

## **Effect of Phosphate Coatings on Fatigue and Wear**

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## **Abstract**

Surface properties such as roughness, hardness and plasticity are critical to preventing wear and fatigue in bearings and gears. For example, to reduce pitting and micropitting on gears, surface roughness needs to be minimized. Instead of “superfinishing” a surface to improve its anti-wear and anti-fatigue properties coatings can be applied. In particular, phosphate coatings are applied to surfaces to prevent corrosion and wear during the initial operation of a machined part (break-in). Our previous research on uncoated surfaces has revealed that the ability of lubricants to reduce friction and form films is critical to the anti-fatigue and anti-wear performance of lubricants. In the current study we have discovered that as the size of phosphate grains on the surface increases wear decreases and friction also decreases, which would improve fatigue life.

## **Introduction**

Extended gear fatigue pitting life is an essential performance requirement for today’s automotive and industrial gear oils [1-3]. Past studies have shown that both gear surface roughness and chemical and physical properties of oils have significant influence on an oil’s ability to prevent the formation of surface pits [1-3]. An oil’s ability to prevent pitting improves if oil film thickness increases and boundary friction decreases [1-3]. The effect of surface roughness on metal fatigue behavior has been studied extensively and is quite well understood [4-8]. It has been well established that reducing surface roughness minimizes the formation of surface micropits which can grow to form pits [7-9].

In order to prevent surface corrosion and prevent wear during initial operation of a machined part, coatings are applied to surfaces [10, 11]. In particular, phosphate coatings and more specifically manganese phosphate ( $MnPO_4$ ) coatings are known to prevent corrosion, prevent welding and reduce friction [10, 11]. However, the characteristics of phosphate coatings can vary with processing conditions [12]. In particular, the amount of the coating on the surface and the morphology of the coating (grain size) can affect the anti-corrosion properties of coatings [12].

Gear wear tests such as ASTM D 6121 are performed on both uncoated and phosphate coated gears [13]. In order to develop lubricants for gear applications the effect of surface coatings on lubricant performance needs to be assessed. Therefore, the effect of phosphate coatings on fatigue life and wear is examined here. In particular, the effect of the amount of  $MnPO_4$  on surfaces and  $MnPO_4$  grain size on fatigue and wear is studied. Our interest in this topic is to determine lubricant properties that need to be optimized in order to prevent wear and increase fatigue life on phosphated surfaces.

## **Experimental**

### *Surfaces Examined*

Six different phosphate coated samples were examined. These surfaces had various amounts of manganese phosphate ( $MnPO_4$ ) deposited on the surfaces and the sizes of the  $MnPO_4$  grains on the surface varied. Figure 1 shows SEM images of several of the surfaces examined. The uncoated steel material to which the coatings were applied was also investigated. Table 1 describes all of the surfaces studied as well as the surface roughness (Ra) and hardness (HRC) of each surface.

