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Research  
Report

## TOF-SIMS Analysis of Lubricant Additives Adsorbed on a Ferrous Material

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### Abstract

The adsorption of model compounds of lubricant additives onto ferrous materials was investigated using time-of-flight secondary ion mass spectrometry (TOF-SIMS). Nineteen types of model compounds, including phosphates, carboxylic acids, alcohols, amines, and esters, were subjected to lubrication tests. The TOF-SIMS spectra of the friction surfaces after hexane washing indicated that amines were physically adsorbed, carboxylic acids and esters were chemically adsorbed, and phosphates were tribochemically reacted onto friction surfaces.

For alcohols, which showed no lubricity, no adsorbed component was detected on the friction surfaces by TOF-SIMS. From the results of investigation of correlation between the TOF-SIMS data and lubrication properties, it was possible to discuss the relationships between the results of TOF-SIMS analysis and lubrication properties such as friction coefficient and wear scar width when making comparisons among similar types of lubricant additives or investigating chemical changes of friction surfaces during lubrication tests.

Keywords

Time-of-flight secondary ion mass spectrometry (TOF-SIMS), Lubrication, Friction surface, Adsorption, Lubricant additives, Tribochemical reaction

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## 1. Introduction

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Lubricant additives, which are added to oils, are known to function by forming an organic and/or inorganic thin film on friction surfaces.<sup>1)</sup> Information concerning the structures of these thin films is extremely important in the analysis of lubrication mechanisms. Conventionally, such information has been obtained through the use of surface analysis techniques, such as x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and reflection infrared spectroscopy.<sup>2-6)</sup> However, these techniques are insufficient for the analysis of the organic chemical structures of monolayer thin films formed on friction surfaces.

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a technique not only suitable for the analysis of thin films, as with XPS or AES, but can also provide information about organic chemical structures.<sup>7)</sup> Accordingly, several studies on the adsorption of a lubricant on a friction surface using TOF-SIMS have been published in recent years, and these studies have verified the suitability of TOF-SIMS for the analysis of friction surfaces.<sup>8, 9)</sup> However, there are few published TOF-SIMS data concerning the chemical adsorption of a lubricant on a friction surface.

Recently, the authors published a series of results concerning TOF-SIMS analysis of eight types of phosphate-type lubricant additive model compounds, eleven types of friction modifier model compounds, and mixtures thereof adsorbed and/or reacted onto the friction surfaces of ferrous base materials.<sup>10-12)</sup> These reports demonstrated that the model compounds were reacted or adsorbed onto the ferrous base materials and formed lubrication films containing these reacted or adsorbed compounds, and that these films affected lubrication properties such as friction coefficient and wear scar width.

This report describes the possibilities of TOF-SIMS analyses for the identification of the chemical structures of lubricant additives adsorbed on friction surface, and for the evaluation of lubricating properties, by providing an overview of the results of these studies.

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## 2. Experiments

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### 2.1 Reagents

The lubricant additive model compounds used for this study included eight phosphates, four carboxylic acids, two amines, three esters and two alcohols. All of the compounds were commercially available reagents purchased from Tokyo Kasei Corporation. The model compounds were dissolved in a paraffinic mineral oil (base oil) for the lubrication tests.

### 2.2 Lubrication tests

The lubrication tests were performed using a Faville-Levally ring-on-block friction test instrument with a load of 230 N, a friction speed of 1.8 m/s, and a temperature of 80 °C for 60 min. Both the test blocks and test rings, which were purchased from Faville-Levally, were made of ferrous material (SAE 01 Steel). Friction coefficient was monitored during the test and the width of the wear scar on the blocks was evaluated using an optical microscope after the test. The friction surfaces of the tested blocks were washed with n-hexane prior to the TOF-SIMS measurements in order to remove unreacted or unadsorbed additives and base oil.

### 2.3 TOF-SIMS measurements

The TOF-SIMS measurements were performed using a Physical Electronics TFS-2100 (TRIFT 2) instrument. High mass resolution spectra of  $M/\Delta M > 5000$  at  $m/z = 27$  ( $C_2H_3^+$ ) or  $m/z = 25$  ( $C_2H^-$ ) were acquired using bunched  $^{69}Ga^+$  ion pulses with an impact energy of 15 keV, an ion current of 600 pA (d.c. current equivalent) for one pulse, a pulse width of 14 ns (700 ps after bunching) and a pulse frequency of 10 kHz. The measured mass range was  $m/z = 5-1000$ . The total ion doses in these measurements were approximately  $< 1 \times 10^{12}$  ions/cm<sup>2</sup>.

