear-in phases, it was obvious that comparisons based on initial friction or friction at any particular time during the first 20 min would have little reliability. This may explain some of the poor friction reproducibility noted by previous workers. In Figs. 6 and 7 the average coefficient of friction (plateau phase) is plotted against load on log-log coordinates. The coefficient varied from 0.04 to 0.12. Friction appeared to be largely independent of ester type and of TCP. The relatively small differences noted between esters can be attributed partly to experimental variation. The PE 6.1 and DPE 6.3 oils generally gave slightly higher friction than TMP 8.8 and sebacate. Thus, no obvious correlation existed between friction and viscosity; a 4:1 range of viscosity apparently had no effect. TCP appeared to have no effect on friction levels, but the data showed less scatter in its presence. It is established that phosphorous compounds lower wear but not friction, and the present data are in agreement (12,21). The moderate decline in friction at loads below 20 kg is suggestive of a hydrodynamic effect, but the wear results did not seem to confirm this. Also, on the basis of past experience at NRL (22), no hydrodynamic effect above a 2.5-kg load was anticipated.

Table 5
Summary of Friction Data With 52100 Steel Balls

Sample	Coefficient of Friction μ_k for Various Loads							
	5-kg		10 kg		20 kg		50 kg	
	Hump	Plateau	Hump	Plateau	Hump	Plateau	Hump	Plateau
Sebacate	0.090	0.036	0.099	0.065	0.127	0.094	0.111	0.091
Sebacate + 1% TCP	0.102	0.052	0.198	0.099	0.125	0.090	0.125	0.109
DPE 6.3	0.130	0.065	0.104	0.075	0.135	0.123	0.136	0.105
DPE 6.3 + 1% TCP	0.137	0.094	0.141	0.083	0.124	0.086	0.104	0.106
TMP 8.8	0.080	0.047	0.099	0.066	0.109	0.085	0.094	0.078
TMP 8.8 + 1% TCP	0.080	0.052	0.127	0.068	0.123	0.097	0.102	0.091
PE 6.1	0.151	0.062	0.137	0.104	0.130	0.106	0.132	0.097
PE 6.1 + 1% TCP	0.104	0.057	0.116	0.076	0.153	0.097	0.123	0.106

Wear and Friction of 440C Stainless-Steel Balls

Data on wear-scar diameters with 440C stainless-steel balls are shown in Table 6 and Figs. 8 through 12. The total range of scar diameters was 0.3 to 2.3 mm. The results are shown as a function of load and ester type in Fig. 8 in the absence of TCP

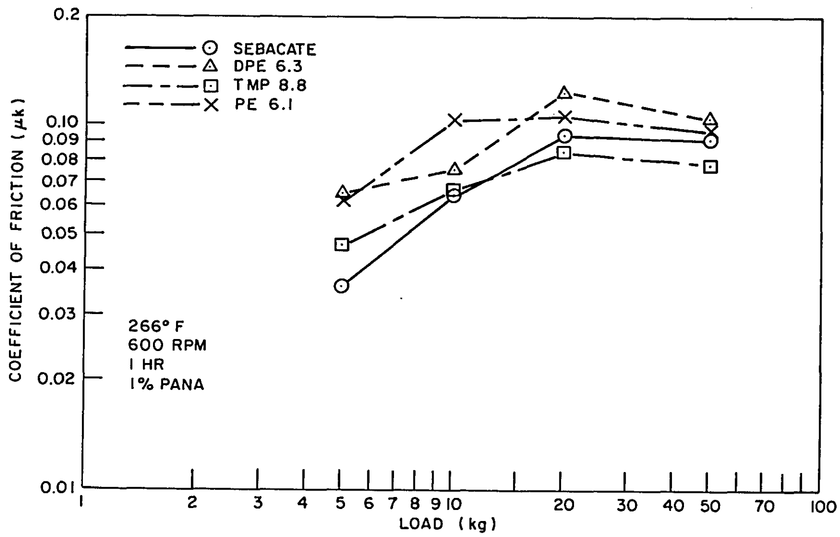


Fig. 6 - Coefficient of friction ("plateau" phase) of 52100 steel with polyol esters and a diester containing no TCP

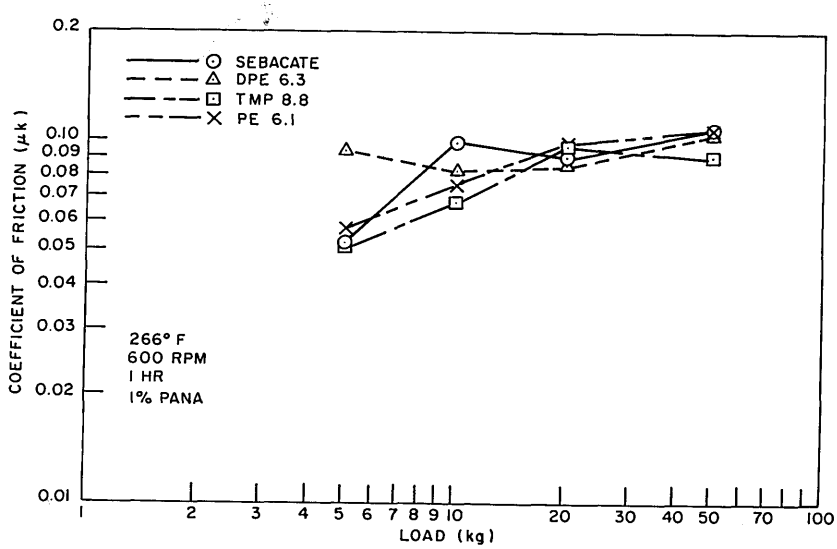


Fig. 7 - Coefficient of friction ("plateau" phase) of 52100 steel with esters containing 1% percolated TCP

Table 6
Summary of Wear-Scar Data with 440C Stainless-Steel Balls

Sample	Diameter of Wear Scars at Various Loads (mm)			
	5 kg	10 kg	20 kg	50 kg
Sebacate	0.261	0.406	0.575	1.51
Sebacate + 1% TCP	0.396	0.478	0.546	1.28
DPE 6.3	0.347	0.555	0.674	1.84 (2.74)*
DPE 6.3 + 1% TCP	0.320	0.511	0.698 (0.840)*	2.33 (3.46)*
TMP 8.8	0.396	0.474	0.820	1.76
TMP 8.8 + 1% TCP	0.373	0.469	0.609	1.39
PE 6.1	0.398	0.491	0.767	1.87 (2.24)*
PE 6.1 + 1% TCP	0.386	0.577	0.805	1.97 (2.04)*
Four esters as a group, no TCP	0.35-0.40	0.41-0.56	0.52-0.82	1.51-1.84
Four esters as a group, 1% TCP	0.32-0.40	0.47-0.58	0.55-0.81	1.28-2.33

*Long axis only of elongated scars.

