Phosphorus Reduction in Plain and Fully Formulated Oils Using Fluorinated Additives

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Abstract**—**The reduction of phosphorus and sulfur in engine oil are the main topics of this paper. Very reproducible boundary lubrication tests were conducted as part of Design of Experiment software (DOE) to study the behavior of fluorinated catalyst iron fluoride (FeF3), and polutetrafluoroethylene or Teflon (PTFE) in developing environmentally friendly (reduced P and S) anti-wear additives for future engine oil formulations. Multi-component Chevron fully formulated oil (GF3) and Chevron plain oil were used with the addition of PTFE and catalyst to characterize and analyze their performance. Lower phosphorus blends were the goal of the model solution. Experiments indicated that new sub-micron FeF3 catalyst played an important role in preventing breakdown of the tribofilm.

Keywords**—**Wear, SEM, EDS, friction, lubricants.

I. INTRODUCTION

INCREASED fuel efficiency and reduced emissions are becoming very important each day. Lubricant serves several purposes such as reducing wear and providing corrosion protection [1]-[4]. The interaction of the lubricant with solid surface results in the formation of a boundary layer with physical and chemical properties that are distinct [5]. The work of Nehme et.al established the importance of a transfer film that was formed as the consequence of the interaction of the lubricating media with the metal surface [6]-[10]. Willermet et.al and Martin et.al established the importance of tribofilms on the surface in boundary lubrication [11], [12].

This paper explored the effect of polytetrafluoroethylene (PTFE) and FeF3 catalyst on the performance of Chevron plain ZDDP (P %), and Chevron GF3 fully formulated oils. The purpose was to gain useful engineering information, and also to use the data to develop equations for minimum wear volume and maximum time for full break down. Emphasis was therefore given to conditions where the additives were working effectively for minimum Zinc dialkyldithiophosphate ZDDP (Phosphorus %). Lubricating oils are normally multi component additive systems. They contain different additives such as viscosity improver, detergents, dispersants and antioxidants. It is known that these additives interact at the surface, affecting the function of the lubricating oil. Therefore, it is important to use ZDDP with base oil alone to check its performance with PTFE and FeF3 catalyst, then compare it to other additives and check the friction and wear phenomenon.

A Plint T53 SLIM modified ball on cylinder machine (Phoenix Tribology, England) was used for all tests. A SAE Timken steel ring (64-66 HRC, 60 mm OD) was the moving body. The surface finish of the rings was examined using a profilometer (Mahr Perthometer M1). Timken Bearing cylinders did not have uniform surfaces and asperities differed from one ring to another. The 66 HRC rings were cleaned with hexane and acetone to remove the machine oil.

The chemistry of the lubricant was measured using ASTM D3120 (for sulfur) and ASTM D5185 (for all other ingredients). For plain Chevron ZDDP OLOA 262 oil, the concentrations were as follow: 7.9% phosphorus, 8.8% zinc, and 16.3% sulfur, and the balance were base oil. For Chevron GF3 fully formulated oil, the data are provided in Table I.

TABLE I
0.05% PHOSPHORUS GF3 FULLY FORMULATED OIL ANALYSIS

Oil Chemistry	Testing Method	Composition PPM
Sulfur	ASTMD3120	1257
Zinc	ASTMD5185	499
Phosphorus	ASTMD5185	446
Silicon	ASTMD5185	7
Aluminum	ASTMD5185	13
Chromium	ASTMD5185	2
Copper	ASTMD5185	1
Manganese	ASTMD5185	0
Iron	ASTMD5185	47
Nickel	ASTMD5185	2
Lead	ASTMD5185	4
Tin	ASTMD5185	6
Sodium	ASTMD5185	9
Boron	ASTMD5185	151
Calcium	ASTMD5185	1156
Magnesium	ASTMD5185	16
Molybdenum	ASTMD5185	74
Barium	ASTMD5185	0
Cadmium	ASTMD5185	0
Vanadium	ASTMD5185	2
Silver	ASTMD5185	2

There were 8 tests from both plain and fully formulated oils. Each test had different concentration of phosphorus, PTFE and FeF3 catalyst, and was run in three replicates. The 2 level factorial design of experiment approach randomly selected these tests. The 2 levels correspond to high and low percentage of each additive. ZDDP: 0.05(P%)-0.1(P %), PTFE: 0%-1%, FeF3: 0.2%-1%. These tests were performed randomly under the same speed and loading conditions (700 rpm and 385 Newton) for 100000 rotations or failure, whichever came first. At the end of each test, the cylinders were ultrasonically cleaned by hexane, and the resulting post wear data were evaluated. The surface was also examined

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using Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS).