The positive and negative TOF-SIMS spectra were obtained for the friction surfaces and non-friction surfaces after lubrication tests, and for the model compounds held on silicon wafers or indium foils.

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## 3. Results and discussion

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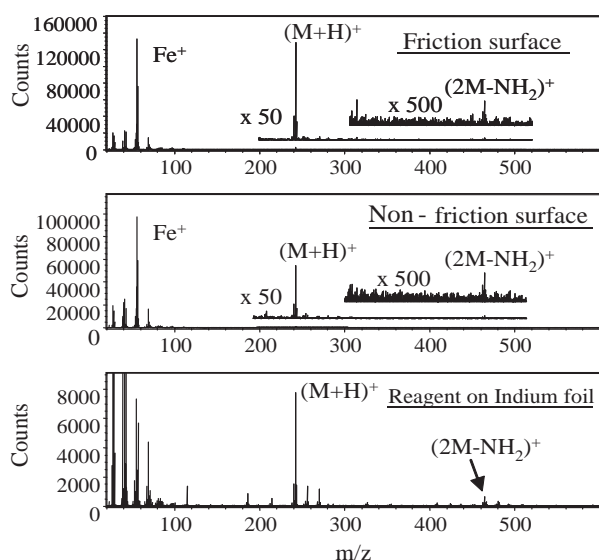
### 3.1 Identification of lubricants

It was determined based the TOF-SIMS spectra of the friction surfaces obtained that lubricant additive adsorption could be classified into three types, i.e.,

physical adsorption, chemical adsorption, and tribochemical reaction. Typical examples of TOF-SIMS spectra obtained for each of the three types from the measurement of friction surfaces are shown in Figs. 1 to 3.

**Figure 1** shows the TOF-SIMS spectra of n-hexadecylamine obtained from a friction surface, a non-friction surface, and indium foil. A quasi-molecular ion, i.e.,  $(M+H)^+$  at  $m/z = 242$ , and a dimer ion, i.e.,  $(2M-NH_2)^+$  at  $m/z = 465$ , which indicates the presence of interaction between amine molecules, were detected in the positive ion spectra for the friction surface and the indium foil.  $(M+H)^+$  was detected in the spectrum for the non-friction surface of the test block as well. These results suggest that n-hexadecylamine was physically adsorbed onto the ferrous base material without undergoing any changes in molecular structure.

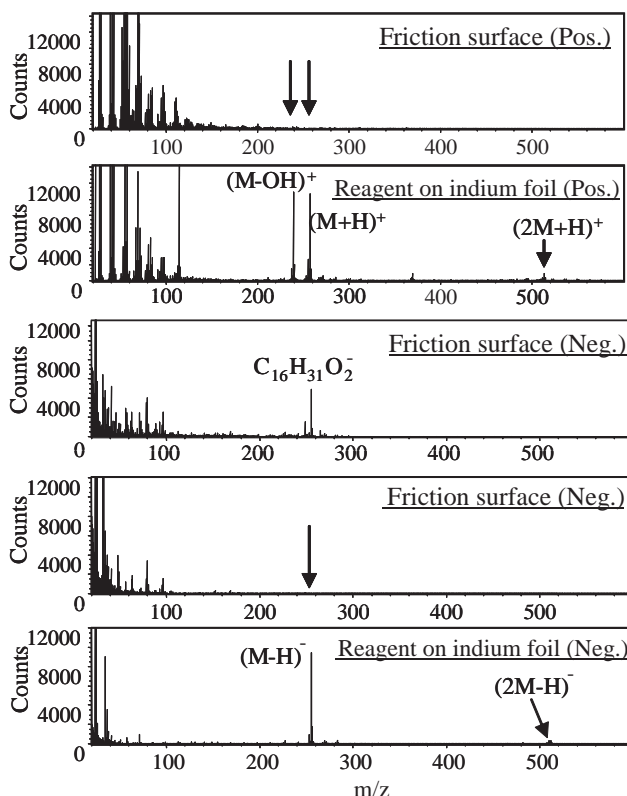
**Figure 2** shows the TOF-SIMS spectra of palmitic acid obtained from a friction surface, a non-friction surface, and indium foil. The TOF-SIMS positive spectrum of palmitic acid carried on In foil showed  $(M+H)^+$  at  $m/z = 257$ ,  $(M-OH)^+$  at  $m/z = 239$ , and  $(2M+H)^+$  at  $m/z = 513$ , which indicates the presence of interaction between the reagent