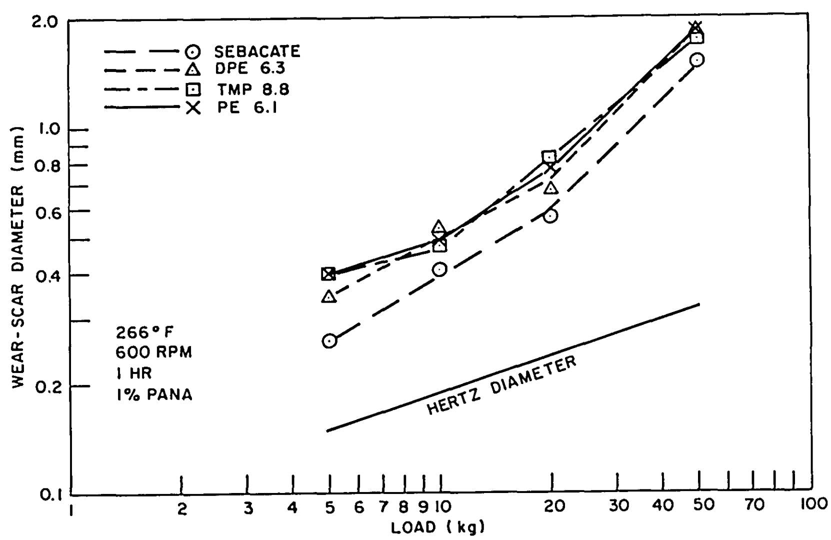


Fig. 8 - Wear rates of 440C stainless-steel balls with polyol esters and a diester in the absence of TCP

and in Fig. 9 in the presence of 1% TCP. As with 52100 balls, the differences between esters were for the most part relatively small and largely attributable to experimental uncertainty, particularly when no TCP was present. The sebacate gave somewhat less wear at all loads. However, this effect possibly was not significant. The load had more effect here than in the case of 52100 balls. The plots were no longer linear and parallel to the Hertz line. There was a sharp upward break in the curves around 20 kg, and the wear values at 50 kg were markedly greater. (The log plot tends to minimize this.) Friction showed no similar break (see below).

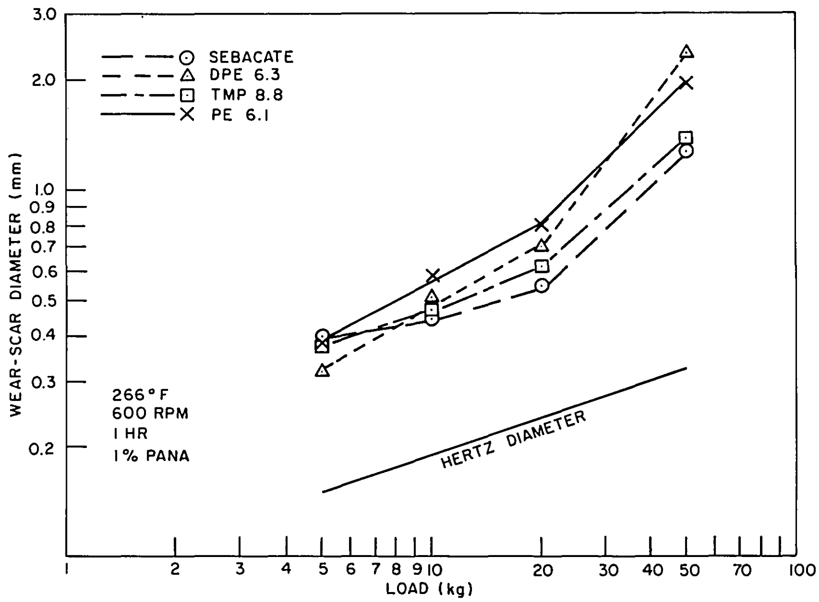


Fig. 9 - Wear rates of 440C stainless-steel balls with polyol esters and a diester in the presence of 1% TCP

Figure 9 showing the wear scars with 1% TCP present is essentially the same as Fig. 8. It was not established that the differences between esters were significant. The effect of TCP is shown directly in Fig. 10 by replotting the data. In contrast to the 52100 results, TCP (percolated) was ineffective in reducing wear at the lower loads in all cases. Differences between each pair of points were not only small, but they were not "ordered," unlike the comparable results with 52100 balls. Thus, TCP (percolated) had no significant effect in any case. In other words, stainless-steel surfaces showed no response to TCP. This may indicate that the chemical and physical activity of the stainless-steel surface was low compared to 52100, and the formation of a protective layer did not occur. It is now generally agreed that the wear-reducing action of phosphate esters is due to the formation of a film of iron phosphates or a mixture of metal phosphates and metal-organic phosphates (12-14). Perhaps high chromium content prevented formation of a satisfactory film. The passivation treatment could be significant here, but since even a slight amount of wear would penetrate the passive layer, it was assumed not to be a factor. Variation in response to TCP between different lubricants is well established (20). These variations are attributed to preferential adsorption of compounds more polar than TCP, possibly traces of acid phosphates (13,23).

Again replotting in Figs. 11 and 12, stainless-steel balls are compared with 52100 balls, first, without TCP and second with TCP. The break at 20 kg and the greatly increased wear of 440C at 50 kg are clearly evident. The increase averaged 127% without TCP and 111% with TCP. At 5 to 20-kg load, wear with stainless steel was essentially the same as with 52100 steel in the absence of TCP and about 1/3 greater in the presence of TCP. The latter reflects the fact that TCP reduced the wear of 52100 balls at the lower loads but not that of the 440C balls.

Reproducibility of the wear data averaged 6 to 12% at the lower loads. At 50 kg reproducibility was poor. The latter is characteristic of transition zones, as noted below.

