Competitive Surface Interactions of Critical Additives with Piston Ring/Cylinder Liner Components under Lubricated Breaking-In Conditions©

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Editor's Note: Most of us never give a second thought to the complex chemical cocktail that tribologists have mixed up in the form of modern motor oil. We just buy a car, change the oil and drive. Our colleagues in industry and academia, however, conduct extensive research to make sure your car engine runs smoothly, lasts a long time, pollutes little and maximizes gas mileage. The following paper describes research to study how different oil additives compete with each other during the break-in process in a new engine's piston ring/cylinder wall contact. You may not know it but a careful balance must be maintained by the oil so that antiwear additives deposit just the right amount of boundary lubricant films where they are needed but at the same time detergent additives make sure that excessive deposits don't build up where they aren't wanted. Engineering today's oils is a tribological challenge but this paper proves that our STLE colleagues are up to the task. Read this one over and even if, like me, you don't fully understand all the chemistry details, I am sure you will agree there's more in that plastic quart bottle than just petroleum!

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Using a commercial mineral based API SJ/SAE 5W-30 engine oil, a series of break-in friction experiments employing a reciprocating tribometer was conducted under simulated engine conditions with actual gasoline engine piston rings (Cr-plated, Mo+NiCrBSi-coated and nitrided) and cast iron cylinder liner combinations. Elemental analyses by energy dispersive X-Ray spectroscopy (EDX) of the wear tracks indicate that the antiwear agent ZDTP displays higher selectivity than the Mg- and Ca-containing detergents toward the tribosurfaces of both rings and liners. In particular, the tribosurface activity of the cast iron cylinder liners reacting with ZDTP is higher than that of the nated piston ring tribosurfaces. The tribosurfaces of all the piston rings sliding against the same cast iron liners exhibit almost the same activity when they react with ZDTP. Stronger interaction occurs between the steel tribosurfaces and the non-metallic functional additive elements (S and P), whose hardness or softness as Lewis acids and Lewis bases can be tailored to produce desired interactions. It is suggested that the tribosurface chemical activity of tribosurfaces, which relies on both the thermodynamic properties of the materials and the triboprocesses involved, plays a role in determining the characteristic surface interactions of functional additive elements.

KEY WORDS
Competitive Surface Interactions; Detergent; Antiwear Agent; Breaking-In Process

INTRODUCTION
Many engine or tribological components, such as piston rings and cylinder liners in a powertrain system, have to go through a break-in process before achieving a steady-state of geometric conformity at the contact surfaces. Such a process is termed “break-in” or “running-in.” This surface break-in process can involve a complex combination of surface interactions of contact geometry, engine configuration, material properties, lubricant chemistry, and environmental conditions. In this complicated process, chemical and thermal effects have the most significant impact on steady-state lubrication. In this paper, the authors have focused on the changes of chemical composition of the tribosurface reaction films during the break-in process. During this process, asperities on the contacting surfaces are smoothed, and the two surfaces gradually come into macro- and micro-conformity (1). As a consequence, abnormal noise and severe wear can be reduced, and stable operation can be achieved when the opposing surfaces begin their normal service life. This same process is followed when conducting tribological tests in the laboratory to study the characteristics of different tribosystems. Breaking-in can be monitored by various means, such as surface finish measurement and analysis before and after the break-in-process, but no generally applicable rule of thumb can be given (1).
The mechanism of piston ring lubrication and the consequent wear phenomena have been a subject of investigation for a considerable time, although much less emphasis has been placed on chemical and metallurgical effects (7). Thus, the purpose of the current research is to study, under lubricated breaking-in conditions, the competitive surface interactions of Ca- and Mg-based detergents and the antiwear agent ZDTP on a variety of actual piston ring surfaces paired with a selected type of cast iron cylinder liner. Test results are then used to interpret the tribological performance of the tribosystems under investigation.

EXPERIMENTAL CONDITIONS
Breaking-in Test and Conditions

The breaking-in test was conducted on an SRV Friction and Wear Tester, as shown in Fig. 1. The upper specimen was a segment of an actual piston ring, and the lower specimen was shaped from real cylinder liner materials. The upper specimen, of length 25 mm and cut directly from Saturn L-4 1.9L piston rings, was reciprocated against cylinder bore materials under a certain Hertzian contact stress. The piston ring specimen was 2.5 mm thick with an outside diameter of 82 mm. The lower cylinder bore specimen was fabricated from Saturn L-4 1.9L cast iron cylinder bore material. The cast iron specimen has a diameter of 24 mm and an arithmetic average roughness (Ra) of 0.3 micron.