**Fig. 1** TOF-SIMS spectra of the friction surface tested with n-hexadecyl amine and of the reagent carried on indium foil.

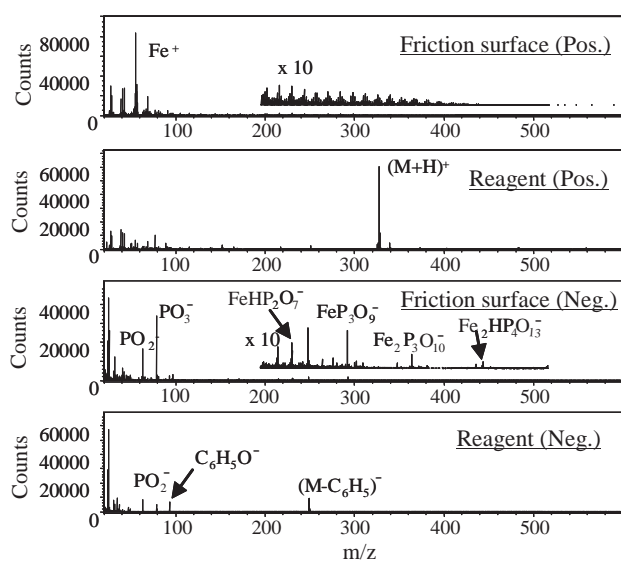
molecules, and the negative ion spectrum showed  $(M-H)^-$  at  $m/z = 255$  and  $(2M-H)^-$  at  $m/z = 511$ . In contrast, the dimer ion  $(2M-H)^-$  at  $m/z = 511$  was not detected in the TOF-SIMS spectra for the friction surface, as in the negative ion spectrum, although  $(M-H)^-$  was detected as in the spectrum for the indium foil and  $(M+H)^+$  and  $(M-OH)^+$  were not detected in the positive ion spectrum. It is well known that carboxylic acids form dimers via strong hydrogen bonding between two carboxyl groups. Therefore, the nondetection of the dimer ion  $(2M-H)^-$  in the spectra for the friction surface indicates that the molecules were in a different state on the friction surface than on the indium foil. These results indicate that the palmitic acid was chemically adsorbed onto the ferrous base material, forming Fe-palmitate under the conditions of lubrication.

**Figure 3** shows the TOF-SIMS spectra of triphenylphosphate obtained from the friction surface and a silicon wafer.  $(M+H)^+$  at  $m/z = 327$ ,



**Fig. 2** TOF-SIMS spectra of the surface of the block tested with palmitic acid and of the reagent carried on indium foil.

which was intensely detected in the spectrum for the silicon wafer, was not detected in the positive ion mass spectrum. This would indicate that no physical adsorption occurred in this lubricant system. Apart from fragment ions originating from lubricants, complex ions of the high-mass region, consisting of  $\text{PO}_3^-$  and Fe, FeO, or FeOH, such as  $(\text{FeHP}_2\text{O}_7)^-$  at  $m/z = 231$ ,  $(\text{FeP}_3\text{O}_9)^-$  at  $m/z = 293$ ,  $(\text{Fe}_2\text{P}_3\text{O}_{10})^-$  at  $m/z = 365$ , and  $(\text{Fe}_2\text{HP}_4\text{O}_{13})^-$  at  $m/z = 445$ , were clearly detected in the negative ion mass spectrum.