Friction results were similar to those with 52100 steel. However, the typical overall shape of the friction-vs-time trace was somewhat different (Fig. 4b). The initial spike was relatively much greater than with 52100 steel or up to five times the subsequent

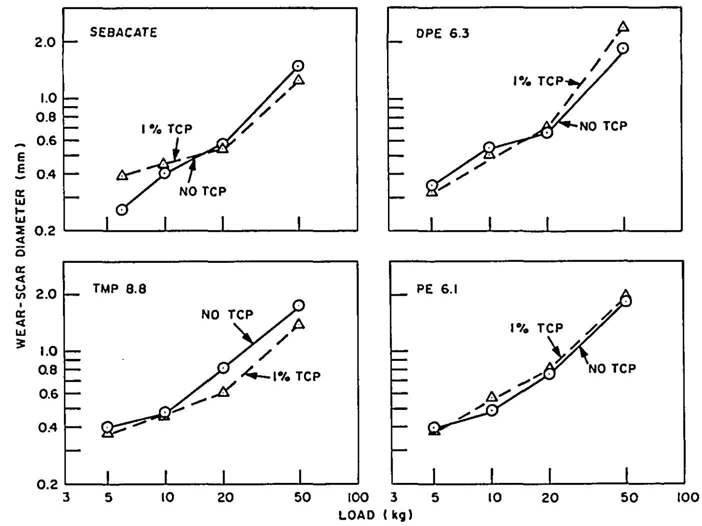


Fig. 10 - Comparison of wear rates of 440C stainless-steel balls with and without 1 % TCP. The test conditions are 266°F, 600 rpm for 1 hr, using 1% PANA.

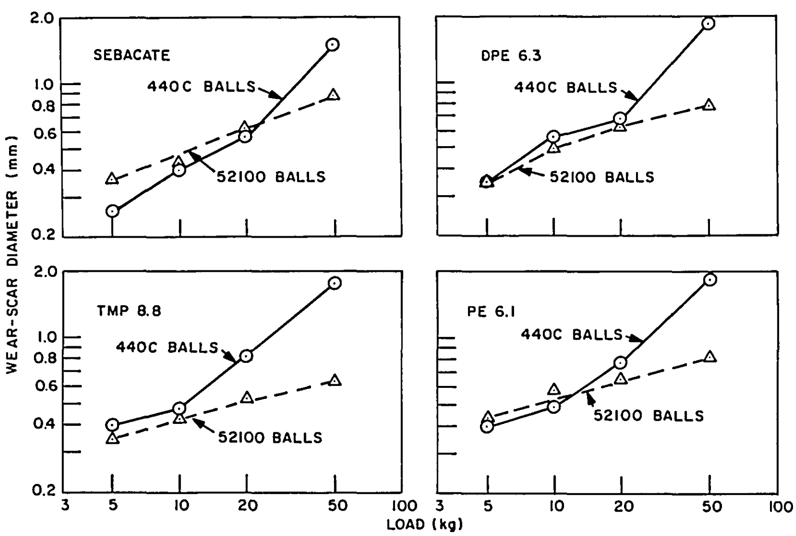


Fig. 11 - Comparison of wear rates of 52100 balls and 440C balls in the absence of TCP. The test conditions are 266°F, 600 rpm for 1 hr, using 1% PANA.

steady friction. It increased with load. These "hard starts" indicated greater initial adhesion of 440C steel. The wear-in phase, as compared to 52100 steel, was less prominent or missing altogether. The initial peak cannot be considered the static friction, inasmuch as there always was a distinct hesitation of a few seconds or less at about the plateau level during the rise to the peak. The ratio of the initial friction peak to the kinetic or steady friction (at given loads) may be a characteristic of the particular metal surfaces. This ratio was an indicator of initial adhesion. It increased with load, as might be expected. Occasionally, other transient rises in friction occurred. These have also been observed by others and called seizures with recovery (19,20). The friction data are presented in Table 7 and Figs. 13 to 17. The discussion will be in terms of the average plateau coefficient. The plotted points in Figs. 13 and 14 as a group show excellent consistency for friction data. A few deviant points at 5 kg are not significant. Values of the friction coefficient with 440C balls were essentially the same as with 52100 balls, varying from 0.07 to 0.12. Again friction generally increased slightly with load with most of the increase occurring between 5 and 10 kg. Friction was not significantly affected by the other variables, namely, ester type, ball alloy, presence of TCP, severe wear, and presence of appreciable metal wear particles. There was no correlation between friction and wear.

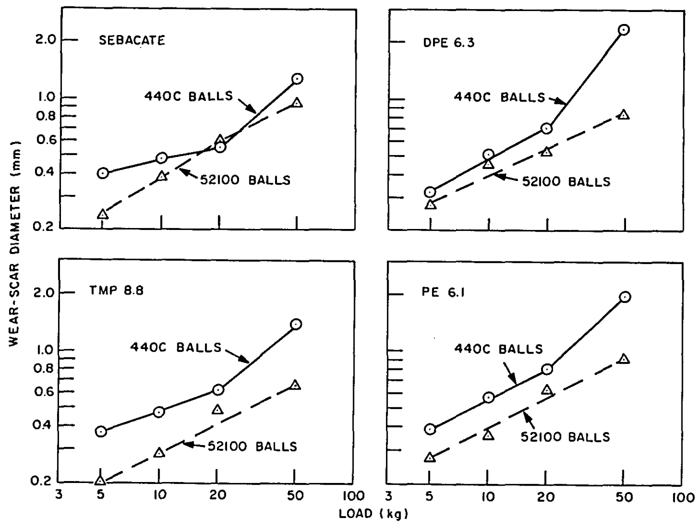


Fig. 12 - Comparison of wear rates of 52100 balls and 440C balls with 1% TCP present. The test conditions are 266°F, 600 rpm for 1 hr, using 1% PANA.