TABLE II
ANOVA (ANALYSIS OF VARIANCE) EQUATIONS FOR WEAR DATA USING DOE

Additives	Wear Volume
Plain ZDDP Oil (0.1 % Phosphorus)	1.246 + 1.741*ZDDP(P%) - 0.288*PTFE – 1.058*CAT –7.0* ZDDP(P%)*PTFE +0.705*PTFE*CAT
Fully Formulated GF3 Oil (0.1 % Phosphorus)	0.683 + 1.741*ZDDP(P%)+ 0.093*PTFE + 0.384*CAT –7.0* ZDDP(P%)*PTFE +0.705*PTFE*CAT

II. RESULTS AND DISCUSSION

A. Analysis

Figs 1, 2 show that the Chevron plain oil was performing better than the fully formulated oil. The model desirability for plain oil is as high as 80% when compared to GF3 oil. It is evident that phosphorus can be reduced in the Chevron plain oil to as much as 0.03% when adding PTFE and catalyst, yet high phosphorus is very significant for the performance of GF3 oil. The model volume equations in Table II show the contribution of the each component in the Design of Experiment. GF3 acceptable performance was tied to the phosphorus percentage in the oil. Equations in Table II show that catalyst was not significant at all. PTFE will contribute to the reduction of wear at very high concentration. Changes in wear were different with oil blends, but it is evident that ZDDP (P %) was crucial for the anti-wear protection in GF3 oil, where PTFE and catalyst contributed greatly to the reduction of phosphorus in Chevron plain ZDDP oil. The protective films formed in GF3 oil experiments were primarily due to ZDDP (P %) and increased PTFE. This can be traced to the modeling equations and the effects of high PTFE concentration, since it is tied to the negative coefficient with ZDDP in the equations that are directly proportional to the decrease in wear. This cannot be said about the plain oil where catalyst is effective in reducing wear. Multiple references [9], [13] have shown that fluorinated catalyst and PTFE will result in fluorinated species bonded on the steel surface. In the Design of Experiment, the plain oil favors these species, where the fully formulated oil at low PTFE concentration favors the organic polyphosphate tribo films.

B. Wear Prediction and Mechanism

The design of experiment software offers prediction and graphical analysis. In the graphical analysis, a limit could be set between certain values of wear or time to failure; then the responses are solved based on the original model and the prediction results are calculated. Figs 3, 4 show the wear and time to failure corresponding to 0.8% PTFE, 0.4% catalyst and 0.05 % phosphorus for the Chevron plain oil and GF3 fully formulated oil. These concentrations were used to perform two ball on cylinder wear tests. The results were acquired and plotted in Figs 5, 6. In Chevron plain ZDDP oil, time to failure occurred at 88000 cycles or 131 minute, wear volume was 0.78 mm^3, wear depth was 9.18, wear width was 916. All results were approximately close to the graphical solution with the exception of wear width. In Chevron GF3 oil, time to failure occurred at 30000 cycles or 42 minutes, wear volume was 0.89 mm^3, wear depth was 10.81, wear width was 940. All experimental results were approximately close to the model predictions.

Fig. 5 indicates that the decomposition of anti-wear additive products took place over a period of time and a solid film that sustained adhesive wear for a long duration was formed in the Chevron plain oil test. It was also evident that steady state friction allowed the formation tribofilm. This was not the case for the fully formulated oil. It is evident that abrasive wear was dominant and anti-wear film was diminished in the early stages of the process (Fig. 6). It is assumed that the stripping of the metal happened toward the end of the test when there was steep rise in friction coefficient without any recovery.