**Fig. 3** TOF-SIMS spectra of the friction surface tested with triphenylphosphate and of the reagent on silicon wafer.

**Table 1** Results of TOF-SIMS analysis and lubricity for 11 model compounds.

Model compounds	Lubricity	Secondary ion species	Adsorbing form
Palmitic acid	○	$(\text{M}-\text{H})^-$ , $(\text{M}+\text{Fe}-\text{H})^+$	Chemical
Oleic acid	○	$(\text{M}-\text{H})^-$ , $(\text{M}+\text{Fe}-\text{H})^+$	Chemical
2-Hydroxypalmitic acid	○	$(\text{M}-\text{H})^-$	Chemical
16-Hydroxypalmitic acid	⊙	$(\text{M}-\text{H})^-$	Chemical
n-Hexadecyl amine	×	$(\text{M}+\text{H})^+$ , $(\text{M}+\text{FeOH})^+$	Physical
Oleil amine	○	$(\text{M}+\text{H})^+$	Physical
Methyl palmitate	×	$(\text{M}-\text{CH}_3)^-$ , $\text{CH}_3\text{OFe}^+$	Chemical
Methyl oleate	×	$(\text{M}-\text{CH}_3)^-$ , $\text{CH}_3\text{OFe}^+$	Chemical
Glycerol monooleate	○	$(\text{M}-\text{Glycerol})^-$ , $\text{CH}_3\text{OFe}^+$	Chemical
1-Hexadecanol	×	Not detected	-
Oleil alcohol	×	Not detected	-

These ions were detected in all of the phosphate-type lubricant systems and are proposed to be fragment ions of Fe-polyphosphates produced by reaction between the phosphate units of the lubricants and the ferrous base material. In the positive spectra, Fe-alcoholate, which is considered to be a reaction product of an alcohol unit of a lubricant and the ferrous base material, was detected for all of the phosphate-type lubricant systems.  $\text{C}_6\text{H}_5\text{OFe}^+$  was detected in the spectra of phenyl ester systems and  $\text{CH}_3\text{OFe}^+$  was detected in the spectra of butyl ester systems. The number of these ions detected is proposed to be an indicator of the reaction probability of a lubricant with a ferrous base material, which is correlated with friction properties.

## 3.2 Correlation with lubrication properties

### 3.2.1 Comparison among different types of lubricants

Since the amounts of adsorbed molecules detected by TOF-SIMS are thought to indicate the lubricity of the lubricant additives, these amounts are assumed to be correlated with friction properties. **Table 1** shows the results of TOF-SIMS analysis of 11 types of model compounds with their lubricity. When the chemical structures of adsorbed molecules differ with each lubricant, as in the present study, it is extremely difficult to use TOF-SIMS data to compare the amounts of adsorbed material seen with each lubricant and to discuss the relationships between the amounts of adsorbed material and lubricant properties, as ionization efficiency is dependent on chemical structure.

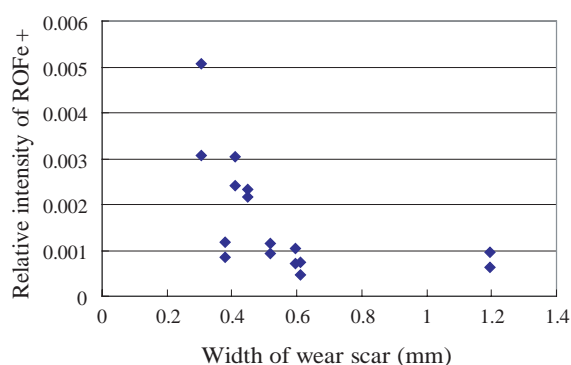
### 3.2.2 Comparison among similar types of lubricants (eight phosphates)

As mentioned in the previous section, the same compounds were formed on the friction surfaces for all phosphate systems, and it is possible to propose, based on TOF-SIMS analysis, that the ionization efficiencies of the reaction products were the same for all systems. Therefore, it is possible to compare the ion intensities of the products formed with each phosphate system and to discuss the relationships between the amounts of products formed and the lubrication properties. **Figure 4** shows the correlations between  $\text{CH}_3\text{OFe}^+$ ,