Table 7
Summary of Friction Measurements with 440C Stainless-Steel Balls

Sample	Coefficient of Friction μ_k at Various Loads							
	5 kg		10 kg		20 kg		50 kg	
	Hump	Plateau	Hump	Plateau	Hump	Plateau	Hump	Plateau
Sebacate	0.094	0.047	0.137	0.090	0.116	0.090	0.128	0.106
Sebacate + 1% TCP	0.062	0.080	0.113	0.078	0.106	0.085	0.113	0.104
DPE 6.3	-	0.128	0.090	0.071	0.144	0.106	0.132	0.122
DPE 6.3 + 1% TCP	0.057	0.057	0.123	0.083	0.118	0.109	0.33	0.130
TMP 8.8	0.142	0.052	0.094	0.087	0.097	0.074	0.189	0.106
TMP 8.8 + 1% TCP	0.142	0.038	0.142	0.111	0.128	0.089	0.109	0.119
PE 6.1	0.227	0.118	0.156	0.094	0.125	0.111	0.321	0.118
PE 6.1 + 1% TCP	0.094	0.066	0.094	0.094	0.132	0.109	0.047	0.113
Four esters as a group	0.094-0.227	0.038-0.118	0.083-0.156	0.054-0.090	0.087-0.125	0.074-0.111	0.128-0.38	0.106-0.163
Four esters as a group + 1% TCP	0.057-0.142	0.038-0.080	0.094-0.142	0.078-0.111	0.106-0.132	0.085-0.109	0.047-0.33	0.104-0.130

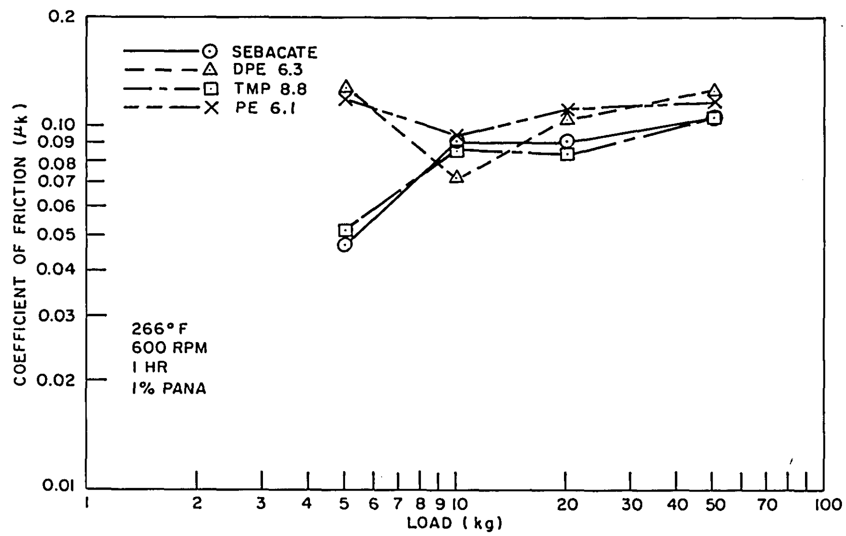


Fig. 13 - Effect of ester type and load on friction coefficients (plateau phase) in four-ball tests using 440C stainless-steel balls with no TCP present

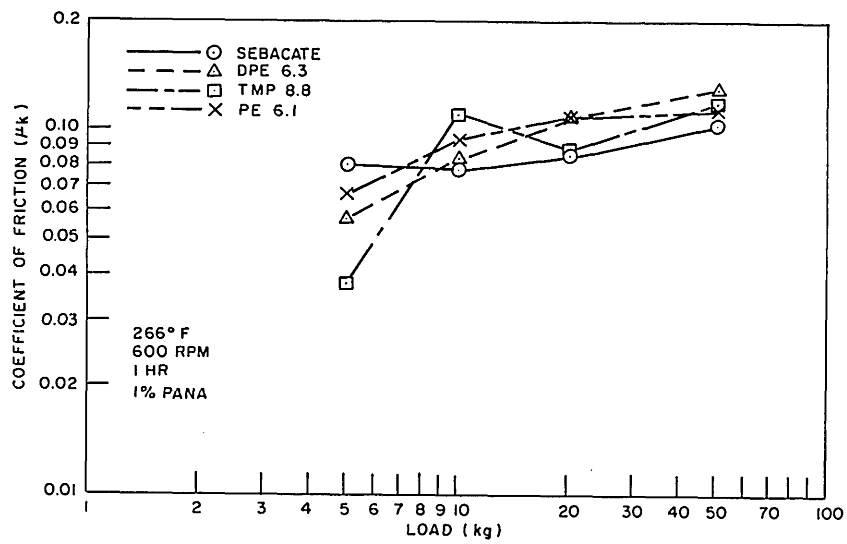


Fig. 14 - Friction coefficients (plateau phase) of esters for 440C stainless-steel balls with 1% TCP added

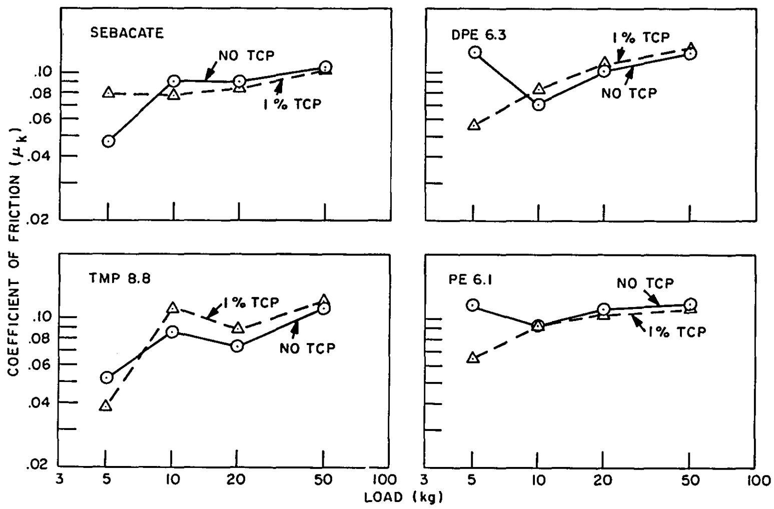


Fig. 15 - Effect of 1% TCP on coefficient of friction (plateau phase) with 440C stainless-steel balls. The test conditions are 266°F, 600 rpm for 1 hr, using 1% PANA.

