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Thesis Outline

Chapter 1: Introduction

In order to improve fuel efficiency for automobiles, it is necessary to reduce undesirable friction loss in automotive engine components by using low viscosity engine oil. Besides, in order to maintain or improve antiwear performance by using the low-viscosity engine oil, it is also necessary to clarify the effects of coexisting additives on the formation and the friction and wear-reducing performance of tribofilms from the low-viscosity oil. The coexistence effects between different additives and ZnDTP are discussed. However, most of these effects are only discussed when there are only two additives: ZnDTP and coexisting additives. In fully formulated oils containing a wider variety of additives, the impact of each additive on ZnDTP remains unclear.

In this study, focusing on polymethacrylate (PMA)-series friction modifiers, also used as viscosity modifiers, the formation of tribofilm and its friction and wear characteristics was investigated based on tribochemical reactions among various additives such as ZnDTP, MoDTC, and PMA-series friction modifiers, to achieve reduction in friction with the low-viscosity engine oil. Several kinds of PMAs having different functional poler groups were added to the engine oil, and then friction tests and several kinds of surface analyses were conducted to evaluate the promotive and inhibitive effects of several PMAs having different poler groups on the friction and wear-reducing performances of ZnDTP and MoDTC containing in the engine oil. In addition, all experimental data were used to construct a linear regression model by calculating the Pearson coefficient to reveal the relation between the chemical composition of tribofilm and the friction reducing performance.

The specific research content of this paper is described below.

1. Investigation of the tribofilm formation and frictional properties of low-viscosity engine oils
2. Effects of multiple coexisting additives on tribofilm formation in fully

formulated low viscosity oil

3. Effect of polar groups on low viscosity lubricants in the presence of friction modifiers
4. Statistical analysis of tribofilms formed in low viscosity engine oils

Chapter 2: Effect of additive combinations on the tribofilm formation and the friction and wear reducing performance of fully formulated 0W-8 oil

As discussed in Chapter 1, to achieve fuel efficiency requirements, an effective way is reducing the viscosity. As the viscosity of the oil decreases, lubricating additives such as friction modifiers and EP agents become more important to ensure low friction and wear. As the main antiwear and EP additive, ZnDTP possibly shows some kinds of synergistic or antagonistic effects with other coexisting additives in lubricating oil. There have been numerous studies conducted to understand the interaction between ZnDTP and other additives as dispersants, detergents, and friction modifiers. However, these interactions were found under binary additive conditions which were ZnDTP and other additives. Since fully formulated (FF) oil is formulated with various types of additives added to base oil, it is necessary to elucidate the coexisting effects of multiple additives on ZnDTP-derived tribofilm formation under conditions close to full formulation.

On the other hand, since 0W-8 oil is a relatively new oil grade, there have not been much research on 0W-8 engine oil. In this study, six kinds of 0W-8 grade engine oil were used to evaluate the effect of different coexisting additive combinations on ZnDTP film formation. Which are 0W-8 engine oil according to the presence or absence of detergent, dispersant, and MoDTC as friction modifier. In order to investigate the formation of tribofilm and its frictional properties, we used a self-made rolling and sliding friction tribometer. After the friction test, wear track formed on the disk were observed using a laser confocal microscope (VK-X250, KEYENCE). In order to investigate the element distribution within the wear scar, elemental mapping was measured using an electron beam probe microanalyzer (EPMA, JXA-8200, JOEL). XPS (PHI5000 Versa Probe, ULVAC-PHI) analysis was used to determine chemical species of the tribofilms.

As results, Ca-based detergent in fully formulated 0W-8 oil showed the antagonistic effect on ZnDTP and MoDTC-derived tribofilm. Dispersant showed the antagonistic effect in fully formulated 0W-8 oil without MoDTC while showed some synergistic effect on ZnDTP-derived tribofilm formation with the presence of MoDTC. Under different additive combinations, the addition of MoDTC had different effects on the ZnDTP-derived tribofilm formation.

Chapter 3: The tribofilm formation and the tribological characteristics of fully formulated 0W-8 oil in the coexistence with the functionalized polymethacrylate

Zinc dialkyldithiophosphate (ZnDTP) is widely used in automotive engine oil as an anti-wear and antioxidant additive. However, because of the poisoning on the exhaust gas purification catalyst and high friction, there has been a strong requirement to reduce the amount of ZnDTP in engine oil. Since it is difficult to find a substitute for ZnDTP, it is important to find a coexisting additive that can remain even promote the formation of ZnDTP-derived anti-wear tribofilm and elucidate the coexisting effect with ZnDTP.

Polymethacrylate (PMA) has been used as a VM to improve viscosity under high temperature condition. PMA, composed of functionalized polar groups such as carboxyl, hydroxyl and amino groups, can be easily adsorbed on metal surfaces, resulting in a thicker, more viscous boundary film. Previous studies by the authors discussed the effects of functionalized PMA on ZnDTP-derived tribofilm formation. The results showed that amino-derived compounds reduced tribofilm formation and increased sulfur content in the tribofilm, whereas carboxyl-derived compounds reduced the friction coefficient while maintaining the formation of tribofilm. However, these findings were obtained only between ZnDTP and functionalized PMAs. It is necessary to clarify the effects of functionalized PMA as coexisting additives in complex conditions as fully formulated oil.