Figure 1: SEM Images of Coated Surfaces

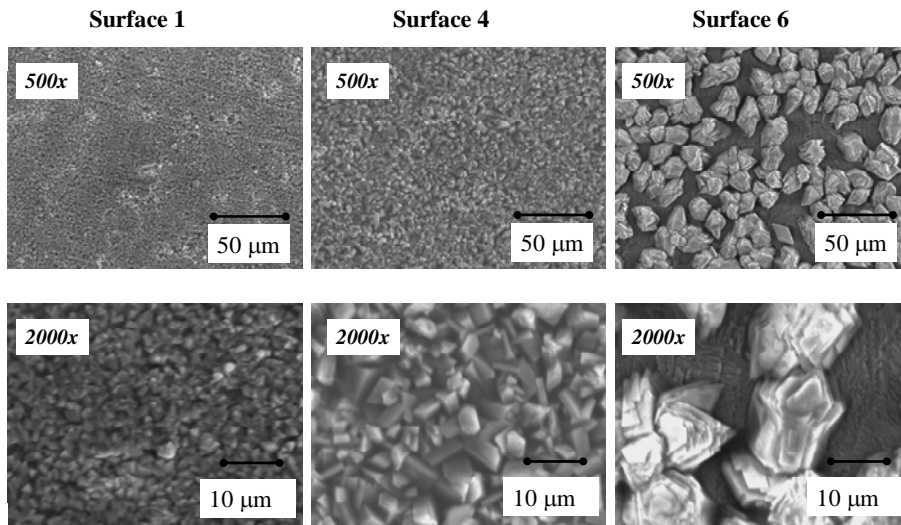


Table I : Surfaces Examined

Surface	Amount MnPO4 (mg/foot <sup>2</sup> )	Average MnPO4 Grain Size (μm)	Surface Roughness Ra (μm)	Hardness (HRC)
Uncoated	0	0	0.66	23.7
1	394	3.5	0.35	20.5
2	445	7.0	0.58	23.6
3	853	2.5	0.41	24.1
4	862	4.5	0.51	22.9
5	1170	9.5	0.61	23.0
6	1206	12.0	1.63	22.6

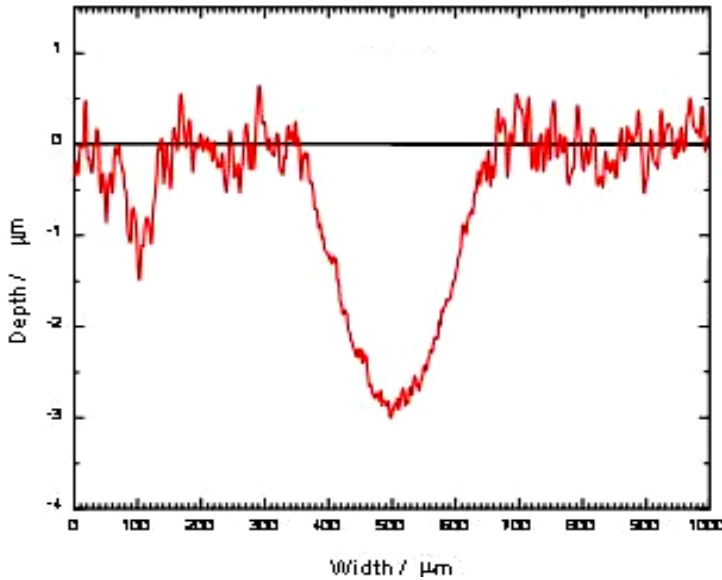
### *Oils Examined*

Two fresh oils which meet both API GL-5 and J2360 gear oil specifications were tested. The ability of oils to form films and reduce friction has been related to gear fatigue life [1-3]. Therefore, the oils tested have different film formation and friction reducing properties (see **Results** for more details).

### *Test Methods*

Wear tests were performed using a PCS Instruments' High Frequency Reciprocating Rig (HFRR). In the HFRR tests, a ball was oscillated across a 1cm x 1cm piece of the surfaces described in Table I. The ball was oscillated at a speed of 20Hz over a two-millimeter path, with an applied load of 700g between the ball and the test surface. The tests were run for 60 minutes at a temperature of 120°C. During the test the boundary friction coefficient for each oil-surface combination was measured. After testing, a surface trace of the wear scar on the test surface was measured using the Micro Analyzer 2000 from Precision Devices Incorporated (PDI). Figure 2 shows a typical PDI wear trace. The cross-sectional area of the wear trace is determined and reported here.

Figure 2: Typical Trace of Wear Scar Cross-section



The EHD film thicknesses of the two oils examined were measured using a PCS Instruments' Optical Interferometer. Film thickness was measured at 100C and entrainment speeds between 0.5 and 1.5 m/s [14].

The boundary friction and film thickness of fluids in combination with the surface roughness of a material can be used to calculate fatigue life in FZG pitting tests [1-3]. For the oil-surface combinations examined here we also report predicted pitting life in FZG pitting tests calculated as described previously [2].