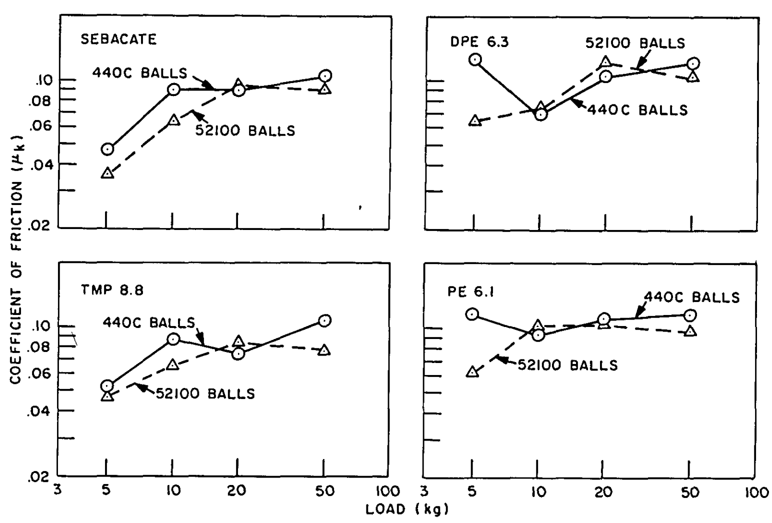


Fig. 16 - Comparison of friction coefficients (plateau values) of 52100 steel balls vs 440C stainless-steel balls with no TCP present. The test conditions are 266°F, 600 rpm for 1 hr, using 1% PANA.

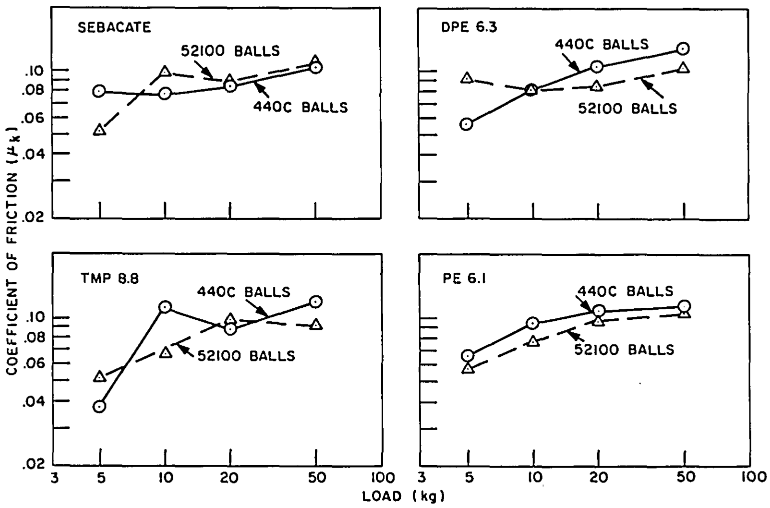


Fig. 17 - Comparison of friction coefficients (plateau phase) of 52100 steel balls vs 440C stainless-steel balls with 1% TCP added. The test conditions are 266°F, 600 rpm for 1 hr, using 1% PANA.

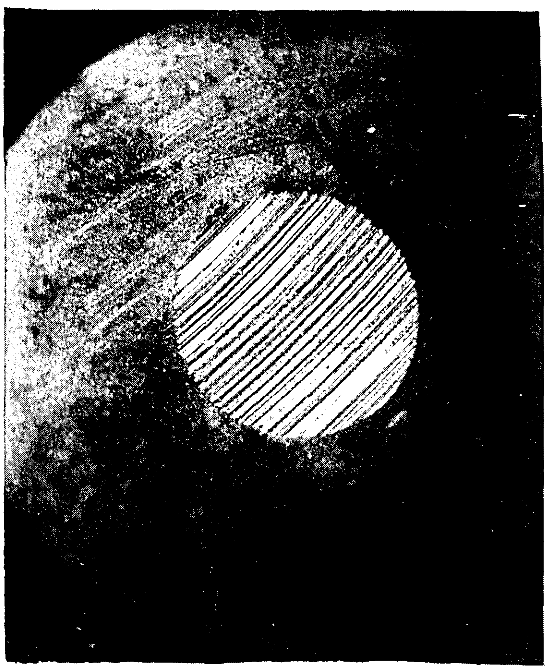


Fig. 18 - Typical wear scar on stationary balls of 52100 steel. Experimental conditions: sample DPE 6.3, 50-kg load, 1% TCP. The original magnification was 50X. Scar diameter was 0.82 mm.

Stainless steel 440C also differed markedly from 52100 steel in the appearance of the wear scars. This was true at all loads. The latter alloy typically gave neat, sharply defined circular scars with an interior structure of fine parallel striations under all conditions; Fig. 18 is an example. With 440C balls, on the other hand, scars were not round and varied considerably in appearance. The variety of shapes is illustrated by the sketches in Fig. 19 and the photomicrographs in Fig. 20. Scars were more or less oval or rectangular, sometimes elongated, often irregular in boundary and not sharply defined. The interior consisted of a relatively small number of smooth, wide, deep grooves, often, at low load, looking like a loose bundle. Sometimes the scar had an envelope and sometimes