Legends: Fc = adjustable normal load; Ph = upper holder for Pc; Pc = clamp for upper specimen as detailed in the right-hand illustration; P = upper specimen; S = lower specimen; Sh = supporter for lower specimen; Fd = piezoelectric transducer for friction force measurement; d = driving system for oscillating sliding.

A two-stage breaking-in process was selected based on several preliminary tests and is diagrammatically displayed in Fig. 2. The breaking-in was terminated when the friction coefficient, indicated by the recording curves, appeared stabilized with maximum variations within +/-0.01.

TRIBOMATERIALS AND LUBRICANTS

In Table 1 lists the detailed elemental compositions, determined by energy dispersive X-ray analyzer (EDX), of the original coated or plated surfaces of all employed tribomate materials (that is materials on mating surfaces). Figure 3 shows the IR spectrum (Bio-Rad Oil Analyzer) of the lubricating oil employed, and Table 2 shows the elemental composition analyzed by Auger Electron Spectroscopy (AES), in which the content of S was determined on a 300T XRF spectrometer (ASOMA Instruments, Inc.) with a China National Standard method GB/T17040-1997. The high content of element S suggests its many sources, including the base oil, ZDTP, and overbased detergents, both the Ca and the Mg detergents, as indicated in Table 2. Absorption at wavenumbers 2900cm⁻¹, 1480-1490cm⁻¹ and 600-900cm⁻¹ identifies the mineral origin of the lubricating oil. Combinations of tribomate materials and lubricating oil in the tribological experiments are listed in Table 3.

CHEMICAL COMPOSITION ANALYSES

After breaking-in, the tribosurfaces were dried, then cleaned with ethanol and ultrasonically cleaned, first by acetone and then by alcohol. The dried tribosurfaces of both upper and lower specimens were analyzed by EDX for elemental composition in the wear tracks.

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| Table 1 – Elemental Composition of Tribomate Surfaces (wt. %) |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|                | Fe  | Cr  | Mo  | B   | Si  | O   | N  | C   | Mn | Ni  |
| Cast Iron Liner | 93.3| 0.4 | -   | -   | 1.9 | -   | -  | 3.0 | 1.3| -   |
| Cr-Plated Ring  | -   | 86.0| -   | -   | -   | 14.0| -  | -   | -  | -   |
| Nitrided Ring   | 83.8| 15.3| -   | -   | 0.7 | -   | 0.3| -   | -  | -   |
| Mo+NiCrBSi      | 1.3 | 2.8 | 73.8| 5.6 | 0.5 | 2.9 | -  | -   | 18.0| -   |
| Coated Ring     | 1.3 | 0.4 | 73.8| 5.6 | 0.5 | 2.9 | -  | -   | 18.0| -   |

| Table 2 – Elemental Composition of API SJ/SAE 5W-30 Engine Oil |
|----------------|----------------|----------------|----------------|----------------|----------------|
| Major Additive Elements | Contents/ppm | Origins                      |
| Mg             | 228            | Detergents              |
| Ca             | 595            |                            |
| Zn             | 1082           | Antioxidant/Antiwear      |
| P              | 919            |                            |
| S              | 5050           | Antioxidant/Antiwear,     |
|                |                | Detergents, Base Oil      |
| Si             | 2.1            | Antifoaming agent         |

| Table 3—Triboc-Contact Pairs and Their Designation Code in SRV Tribotests |
|----------------|----------------|----------------|----------------|----------------|----------------|
| Cr Plated Ring/ Cast Iron Liner | I-Cr/Fe         |
| Mo+NiCrBSi coated Ring/ Cast Iron Liner | I-Mo/Fe          |
| Nitrided Stainless Steal Ring/ Cast Iron Liner | I-Ni/Fe           |

Fig. 3—Infrared trace of API SJ/SAE 5W-30 engine oil.