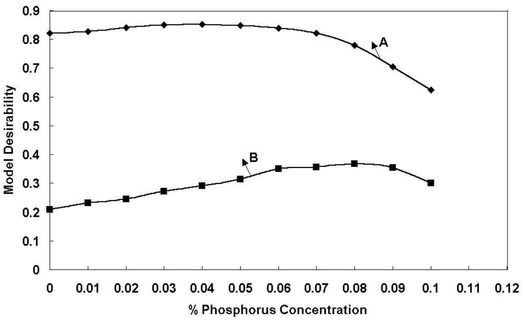

Fig. 1 Desirability of the model to target minimum phosphorus for chevron oil using the variation of Catalyst and PTFE: (A) is for Chevron plain oil, (B) is for Chevron GF3 oil

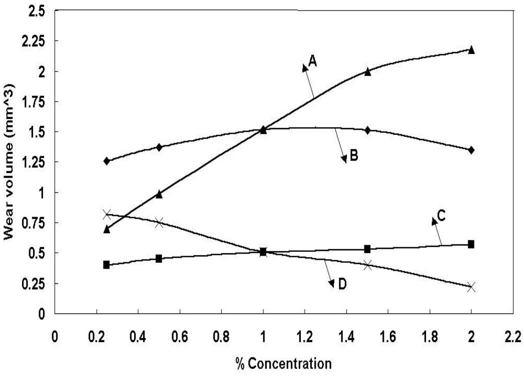

Fig. 2 Wear volume variation with respect to PTFE and catalyst concentration (A) represents the variation of Chevron GF3 with respect to catalyst Concentration, (B) represents the variation of Chevron GF3 with respect to PTFE Concentration, (C) represents the variation of Chevron plain oil with respect to PTFE Concentration, (D) Represents the variation of Chevron plain oil with respect to catalyst Concentration

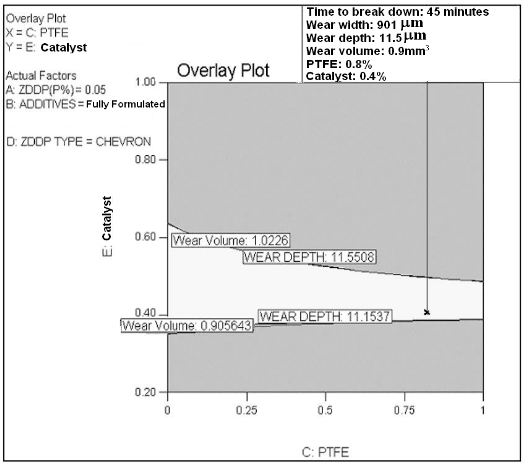

Fig. 3 Graphical solution and predictions for the DOE equations

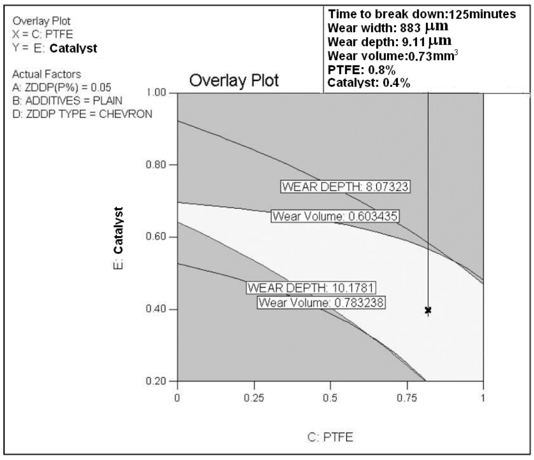

Fig. 4 Graphical solution and predictions for the DOE equations

To identify the anti-wear function of ZDDP (P%), FeF3 catalyst, and PTFE in the present study; Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) of 0.05% Phosphorus Chevron plain oil with 0.8%PTFE and 0.4% FeF3 catalyst was compared to SEM and EDS of 0.05% phosphorus GF3 Chevron oil with 0.8%PTFE and 0.4% FeF3 catalyst (Fig. 7). The wear track for the plain oil is smooth and suggests that adhesive wear was dominant during the process. In addition, polyphosphate chains and fluorinated species are presumed to be the driving force in the formation of anti-wear additive film. The improvement in the GF3 fully formulated oil was not very significant and abrasive wear dominated the process.