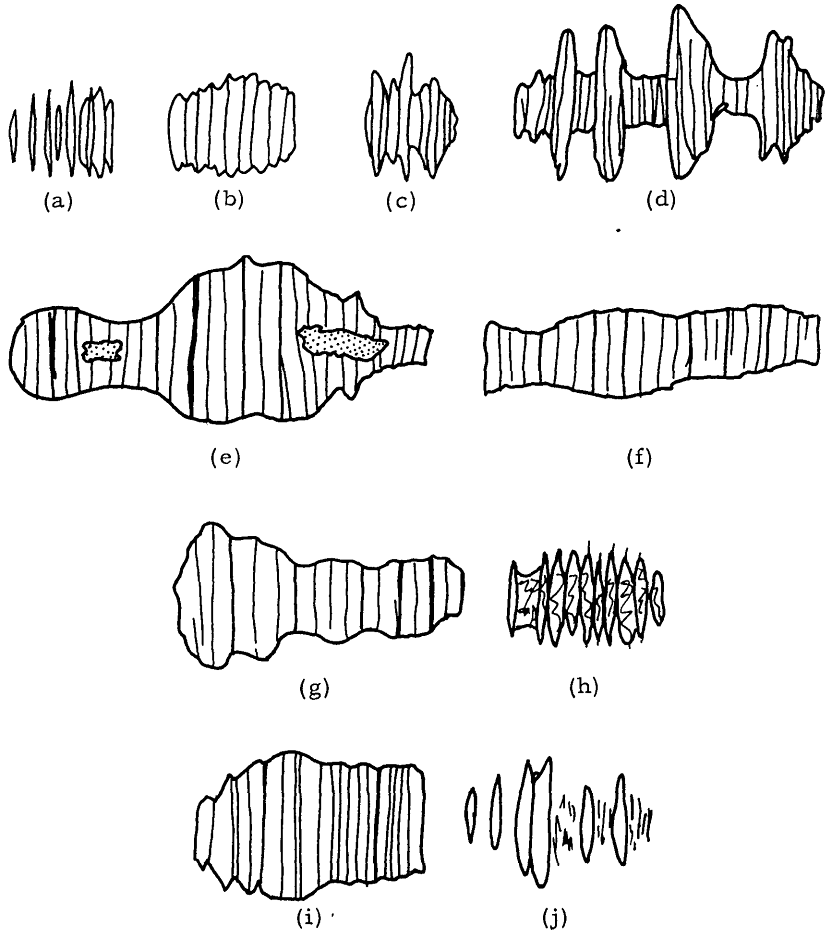
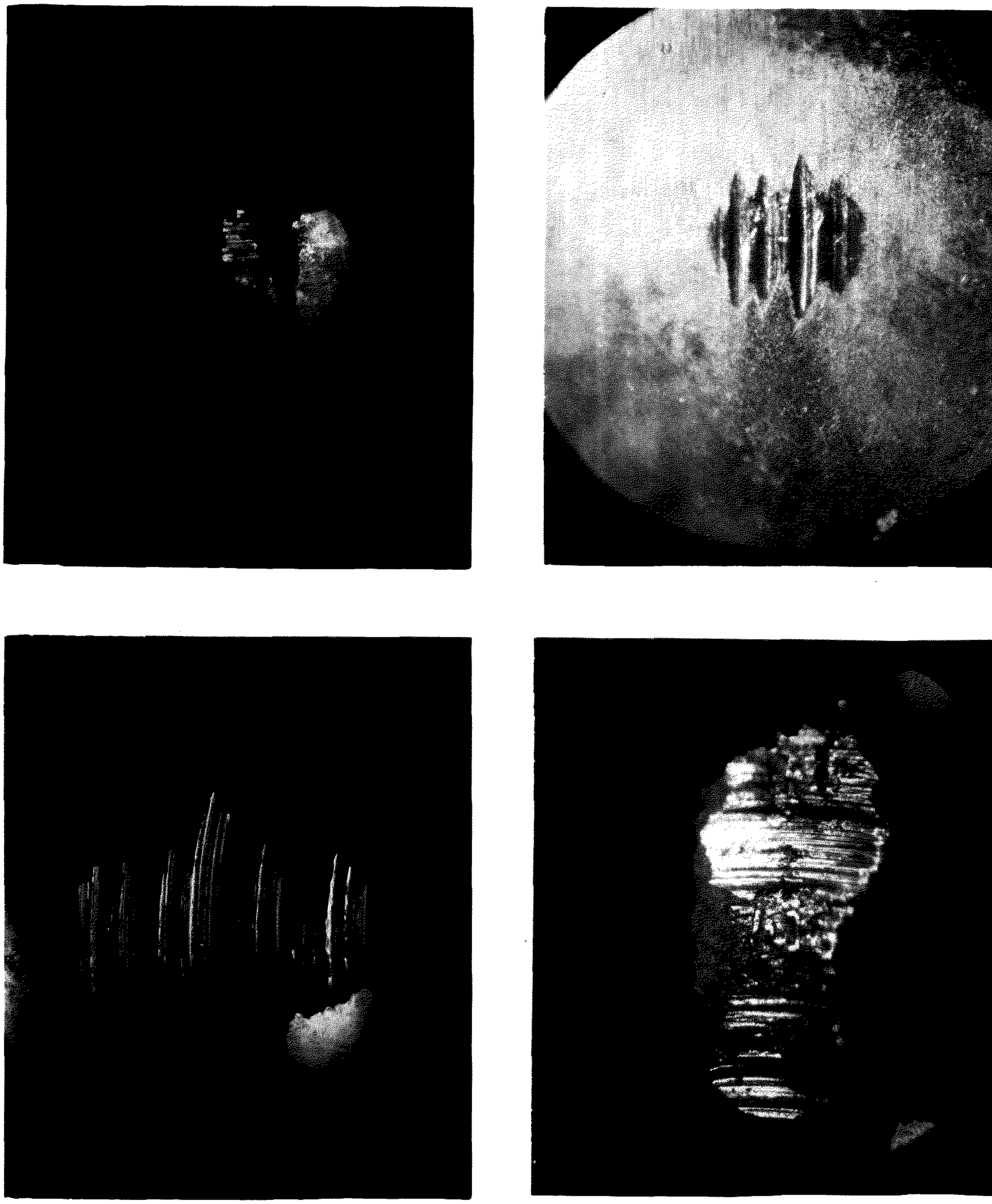


Fig. 19 - Sketches of wear scars formed on 440C stainless-steel lower balls showing the variety of scar shape with and without 1% TCP: (a) DPE 6-3 under a 5-kg load with TCP present, (b) DPE 6.3 under a 20-kg load, (c) PE 6.1 under a 10-kg load with 1% TCP present, (d) DPE 6.3 under a 20-kg load, (e) DPE 6.3 under a 50-kg load with 1% TCP present, (f) DPE 6.3 under a 50-kg load, (g) PE 6.1 under a 50-kg load, (h) sebacate under a 5-kg load, (i) TMP 8.8 under a 50-kg load with 1% TCP present, and (j) sebacate under a 20-kg load with 1% TCP present.

there was none. Sometimes fine striations and irregular granular areas appeared between or superimposed on the grooves. The latter were probably areas of adhesion. In some cases they were identified as pits, which indicated severe adhesion and welding. The large grooves had a polished look; this appearance was independent of the presence of TCP. It was obvious that the mechanism of wear differed from that of 52100 steel at all loads and was not a desirable type. The worst scars occurred at 50 kg with DPE 6.3 and with TCP present. TMP 8.8 gave the scars with the "best" appearance. However, due to the reduced reproducibility at 50 kg, the significance of these observations may be limited.