*Statistical Methods*

The effect of surface coatings on wear, boundary friction and predicted pitting life can be described using the following equation:

$$\text{Performance} = A + B * \text{amount of MnPO4} + C * \text{grain size} + D * \text{Oil Effect} \quad \text{Eq. 1.}$$

In this study performance can refer to wear ( $\mu\text{m}^2$ ), boundary friction coefficient or predicted pitting life (hrs to pitting). Oil Effect is the difference in performance between Oil 1 and Oil 2. The values of the constants A, B, C and D are determined using standard statistical techniques [15]. Coefficients A and D would have the same units as performance ( $\mu\text{m}^2$ , friction coefficient or hrs to pitting). Coefficients B and C would have units of performance ( $\mu\text{m}^2$ , friction coefficient or hrs to pitting) divided by the factor affecting performance (amount of MnPO4, grain size). For example, coefficient B in a model for wear would have units of  $\mu\text{m}^2 / (\text{mg}/\text{foot}^2)$  so that when B is multiplied by the amount of MnPO4 ( $\text{mg}/\text{foot}^2$ ) this term would have the units for wear ( $\mu\text{m}^2$ ). In addition, once the values of B and C are known the

relative effect of amount of MnPO<sub>4</sub> and grain size on wear, boundary friction or predicted pitting can be calculated (see **Results** for calculations).

## Results

### *Effect of Coating on Wear*

Table II shows the wear scar cross-sectional areas for HFRR tests performed on the surfaces described in Table I in combination with Oil-1 or Oil-2. Oil-1 was designed to form thicker EHD films than Oil-2, but does not reduce friction as well as Oil-2 (see *Effect of Coating on Boundary Friction* section). HFRR wear tests are designed so that the formation of EHD films is minimized, so the differences in oil performance should be a result of the different surface active agents in the two fluids rather than their ability to form EHD films. Oil-2 prevents wear better than Oil-1 on all surfaces because of the differences in surface active agents in these two oils. More importantly, wear resistance varies with surface morphology. Wear tests performed with Oil-1 indicate that the best surfaces to prevent wear are the uncoated surface, surface 2 and perhaps surface 5. Wear tests performed with Oil-2 indicate the best surfaces to prevent wear are the uncoated surface, surface 2 and surface 5.

Table II : Wear on Coated Surfaces

Surface	Wear Scar Produced from Tests with Oil-1 ( $\mu\text{m}^2$ ) (a)	Wear Scar Produced from Tests with Oil-2 ( $\mu\text{m}^2$ ) (a)
Uncoated	7800(1000)	4400 (300)
1	10600 (400)	6300 (1300)
2	7100 (200)	5600 (600)
3	14000 (600)	6100 (200)
4	13100 (1600)	6800 (1700)
5	9000 (1000)	5300 (300)
6	10200 (2000)	6600 (600)

(a) The values in parentheses are the standard deviations in the wear scar measurements

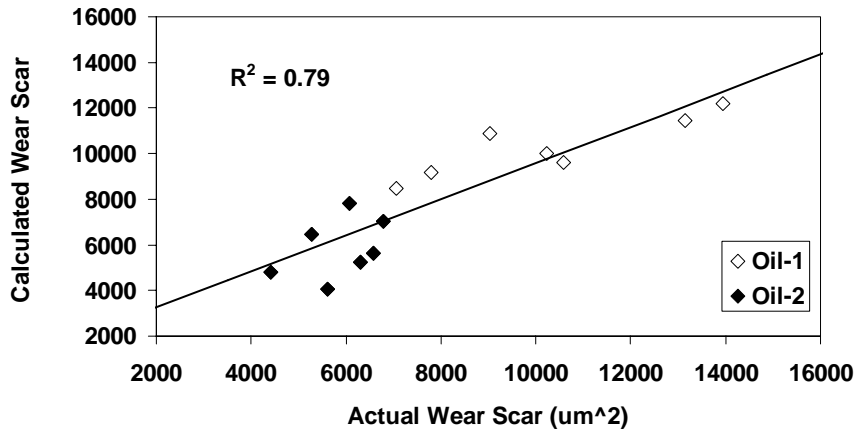
The effect of surface characteristics on wear are determined by correlating the wear data in Table II to the surface characteristics shown in Table I using Equation 1. Figure 3 shows that the correlation has an R-square value of 0.79. The wear data generated using Oil-1 is shown as the open diamonds and the wear data generated using Oil-2 are shown as the closed diamonds. The correlation equation relating wear to surface characteristics is as follows:

$$\text{Wear Scar} = 4800 + 4.7 * \text{amount of MnPO}_4 - 405 * \text{grain size} + 4390 * \text{Oil 1 vs Oil 2} \quad \text{Eq. 2.}$$

This equation shows that on average Oil-1 produces larger wear scars than Oil-2 which is evident in Table II. The equation also shows that as the amount of MnPO<sub>4</sub> on the surface increases, wear increases, but as grain size increases wear decreases. The relative effect of amount of MnPO<sub>4</sub> and grain size on wear can be determined using Equation 2. In Table I the amount of MnPO<sub>4</sub> on the surface varies from 0 to 1206 mg/ft<sup>2</sup> and average grain size varies from 0 to 12 $\mu\text{m}$ . The greatest effect that the amount of MnPO<sub>4</sub> has on wear is 1206\*4.7 or +5670 $\mu\text{m}^2$ . The greatest effect that grain size has on wear is -405\*12 or -4860 $\mu\text{m}^2$ . Therefore, the absolute effect of the amount of MnPO<sub>4</sub> on wear is

slightly greater than the absolute effect of grain size on wear. Correlations between surface roughness surface hardness and wear were also attempted but these factors did not have a statistically significant effect on wear. In addition, surface roughness and hardness are not correlated to the amount of MnPO4 or grain size. Therefore, the effects of the MnPO4 coating characteristics (amount and grain size) on wear cannot be explained by differences in surface roughness or hardness due to the coatings.

Figure 3: Correlation Between Wear and Surface Characteristics



*Effect of Coating on Boundary Friction*

Table III shows the boundary friction coefficients measured during the HFRR tests performed on the surfaces described in Table I in combination with Oil-1 or Oil-2. Oil-1 was designed to form thicker EHD films than Oil-2, but does not reduce friction as well as Oil-2. In addition, friction varies with surface morphology. Boundary friction coefficients measured when performing tests with Oil-1 are lowest on the uncoated surface and surface 2. Boundary friction coefficients measured when performing tests with Oil-2 are lowest on the uncoated surface and surfaces 1 and 6.

Table III : Boundary Friction Coefficients Measured on Coated Surfaces

Surface	Boundary Friction Coefficient from Tests with Oil -1 (a)	Boundary Friction Coefficient from Tests with Oil-2(a)
Uncoated	0.109 (0.001)	0.083 (0.001)
1	0.113 (0.003)	0.089 (0.001)
2	0.109 (0.001)	0.092 (0.001)
3	0.116 (0.001)	0.106 (0.007)
4	0.112 (0.004)	0.098 (0.007)
5	0.111 (0.002)	0.106 (0.001)
6	0.112 (0.002)	0.086 (0.005)

(a) The values in parentheses are the standard deviations in the friction coefficients