III. CONCLUSION

In this article Design of Experiment (DOE) limits the scope of work by analyzing several factors and presents meaningful responses. Stand-alone experiments of one factor at a time will take longer without even reaching a conclusion. The model gave simple and accurate predictions on the performance of PTFE and catalyst additives in Chevron plain and fully formulated oils. The performance predicted by the model tended to be closer to that of ideal situation. In experimental tests, there will always be errors and uncertainties associated with uneven surfaces, or large abrasive particles that cause large fluctuation of friction and render wear results with accuracies in the order of 75% [13]. Such errors in tribology should be acceptable.

After analyzing GF3 with other plain oil formulations in the design matrix, it became clear that the formation of anti-wear film was reduced due to other interactions. It was certain that the role of FeF3 catalyst was totally diminished based on the conditions of these tests. Steady state coefficient never existed and abrasive wear dominated the process. The role of GF3 and anti-wear additives were deeply explored by the extensive analysis of the DOE model. Therefore the other chemistries in GF3 should be investigated.

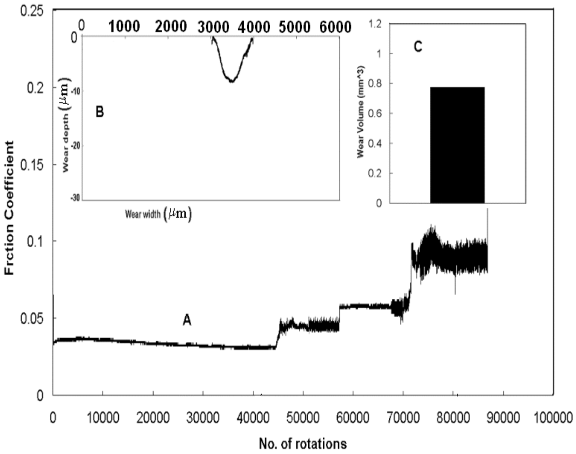

Fig. 5 Experimental data for the responses predicted by the model for plain ZDDP oil (0.05 P%): (A) represents frictional data and break down steps, (B) represents Wear width and depth, (C) represents Wear volume

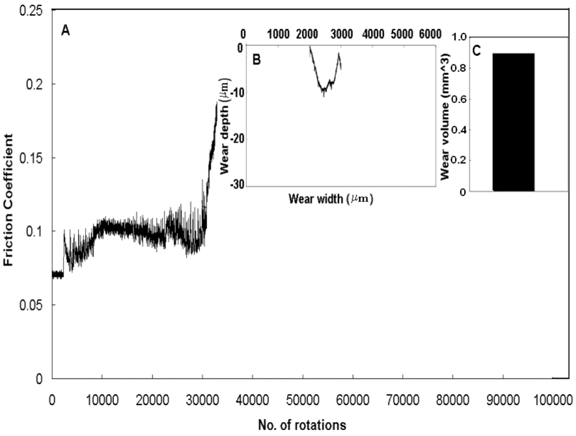

Fig. 6 Experimental data for the responses predicted by the model for Chevron GF3 oil (0.05 P%): (A) represents frictional data and break down steps, (B) represents Wear width and depth, (C) represents Wear volume

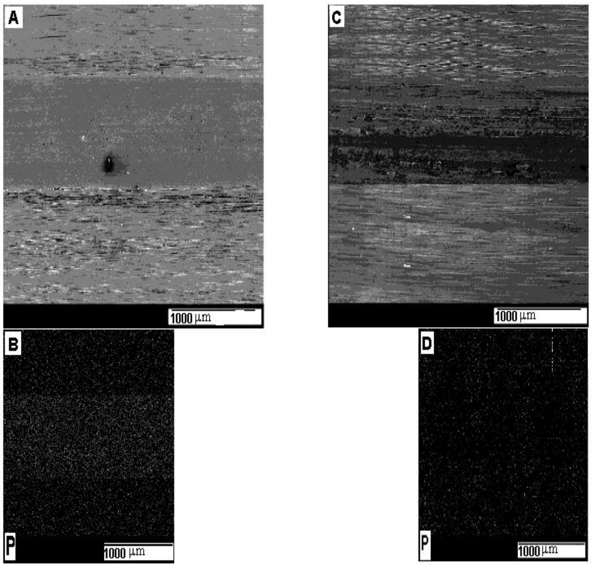

Fig. 7 SEM and EDS images showing the wear track and phosphorus concentration. (A) and (B) represent Chevron plain oil, (C) and (D) represent Chevron GF3 fully formulated oil

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