With PE 6.1 and DPE 6.3 at a 50-kg load and to some extent at 20 kg, there was high wear of the rotating ball with accumulation of a large amount of metal particles in the oil in the sample cup. These had a wide range of particle size including some slivers up to 1/8 in. long. TCP gave little or no improvement. In the most extreme case the top ball came out with a profile as shown in Fig. 21. Thus, in these cases the rotating



(c) (d)

Fig. 20 - Wear scars on 440C stainless-steel balls: (a) PE 6.1 under a 20-kg load with 1% TCP. The original magnification was 25X, (b) DPE 6.3 under a 20-kg load with no TCP. The original magnification was 50X, (c) PE 6.1 under a 50-kg load with 1% TCP. The original magnification was 25X, (d) DPE 6.3 under a 50-kg load with 1% TCP. The original magnification was 25X.

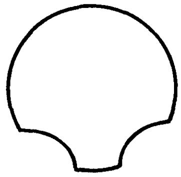


Fig. 21 - Profile view of rotating top ball showing extreme wear obtained with PE 6.1 and DPE 6.3 at a 50-kg load using stainless-steel balls, with or without TCP

ball wore at a much greater volume rate than the stationary balls. There was little correlation between the two wear rates. The significance of the accelerated wear of the rotating ball is not clear. Possibly wear particles of sufficient size or amount caused the superposition of a self-accelerating or avalanche-effect abrasive wear process. If so, the wear situation would be unstable, and poor reproducibility would be expected (as found); hence, a shorter test duration might be more useful.

A similar example of extreme wear of the rotating ball occurred in a previous investigation by the Shell Development Co. when certain phosphorous esters were tested neat in the four-ball EP machine to determine the weld load (24). It was explained by postulating that the decomposition products of the organophosphorous compounds, released by the high temperature of the rubbed surfaces of the balls, severely attacked the steel, forming a phosphorous film which prevented welding but produced excessive wear. Except for the same end result, the present situation is not comparable as to operating conditions and is different in other respects, notably the absence of corrosiveness away from the area of contact and occurrence of the rapid wear in the absence of TCP. Hence, the foregoing mechanism involving corrosive wear by phosphates is not applicable.

It is obvious from the experiments described that boundary lubrication of 440C stainless steel is more difficult than that of 52100 steel and that PE 6.1 and DPE 6.3 appeared to make especially poor combinations with 440C. While wear rates with 440C were about the same as for 52100 steel at 20 kg and below (in the absence of TCP at least), the kind of wear was different and apparently unfavorable, and the load-carrying capacity was reduced. The moderate wear-reducing effect of TCP at low loads with 52100 steel was absent with stainless-steel balls. The importance of adhesion and seizures in the friction and wear of 440C steel, especially at high load, was revealed by the appearance of the wear scars and by transients in the friction traces. The 50-kg test results reflected a transition to a region of rapid, destructive wear which would not be tolerated in practical machines.

The idea of a transition from a mild to a severe type of wear at some point with increased load or other variable is amply illustrated in the literature of wear testing (25-28). According to one viewpoint (29), it takes place when the load or contact stress exceeds 1/3 the indentation hardness of the metal. With 440C steel at 50 kg, the initial contact stress was just under the 1/3 point. Elsewhere the transition point is taken as the point where seizure takes place. In the four-ball EP machine, as distinguished from the four-ball wear machine, this point is quite obvious when wear is plotted against load. There is a sharp upward discontinuity at the "seizure load." At loads above this point stable wear again occurs but at a higher level. An established feature of transition zones in wear regime is poor reproducibility of the wear scars (21,22,27,30). In other words, a rapid increase in wear occurs over a small change in load (or other variable). The present work bore this out—a 50-kg load on 440C steel was in a transition region between low and high wear regimes. The mild-type wear is said to take place by plowing (abrasion) combined with microadhesion, and the scars are quite regular and look like those obtained here with 52100 steel. In the severe type, wear takes place by macroadhesions, and the scars become somewhat irregular and smeared. It is not clear how well the latter picture fits the present results (440C at 50 kg). The irregularity of scar shape was perhaps greater than would be expected for mild wear, but wear still involved plowing or grooving; adhesions and seizures were superimposed.

Effect of TCP Polar Impurities

The effect of unpercolated TCP was studied in connection with the Navy gyro bearing program. The antiwear activity of commercial TCP has been ascribed to trace impurities, presumably acidic substances such as acid organic phosphates (12-14). Furthermore, percolation is said to remove the active factors. Thus, following the absence of wear reduction with the percolated TCP using stainless-steel balls, an unpercolated sample which had given good results in the 1-rpm gyro test at M.I.T. and was said to contain the "active factor" was tried (30). This was added to two of the esters and compared with percolated TCP at 20 and 50 kg loads. Preliminary results are shown in Table 8. The use of a 3% additive in addition to 1% was merely a further attempt to detect the expected effect rather than a comparison of concentrations. At a 20-kg load it is seen that there were essentially no significant differences. At 50 kg possible differences were obscured by the poor reproducibility and irregular shape of wear scars in a transition zone. Friction was unaffected. On the other hand, the appearance of the wear scars was improved in at least 2/3 of the cases. These tended to be rounder and look more like the good scars obtained with 52100 steel balls. This observation may be significant and indicate a change in the mechanism if not the rate of wear.

Table 8
Effect of Unpercolated TCP on Wear and Friction of 440C Balls

TCP Additive*	Dia. of Wear Scar at Two Loads (mm)		Coeff. of Friction at Two Loads	
	20 kg	50 kg	20 kg	50 kg
DPE 6.3				
none	0.601 0.674	1.14 1.84	0.106 0.080	0.122 0.163
1% P	0.698	2.33	0.109	0.130
1% U	0.708	1.28	0.095	0.120
3% U	0.482	0.83 0.99	0.113	0.108 0.111
Sebacate				
none	0.516	1.51	0.087	0.106
1% P	0.546	1.28	0.085	0.104
1% U	0.481	0.94	0.092	0.105
3% U	0.503	1.50	0.094	0.099

*P = percolated; U = unpercolated (Barden)

Another group of wear tests using 52100 balls was carried out (Table 9 and Fig. 22). The additive in this case was not from the gyro program. The data show that nonpercolation appeared to reduce the wear by small amounts at 5 kg and not at all at 50 kg. Hence, the results at 50 kg agree with the conclusion above and should be more reliable due to absence of severe wear.