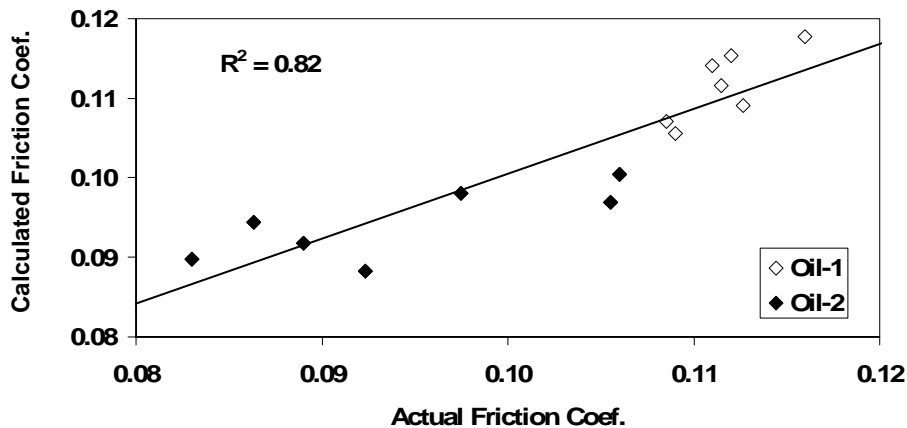
The effect of surface characteristics on friction is determined by correlating the friction data in Table III to the surface characteristics shown in Table I using Equation 1. Figure 4 shows that the correlation has an R-square value of 0.82. The friction coefficients measured using Oil-1 are shown as the open diamonds and the friction coefficients measured using Oil-2 are shown as the closed diamonds. The correlation equation relating friction coefficients to surface characteristics is as follows:

$$\text{Boundary Fr. Cf.} = 0.090 + 0.00002 * \text{amount of MnPO4} - 0.0012 * \text{grain size} + 0.017 * \text{Oil 1 vs Oil 2}$$

Eq. 3.

This equation shows that on average Oil-1 produces higher friction coefficients than Oil-2 which is evident in Table III. The equation also shows that as the amount of MnPO4 on the surface increases, friction increases, but as grain size increases friction decreases. The relative effect of the amount of MnPO4 and grain size on friction can be determined by using Equation 3 in the same manner as the effect of these surface parameters on wear was determined. The greatest effect that the amount of MnPO4 has on friction is  $1206 * 0.00002$  or  $+0.024$ . The greatest effect that grain size has on friction is  $-0.0012 * 12$  or  $-0.014$ . Therefore, the absolute effect of the amount of MnPO4 on friction is greater than the absolute effect of grain size on friction.

Figure 4: Correlation Between Boundary Friction and Surface Characteristics



#### *Effect of Coating on Predicted Pitting*

The film formation and boundary friction reducing properties of oils have been correlated to fatigue life measured in FZG pitting tests [1-3]. The thicker the film formed by a lubricant and the lower the boundary friction the longer the hours to pitting in FZG tests [1-3]. Figure 5 shows that Oil-1 forms thicker EHD films at 100°C than does Oil-2. However, Table III shows that Oil-2 reduces boundary friction better than Oil-1 on the various coated surfaces. In addition, the roughness of gear surfaces affects the hours to pitting in FZG tests with smoother surfaces having longer fatigue lives [1-3]. To assess the effect of surface coatings on fatigue life, predicted hours to pitting in FZG tests are calculated

for each oil on each surface using the film thickness data shown in Figure 5, the boundary frictional data shown in Table III and the surface roughness data shown in Table I. The results of these calculations are shown in Table IV. The predicted fatigue life for Oil-1 on all surfaces is greater than for Oil-2 on all surfaces. In addition, the predicted fatigue life for Oil-1 does not vary significantly as the surfaces are varied. That is the predicted hours to pitting for Oil-1 range from 292 hours on surface 3 to 306 hours on the uncoated surface and surface 2. On the other hand, the predicted hours to pitting determined for Oil-2 on the various surfaces range from 216 hours on surface 3 to 263 hours on the uncoated surface. Therefore, fatigue life is good when Oil-1 is tested with any surface but can fluctuate significantly when Oil-2 is tested.