RESULTS AND DISCUSSION

Elemental composition is widely employed to characterize the chemical state of wear tracks. Since most additives can be chemically characterized by specific functional elements in their molecules, an indirect way to understand the distribution of additive types on tribosurfaces is through identifying the additive-specific elements. In commercial engine oil formulations, detergents, antioxidant and antiwear agents are among the key constituents of the additive package. Generally, detergents are the alkali earth metallic salts of sulfonates, phenates and salicylates. The alkaline-earth metals, usually magnesium (Mg) or calcium (Ca), can therefore be regarded as the functional elements to specify and identify types of the formulated detergents. As shown in the atomic emission spectroscopic data shown in Table 2, both Mg and Ca are present as detergent components. Separately or in combination, these two elements can be taken as detergent indicators. Another major category of polar additives of tribiochemical importance in commercial fully formulated engine oils is the zinc salts of alkyl or aryl dithiophosphates, which have the dual role of providing both antioxidant and antiwear performance. For these multipurpose additives, S, P and Zn can be taken either separately or in combination, as their indicators. Due to the presence of other functional additives in fully formulated engine oils, the element indicators designated above can be cited only as a suggestion of the residence of antioxidants on the worn tribosurfaces. For the surface active detergents and antiwear agent, quantity values of their elemental indicators in the wear tracks are a good estimation of their interactions with tribosurfaces. With this approach, it is desirable to obtain knowledge of the adsorption and/or reaction properties of the additives in fully formulated mineral oils. In the following discussions, semi-quantitative estimations will be made, considering the lack of a well-defined relation between the elemental analysis results of AES and EDX, about the preferential residence of functional additive elements on tribosurfaces and tribiochemical activity of tribosurfaces toward functional additive elements.

PREFERENTIAL RESIDENCE OF FUNCTIONAL ADDITIVE ELEMENTS ON TRIBOSURFACES

In terms of the individual and combined element indicators defined above for the detergents and antiwear agent, Figs. 4-6 compare the distribution characteristics of major functional additive elements on the contacting areas of each of the tribomates.
It is obvious that various polar additive molecules in engine oil have different types of surface interactions with the tribosurfaces of differing chemical compositions due to the varied adsorption/interaction activity or selectivity of the additives, as summarized below.

Whether one considers the piston rings (of differing chemical nature) or the cylinder liner (of cast iron), they all demonstrate higher surface activities toward the antitrust agent than they do toward the detergents. Such a fact implies that ZDTP is an effective antitrust agent when lubricating all these tribosurfaces under mixed or boundary conditions. In comparison, the tribosurface activity of the cast iron cylinder liners toward ZDTP is invariably higher than that of the corresponding tribosurfaces. It is noted that, for the tribosurfaces of all the piston rings, similar activity toward ZDTP is demonstrated when pairing with the same cast iron cylinder liners, while for the activity of tribosurfaces of the cast iron cylinder liner their activity toward ZDTP depends heavily on the nature of the pairing piston rings. The surface activities with ZDTP can be ranked as follows: (Starting with the greatest interaction) Fe/Mo-coated > Fe/Cr-plated > Fe/nitrivated (least interaction).

The tribosurfaces of piston rings of different chemical nature confer varied activities toward individual functional additive elements S, P, and Zn from ZDTP. For the Mo-coated piston ring, its tribosurface exhibits activity in a decreasing order of S > P > Zn, while for the Cr-plated and nitrivated tribosurfaces, P becomes the most richly distributed element. Interestingly, for the nitrivated piston ring, S assumes a relatively prominent role, in contrast to S from the Cr-plated piston ring. Residence of Zn on the three tribosurfaces varies, and particularly only trace amounts of Zn have been detected on the Mo-coated tribosurface. In the case of the cast iron tribosurface, its activity toward the functional elements of ZDTP follows the decreasing order of P > S > Zn when mating with the Cr-plated tribosurface. When it is mated with either Mo-coated or nitrivated tribosurfaces, its activity toward the functional elements of ZDTP follows the decreasing order of S > P > Zn. Zn always ranks in last place in terms of the atomic population among the three functional elements of ZDTP. These facts suggest again that activity of the cast iron tribosurface toward the functional elements of ZDTP is dependent, to some extent, upon the chemical nature of its triborates.