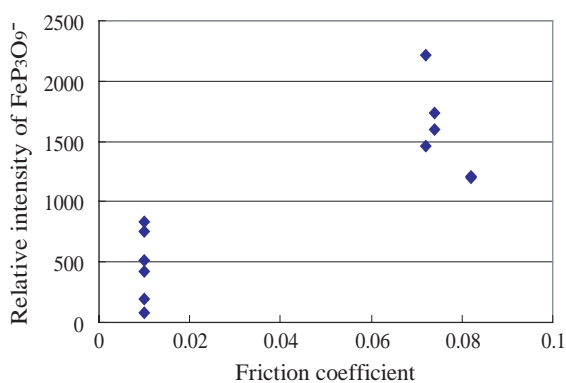
$C_6H_5OFe^+$ , and  $FeP_3O_9^-$  and friction coefficient or wear scar width. This figure shows that the amount of  $FeP_3O_9^-$  present tended to be large in lubrication systems whose friction coefficient was large and that the amounts of  $CH_3OFe^+$  and  $C_6H_5OFe^+$  were inversely correlated with wear scar width.

### 3. 2. 3 Chemical changes to friction surfaces during lubrication tests

As mentioned above, it is possible to discuss the relationships between amounts of products formed and lubrication properties for the same products. Therefore, it is also possible to investigate changes in ion intensities over the course of testing time for the same mixture system. As an example, we focused on a mixture of tri-n-butylphosphite and palmitic acid and investigated the changes in ion intensities by TOF-SIMS analysis of friction



(a)



(b)

**Fig. 4** Relationships between relative intensities of ions originating from reacted or adsorbed compounds and lubricities.

(a)  $[ROFe^+]$  versus width of wear scar

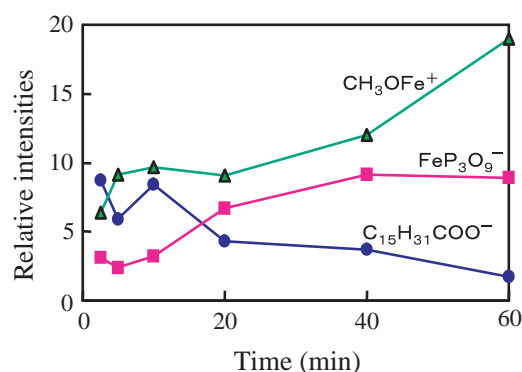
(b)  $[FeP_3O_9^-]$  versus friction coefficient

surfaces 2.5, 5, 10, 20, 40, and 60 min after starting the test. **Figure 5** shows the relative intensities of  $C_{15}H_{31}COO^-$ ,  $FeP_3O_9^-$ , and  $CH_3OFe^+$  plotted against testing time. Based on the results shown in Fig. 4, it is assumed that  $C_{15}H_{31}COO^-$  and  $CH_3OFe^+$  originate from lubrication films that function by reducing the friction coefficient and that  $FeP_3O_9^-$  originates from Fe-polyphosphate, which increases the friction coefficient. In Figure 5, the amount of  $C_{15}H_{31}COO^-$ , which indicates the chemical adsorption of palmitic acid, was largest at the early stages of the test but decreased with testing time. Conversely, the amounts of  $FeP_3O_9^-$  and  $CH_3OFe^+$ , which indicate phosphate component reactions, were relatively small at the early stages of the test and increased with testing time. It can therefore be assumed that the behavior of  $C_{15}H_{31}COO^-$  and  $FeP_3O_9^-$  functioned to increase the friction coefficient with testing time and that the behavior of  $CH_3OFe^+$  functioned to reduce it.

## 4. Conclusion

The adsorption or reaction of lubricant additives onto ferrous material was investigated by TOF-SIMS analyses of the friction surfaces. The following conclusions were obtained.

- (1) For all types of lubricant additives, with the exception of alcohols, fragment ions originating from adsorbed additives were detected by TOF-



**Fig. 5** Changes in relative intensities of ions originating from reacted or adsorbed compounds during the lubrication test using a mixture of tri-n-butylphosphite and palmitic acid.

SIMS analysis of friction surfaces.

- (2) The forms of adsorption can be classified into three types, i.e., physical adsorption, chemical adsorption, and tribochemical reaction.
- (3) It is possible to discuss the relationships between the results of TOF-SIMS analysis and lubrication properties when making comparisons among similar types of lubricant additives or when investigating chemical changes of friction surfaces during lubrication tests.

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