It must be concluded that the foregoing experiments failed to confirm a substantial difference in wear and friction behavior between percolated and unpercolated TCP. At a 5-kg load a small improvement due to nonpercolation was indicated. In contrast to these

Table 9
Effect of Unpercolated TCP on Wear of 52100 Steel Balls
Lubricated with PE 6.1

TCP Additive	Temp (°F)	Dia. of Wear Scar at Two Loads (mm)	
		5 kg	50 kg
Percolated	140	0.396	0.893
Unpercolated	140	0.294	0.848
Percolated	392	0.284	0.920
Unpercolated	392	0.250	0.947

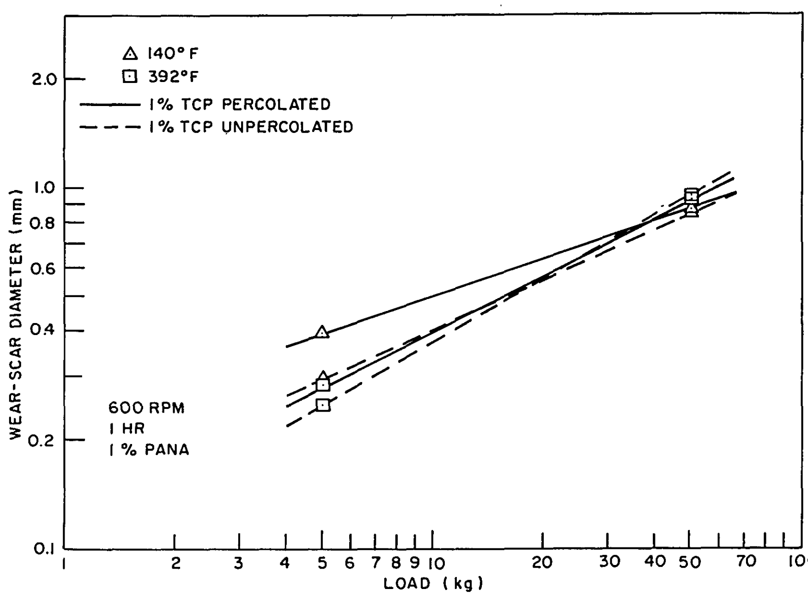


Fig. 22 - Effect of nonpercolation of TCP additive using 52100 steel balls in PE 6.1 at 140°F and 392°F

results, bearing life, as defined in the M.I.T. gyro bearing test, was over 200 hr, with a TCP corresponding to unpercolated TCP and less than 1 hr with a TCP not containing the "active factor." Thus, in the four-ball tests a very large or qualitative difference was sought, but none was found. Perhaps the discrepancy is not surprising in view of the many points of non-comparability between the NRL four-ball tests and the M.I.T. gyro bearing tests. To elucidate the M.I.T. results, further work on TCP would be required, possibly involving the addition of known amounts of polar hydrolysis products, such as hydrogen dicresyl phosphate.

SUMMARY AND CONCLUSIONS

Using type 52100 steel balls in a four-ball wear machine, basic friction and wear data were obtained on a representative of each of the three classes of neopentyl polyol esters of commercial interest. Generally there was little or no difference between the wear behavior of different polyol ester types. In addition there was no significant difference between the polyol esters and a conventional diester lubricant. TCP reduced the wear moderately at the lower loads but not at the higher loads. This behavior was in agreement with that of TCP in conventional petroleum lubricants.

Similar friction and wear studies were made with type 440C stainless steel. It was found that 440C steel was significantly different from and inferior to 52100 steel in its wear properties in several respects. This information is of interest, because 440C has begun to replace 52100 generally in ball bearings for Navy use. The type of wear or wear mechanism was different – and presumably unfavorable – at all loads studied, as shown by the abnormal, irregular appearance of wear scars and to some extent by friction traces. Secondly, above a 20-kg load, wear entered a severely destructive regime. Wear scars became sharply larger and more variable in size and shape. Thus, load-carrying ability was less than with 52100 steel. Again no significant difference between the wear behavior of the several esters was established. Further, TCP had no beneficial effect with 440C steel, while it reduced wear moderately at lower loads with 52100 steel.

Friction results with both metals were similar. Improved dynamic recording of friction torque revealed the presence of a run-in period of 15 to 20 min followed by a plateau or constant friction phase at a lower level. Occasional transient rises in friction suggested limited seizures with recovery. Plateau values of the friction coefficient were suitable for comparison purposes. The average friction coefficient (plateau) increased slightly with load, especially between 5 and 10 kg, but was largely insensitive to the other operating variables, namely, ball-alloy type, ester type, and the presence of TCP and severe wear. Thus, friction did not correlate with wear. Also experimental variability was greater than in the case of wear scars. Hence, friction measurement was less useful than wear for studying lubrication variables.

The effect of nonpercolation of TCP was studied briefly, because it has been reported that the antiwear effect of TCP is due to polar impurities rather than the neutral ester itself. While results of the present experiments were not clear-cut, they failed to confirm any substantial difference in wear between percolated TCP and the unpercolated TCP available. A possible small improvement in wear at 5 kg was indicated with the unpercolated additive. Appearance of wear scars on 440C stainless steel, using the unpercolated additive, was improved and more like those observed on 52100 steel. The differences in wear behavior between 440C stainless steel and 52100 steel are of interest because of the trend to the use of the former in ball bearings, but it must be borne in mind that the wear situation in a rolling contact bearing is very different from the sliding contact of the four-ball machine.

The primary purpose of the study was to provide a basis of reference with which to compare potential antiwear and EP additives for neopentyl polyol ester lubricants. An investigation is currently being conducted to explore for additives which will be more effective than TCP. Since no significant differences were found among the three ester types, pentaerythritol esters have been selected as the base lubricant for all future work.

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13. ABSTRACT

Wear and friction properties of three representative neopentyl polyol esters, together with the common diester lubricant base, bis(2-ethylhexyl)sebacate, were studied with the four-ball wear machine in the presence and in the absence of tricresyl phosphate. The rubbing surfaces were 440C stainless steel and 52100 steel.

With 52100 low-chromium steel balls, wear rates were largely independent of ester structure and viscosity. Percolated tricresyl phosphate reduced wear moderately at low loads only. Stainless steel 440C gave results significantly different from those with 52100 steel at all loads. Wear was greatly increased at a load of 50 kg. Tricresyl phosphate was ineffective under all conditions. Friction showed little or no correlation with wear or the variables examined.

Experiments with the "as-received" tricresyl phosphate additive failed to confirm the substantial difference between percolated and unpercolated tricresyl phosphate found at the Massachusetts Institute of Technology with a different test method in connection with the Navy gyro bearing program.

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Friction						
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