Tribosurface activities of the three kinds of piston rings and the cast iron cylinder liner toward the detergents also show a great disparity. Generally, tribosurfaces of the cast iron cylinder liner are more active toward the detergents than tribosurfaces of the piston rings of a different chemical nature. Among the tribosurfaces of the piston rings, their activity toward the detergents ranks as follows: (greatest) nitrivated > Cr-plated > Mo-coated. Considering the relatively significant distribution of the functional element S on the nitrivated piston ring tribosurface, it is expected that a nitrivated piston ring might be among the best candidates for gasoline engine applications.

As for the detergent types, except for the Cr-plated tribosurface which shows greater activity toward the Mg-containing detergent than toward a Ca-containing detergent, both the Mo-coated and nitrivated tribosurfaces are more active toward a Ca-containing detergent than toward a Mg-containing detergent. With regard to the tribosurface of a cast iron cylinder liner, it always exhibits higher activity toward the Mg-containing detergent than toward the Ca-containing detergent. For easy comparison, and quick learning of the selectivity of major functional additive elements toward the tribosurfaces of differing chemical composition, a different way of displaying the residence of both the detergent and the antitrust agent indicators is depicted in Fig. 7.

From Fig. 7 it is easy to rank all the functional additive element indicators in terms of their preferential residence on both the piston ring tribosurfaces of different type and the cast iron cylinder liner tribosurface.

Overall, tribosurfaces of the Cr-plated piston ring show stronger interaction with ZDTP than with the detergents. In terms of "high-

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Fig. 7—Interactive activity and selectivity between functional additive elements and tribosurfaces.

(a) Piston rings  
(b) Cylinder liner

to low-selectivity order by which the functional additive elements interact with the Cr-plated tribosurface, the following rank order is observed: P > Zn > Mg > S > Ca.

The Mo-coated piston ring tribosurfaces distinguish themselves by remarkably high interactive selectivity toward the element S. Also, in terms of high-to-low-selectivity order, the ranking is S >> P >> Ca > Zn = Mg for the Mo-coated tribosurfaces (both Mg and Zn experience almost no interaction). Such an order suggests that tribosurfaces of Mo-coated piston rings possess higher interactive selectivity toward non-metal atoms than toward metal atoms.

Generally, tribosurfaces of nitrided piston rings exhibit a little higher interactive selectivity towards ZDTP than towards the detergent, as suggested by the from-high-to-low-selectivity order that P > S > Ca > Zn = Mg.

In a similar way, inferences can be drawn from Fig. 7(b) for the interactive activity and selectivity between functional additive elements and tribosurfaces of cast iron cylinder liners. But more importantly, it is noted that even those functional additive elements assume different quantities on the cast iron tribosurfaces. An explanation is that the cast iron surfaces that were initially identical, have been modified by sliding.

In summary, since the operating parameters remain the same for all the tribosystems, the varied tribosurface activities should be attributed to the composition and structure of the coatings or permeated layers. This means that, under given tribological conditions, it might be possible to control the surface activity of the tribosurfaces in a positive way.

TRIBOCHEMICAL ACTIVITY OF TRIBOSURFACES TOWARD FUNCTIONAL ADDITIVE ELEMENTS

The characteristic residence of functional additive elements on the active tribosurfaces in a given tribosystem implies that there exists some specific chemistry that is dominating the chemical phenomena involved. Due to the paucity of tribocchemical data for triboelements, only approximate explanations can be made using general chemistry concepts. One popular approach is the attempted application of the Hard and Soft Acids and Bases (HSAB) Principle based on the Lewis acid-base concept (4), (8). For use of this principle in the cases concerned here, a schematic illustration of the interaction (for tribosurfaces) and selectivity (for functional additive elements) between the tribosurfaces and functional additive elements is shown in Fig. 8. The bold arrow, the richer the corresponding functional element residing on the designated tribosurface.

According to the Lewis acid and base concept, S and P are Lewis bases, and tribosurfaces of Cr, Mo and Ni are Lewis acids. In terms of electronegativity ($\chi$, which is directly proportional to the electronic affinity, E.A.) and atomic size, S is a softer Lewis base than P; Mo is a softer Lewis acid than Cr and Ni when estimated by their ionization potentials (IP) and atomic sizes. In light of the HSAB principle, S tends to react more with the Mo + NiCrBSi tribosurface than with the Cr-plated tribosurface, and P tends to react more with the Cr-plated tribosurface than with the Mo + NiCrBSi tribosurface. Thus, it can be summarized that among the non-metal functional additive elements, those with higher electronegativity and larger atomic size show stronger selectivity onto the tribosurfaces whose major constituent elements possess higher ionization potential and larger atomic size.