Figure 5: EHD Film Thickness of Oil-1 and Oil-2

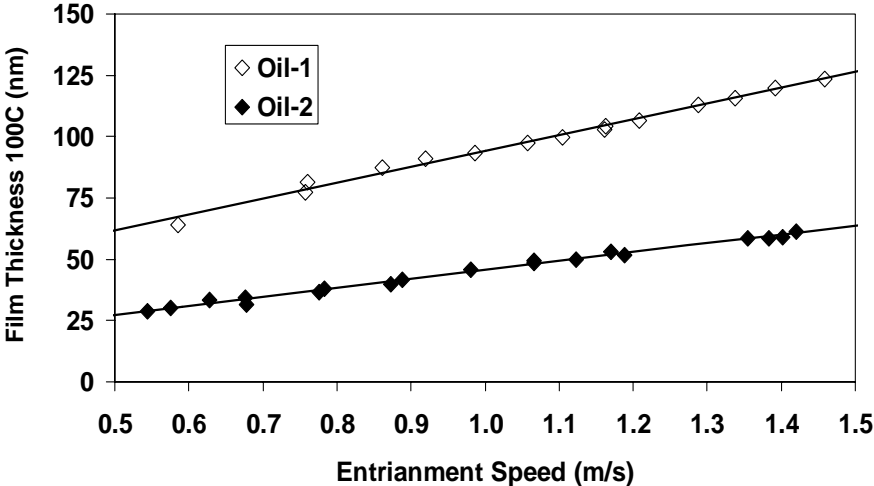


Table IV : Predicted Hours to Pitting Calculated for Each Oil/Surface Combination

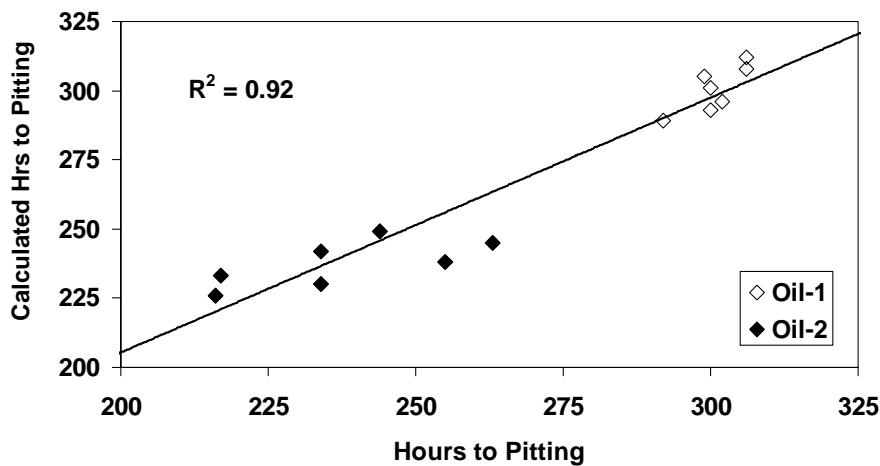
Surface	Predicted Hours to Pitting from Tests with Oil-1	Predicted Hours to Pitting from Tests with Oil-2
Uncoated	306	263
1	299	234
2	306	244
3	292	216
4	300	234
5	302	217
6	300	255

The effect of specific surface characteristics on predicted fatigue life is determined by correlating the data in Table IV to the surface characteristics shown in Table I using Equation 1. Figure 6 shows that the correlation has an R-square value of 0.92. The fatigue lives calculated for Oil-1 are shown as the open diamonds and those calculated for Oil-2 are shown as the closed diamonds. The correlation equation relating fatigue life to surface characteristics is as follows:

Predicted Hours to Pitting =  $245 - 0.030 \cdot \text{amount of MnPO}_4 + 2.38 \cdot \text{grain size} + 63 \cdot \text{Oil 1 vs Oil 2}$  Eq. 4.

This equation shows that Oil-1 protects surfaces from pitting better than Oil-2 which is evident in Table IV. The equation also shows that as the amount of MnPO<sub>4</sub> on the surface increases, hours to pitting decreases, but as the grain size increases hours to pitting increases. The relative effect of amount of MnPO<sub>4</sub> and grain size on wear can be determined by using Equation 4. In Table I the amount of MnPO<sub>4</sub> on the surface varies from 0 to 1206 and average grain size varies from 0 to 12. The greatest effect that the amount of MnPO<sub>4</sub> has on predicted hours to pitting is  $1206 \cdot -0.030$  or -36 hours. The greatest effect that grain size has in wear is  $+2.38 \cdot 12$  or +29 hours. Therefore, the absolute effect of the amount of MnPO<sub>4</sub> on fatigue life is slightly greater than the effect of grain size on fatigue life.