According to the results in Chapter 2, with the increase in the types of additives in 0W-8, the friction and wear of fully formulated oil without FM increased significantly. In this chapter, Oil-A was used to discuss the effects of functionalized PMA as coexisting additives in fully formulated oil. Five kinds of oil were used to evaluate the effect of PMA-series polar compounds in fully formulated 0W-8 oil. Then, time change experiment of those samples were tested.

As results, PMA with functionalized groups significantly increased the uniformity of the tribofilm and reduced the friction coefficient and wear in fully formulated oil. PMA with functionalized groups showed stronger promotional effects on ZnDTP-derived tribofilm formation in fully formulated oil than in base oil. However, those PMAs could not prevent other coexisting additives from damaging the formation of ZnDTP-derived deposited tribofilm. The addition of PMA-OH and PMA-COOH generated longer polyphosphate chain length, more calcium and less sulfur and zinc could significantly reduce friction and wear. The addition of PMA-N generated longer polyphosphate chain length in earlier period to significantly reduce friction and wear. While with the coordination complex formation during further friction, the anti-wear tribofilm lost the durability.

Chapter 4: Effect of friction modifiers with polar group on tribofilm formation and the tribological characteristics of the fully formulated 0W-8 oil

Friction modifiers (FMs) are widely used in engine oil to reduce friction. Friction modifiers can be categorized as organic or inorganic. The inorganic friction modifiers are organomolybdenum-type such as MoDTC which formed low shear strength compounds in sliding contacts to reduce friction. The interaction between ZnDTP and FMs has been widely discussed. Since the additives in a base oil have complex synergistic and antagonistic interactions with each other, it is necessary to study the interaction between ZnDTP and FMs under fully formulated oil condition.

Chapter 3 discussed the effect of PMA-series polar compounds on the formation of tribofilm and their tribological characteristics in fully formulated 0W-8 oil containing no friction modifier. The findings indicated that PMAs showed synergistic and antagonistic effect on them dependent on the kind of functional groups. It is necessary to verify whether polar groups of low molecular organic compounds except for PMAs exhibited the similar effects in order to understand the role that PMAs plays in the fully formulated 0W-8 engine oil. In this chapter, three kinds of low molecular organic compounds that act as FM were prepared for the addition to Oil-A. Those were N-Dimethyloctadecylamine (DMODA) which has amino group, Glycerinmonoolate (GMO) which has hydroxy group and Oleic Acid (Ola) which has carboxy group.

In addition, the interaction between ZnDTP and MoDTC has been introduced in Chapter 1. Due to the competitive adsorption between ZnDTP and MoDTC on metal surfaces, there are possibility that the addition of MoDTC hinders the growth of ZnDTP-derived tribofilm. ZnDTP might provide sulfur to form MoS_2 from MoS_2-xOx, leading to increased formation of MoS_2 instead of MoO_3. In Chapter 2, the interaction between ZnDTP and MoDTC in fully formulated 0W-8 oil were discussed. In this chapter, the effects of functionalized PMA on tribofilm formation and the tribological characteristics of the fully formulated 0W-8 oil containing MoDTC will be discussed.

As results, polar group could increase polyphosphates chain lengths in fully formulated 0W-8 oil both organic and inorganic friction modifiers. DMODA and ola showed complex effect that chain length of polyphosphates increased while P, Zn and S from ZnDTP-derived tribofilm were reduced. GMO show synergistic effect in fully formulated 0W-8 oil that increased polyphosphates chain lengths while promote FeS/FeS2 formation which significantly increasing sulfur and maintained the intensity of other elements from ZnDTP-based tribofilm. However, more sulfur reduces lubrication ability. PMA with and without functionalized groups significantly increased the length of polyphosphate chain to have thicker deposited films in fully formulated oil with MoDTC. While the addition of PMA-OH and PMA-COOH reduce sulfur in fully formulated 0W-8 oil which reduced the ratio of MoS_2

Chapter 5: Statistical analysis on the correlation between the elemental intensity of tribofilms and the corresponding coefficients of friction obtained with fully formulated 0W-8 engine oils

In Chapter 2, by conducting tribological experiments, it was discussed the effects of multiple coexisting additives on tribofilm formation in fully formulated 0W-8 oil. In Chapter 3, change in chemical structure of tribofilm by addition of PMA-series polar compounds was evaluated, and then the effect of polar groups including in FMs and PMAs on tribofilm formation and tribological characteristics of the 0W-8 oil in chapter 4. However, those results for each set of formulations were discussed separately. All data need to be discussed as a whole in order to discover common findings and knowledges through all experiments.

Pearson's linear correlation coefficient (r), as the most commonly used linear correlation coefficient, has been widely used in various types of research fields, such as geophysics, transportation, optics, etc. Linear logistic regression as a data-driven method enables exploration of multiple variables and provides an advanced explanation. In this chapter, the experimental data obtained from the previous chapters will be analyzed statistically. From a statistical point of view, the relation between the intensity of each element and the friction in the generated lubricating film was clarified.