As the tribocchemical status of nitrided tribosurfaces is not clear, the interaction between the elements S or P and the nitrided tribosurface is not easily understood. However, as more P than S resides on the nitrided tribosurface, it is presumed that Fe assumes a lower positive electronic state in the running-in and thus tends to complex more with P, which is less electronegative than S, and Fe has corresponding chemical hardness similar to the lower positive electronic state.

It is immediately evident that the inference drawn above cannot be applied to the distribution of S and P on the cast iron tribosurfaces.

In terms of inherent thermochemical activity, the cast iron tribosurfaces should behave the same toward S or P, without regard to their tribonates of different chemical identity. It is noted, however, that the tribosurfaces of cast iron cylinder liners exhibit different activities towards the same functional elements, either S or P, from ZDTP, as indicated in Fig. 8(b). Thus, it is inferred that, in spite of the contributions from the thermodynamic properties of the tribosurfaces, interactions between tribosurfaces and functional additive elements are more dependent on the tribocchemical activity acquired in situ by the tribosurfaces. By comparing the complexation tendency of S and P on the cast iron tribosurface shown in Fig. 8(b), it can be surmised that Fe will become more ionized when in tribocchemical interaction with the Mo + NiCrBSi tribosurface of stronger total ionization tendency.

SUMMARY

Using a commercial mineral based API SI/SAE 5W-30 engine oil, a series of breaking-in friction experiments employing a reciprocating tribotester was conducted under simulated engine conditions with actual gasoline engine piston rings (Cr-plated, Mo+NiCrBSi-coated and nitrided) and cast iron cylinder liner combinations. Surface analysis results by EDX can be summarized as follows:

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1. Tribosurfaces of both the piston rings of different chemical nature (Cr-plated, Mo-coated and nitrided) and the cast iron cylinder liner demonstrate higher activity toward the antiwear agent ZDTP than they do toward the Mg- and Ca-containing detergents. This allows ZDTP to interact preferentially with activated tribosurfaces to provide in situ boundary film lubrication under severe operating conditions.

2. Almost the same activity toward ZDTP is demonstrated for the tribosurfaces of all the studied piston rings when they are mated with the same cast iron cylinder liners. In comparison, tribosurface activity of the cast iron cylinder liners towards ZDTP is invariably higher than that of each of its tribonate surfaces, namely, the piston ring tribosurfaces.

3. Stronger interaction occurs between the alloy tribosurfaces and the non-metallic functional additive elements (e.g. S and P) when they act as Lewis acids and Lewis bases, respectively, and exhibit similar hardness or softness.

4. It is the tribocochemical activity of tribosurfaces that governs the characteristic residence and distribution of functional additive elements. It is suggested that the tribocochemical activity of a tribosurface be imparted by both the thermodynamic properties of the tribomaterials and the triboprocess in which they are involved in a given tribosystem.

5. Detergent types (Mg, Ca) exhibit different preferential residence on tribosurfaces having a differing chemical nature (this effect is under investigation). Structurally specific detergents are needed to clarify their lower selectivity, as compared to ZDTP, toward tribosurfaces on the one hand, and differences in the preferential residence between different alkaline-earth metallic detergents on the other hand.

CONCLUSIONS

The surface interaction mechanisms of engine oil additives with piston ring/cylinder liner components under lubricated breaking-in conditions are critical to our engineers and research scientists to understand engine oil additive chemistry and fundamental friction-reducing mechanisms. The improved surface engineering approaches described in this paper can help powertrain design engineers to identify quickly and inexpensively candidate engine materials and energy-conserving lubricants that will improve fuel economy, reduce wear, and consequently help avoid federal penalties.

REFERENCES

(3) Yamaguchi, E. S. and Ryason, P. R. (1996), "Structures of Adsorbed Zinc Dithiophosphates and Their Relationship to Engine Wear," Tribology, 3-2, pp 123-135.