Figure 6: Correlation Between Fatigue Performance and Surface Characteristics



## Discussion

Extending gear fatigue pitting life and preventing wear are essential performance requirements for today's automotive and industrial gear oils. Surface properties such as roughness, hardness and plasticity are critical to protecting gear surfaces [1-3]. For example, to reduce pitting and micropitting on gears, surface roughness needs to be minimized [4-9]. Instead of "superfinishing" a surface to improve its anti-fatigue and anti-wear properties, coatings can be applied to surfaces. In particular, phosphate coatings are applied to surfaces to prevent corrosion and wear during the initial operation of a machined part (break-in) [10-12]. However, the characteristics of phosphate coatings can vary with processing conditions [12].

In order to develop lubricants for gear applications the effect of surface coatings on lubricant performance has been assessed. Wear on phosphate-coated surfaces can be reduced by decreasing the

amount of phosphate on the surface or by increasing phosphate grain size (see Equation 2). Interestingly, these physical characteristics of coatings do not correlate to changes in the roughness or hardness of the surface. Furthermore, in this study surface roughness and hardness do not significantly affect wear. Perhaps, wear on coated surfaces is caused by abrasion of the surface by MnPO<sub>4</sub> particles released from the surface. This possible mechanism for surface damage has not been investigated here. Of more importance to the lubricant developer, the correct choice of surface active agents can be used to prevent wear (compare results for Oil 1 and Oil 2 in Table II). However, the anti-wear performance of even the best lubricant (Oil 2) will vary if the characteristics of the phosphate coating vary (see Table II).

Past studies have shown that an oil's ability to prevent pitting improves if oil film thickness increases and boundary friction decreases [1-3]. Table III and Equation 3 show that boundary friction coefficients vary as surface morphology of phosphate coated surfaces vary. In particular, friction coefficients increase as the amount of phosphate on the surface increases and they decrease as phosphate grain size increases. These effects of surface morphology on friction along with the variation in surface roughness for coated surfaces (see Table I) affect the fatigue life of oil/surface combinations (see Table IV and Equation 4). In particular for Oil-2, which forms thin EHD films, predicted fatigue life decreases as the amount of phosphate on the surface increases and predicted fatigue life increases as phosphate grain size increases. For Oil-1, which forms the thicker EHD film, surface morphology has very little effect on predicted fatigue life. Therefore, to best optimize fatigue life on phosphate surfaces oils formulated to form thick EHD films should perform better than oils formulated to control friction.

Overall, Table II and Table IV show that lubricants prevent wear and improve fatigue life best when uncoated surfaces are used. However, phosphate coated surfaces are needed to prevent corrosion and prevent wear during break-in conditions [10, 11]. Therefore, until new cost-effective coatings or surface finishing techniques are developed, lubricants will need to be developed that prevent wear and improve fatigue life on phosphate coated surfaces. To optimize the ability of lubricants to protect surfaces the characteristics of the phosphate coating need to be well controlled. Equations 2, 3 and 4 indicate that an optimized phosphate coating would contain large phosphate grains and a minimal amount of phosphate on the surface.

## Conclusions

- Wear on phosphate coated surfaces increases as the amount of coating on the surface increases and decreases as phosphate grain size increases.
- The anti-wear performance of oils formulated to minimize wear will vary as the morphology of phosphate coatings vary.
- Boundary friction on phosphate coating surfaces increases as the amount of coating on the surface increases and decreases as phosphate gain size increases. These variations in friction affect fatigue life on phosphate coated surfaces. Fatigue life decreases as the amount of coating on the surface increases and fatigue life increases as phosphate grain size increases.
- The fatigue life performance of an oil formulated to form thick EHD films does not vary significantly as the morphology of phosphate coatings vary.
- The optimal phosphate coating to prevent wear and improve fatigue life would contain large phosphate grains and a minimal amount of phosphate on the surface.

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