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Research Report

TOF-SIMS Analysis of Engine Oil Additives Adsorbed onto Friction Surfaces

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Report received on Oct. 20, 2011

ABSTRACT This report describes the analytical results of friction surfaces tested in engine oils containing typical additives such as polyisobutenyl succinimide, Ca-sulfonate, Zn-dithiophosphate, and Mo-dithiocarbamate by time-of-flight secondary ion mass spectrometry (TOF-SIMS). Two types of lubricating oil containing the above additives as models for real engine oils were prepared. The test specimens used were stainless steel (SUS) blocks and SUS blocks hard-coated with chromium nitride or titanium nitride. The TOF-SIMS results showed that the adsorption behavior of the additives on the test blocks was strongly influenced by the oil components and the friction surface materials. The results suggest that the difference in friction coefficient among engine oils and sliding materials can be explained by the adsorption properties of Mo-dithiocarbamate.

KEYWORDS TOF-SIMS, Engine Oil, Lubricant Additives, ZnDTP, MoDTC, Friction Coefficient

1. Introduction

Lubricant additives which are added into oils are known to function by forming an organic and/or inorganic thin film on the friction surface, and understanding the structure of such a film is extremely important for the analysis of the lubrication mechanism. 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.[1-5] However, these techniques are insufficient for the analysis of the organic chemical structures of monolayer thin films formed on friction surfaces, because their main function is elemental analysis.

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a suitable technique for the analysis of thin films, as are XPS and AES, but TOF-SIMS can also provide information on organic chemical structures.[6] Accordingly, several studies using TOF-SIMS to examine the adsorption of a lubricant on a friction surface have been published, all of which have verified the suitability of TOF-SIMS for the analysis of friction surfaces.[7,8] Recently, the authors published a series of results concerning the TOF-SIMS analysis of eight kinds 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.[9-12] These reports demonstrated that the model compounds were reacted or adsorbed onto the ferrous base materials to form lubricating films, and that these films affected lubrication properties such as the friction coefficient and wear resistance. Subsequently, the authors have attempted to analyze lubrication phenomena in real-world friction surfaces lubricated with engine oils or automatic transmission fluids by TOF-SIMS. This report describes the results of TOF-SIMS analysis of friction surfaces tested in engine oil as a real-world sliding part used in the automobile industry.

2. Experimental

Friction tests using experimental engine oils or a simple additive system containing a single additive were performed. For the simple additive systems, Zn-dithiophosphate (ZnDTP), Mo-dithiocarbamate (MoDTC), Ca-sulfonate, and polyisobutenyl succinimide were used. Each additive was dissolved into a paraffinic base oil. For the experimentally prepared model engine oils, two types of model engine oil (A and B) were used. Engine oil A contained ZnDTP, Ca-sulfonate, and polyisobutenyl succinimide, in addition to the paraffinic base oil. Engine oil B contained MoDTC in addition to the same additives and base oil as engine oil A.

Friction tests were performed with a Faville-Levally ring-on-block-type friction test instrument under a normal load of 300 N, a sliding speed of 0.3 m/sec, and an oil temperature of 80°C for 0.5 hours. A schematic illustration of the lubrication test is shown in **Fig. 1**. The friction coefficient was evaluated at the end of each test. For the friction tests in simple additive systems, stainless steel (SUS) test blocks were used. The friction tests in model engine oil employed untreated SUS blocks and two types of hard-coated SUS blocks: SUS blocks coated with titanium nitride (TiN) or chromium nitride (CrN). The friction surfaces of the tested blocks were rinsed with n-hexane by immersing and shaking for about 1 minute in fresh solvent three times before the TOF-SIMS measurements.

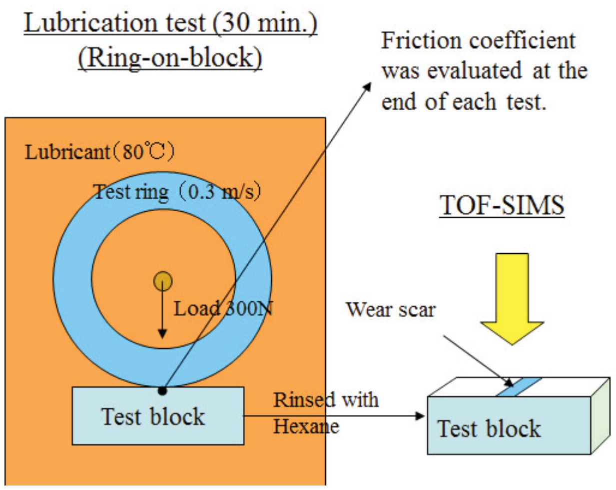

Fig. 1 Schematic illustration of the lubrication test and preparation for TOF-SIMS analysis.

TOF-SIMS measurements were performed with a Physical Electronics TFS-2100 (TRIFT2) instrument. High mass-resolution spectra of M/dM > 5000 at m/z 27 ($C_2H_3^+$) or m/z 25 (C_2H^-) were acquired using a bunched $^{69}Ga^+$ ion pulse with an impact energy of 15 keV, an ion current of 600 pA per pulse, and a pulse frequency of 10 kHz. The total ion dose in each of these measurements was approximately < 1×10^{12} ions/cm^2. High lateral-resolution images were acquired using an unbunched $^{69}Ga^+$ ion pulse with an impact energy of 25 keV.

3. Results and Discussion

3. 1 TOF-SIMS Spectra of Friction Surfaces Tested in Simple Additive Systems

Table 1 shows, for each additive system, the friction coefficient and the adsorbed components detected by TOF-SIMS. The results show that, for all of the additives, the adsorbed components originating from the additives were detected by TOF-SIMS measurements of the friction surfaces. For example, the TOF-SIMS spectrum of a friction surface for the ZnDTP system is shown in **Fig. 2**. As shown in Fig. 2, the spectrum of the friction surface was much different from that of ZnDTP on a silicon wafer. For example, molecular ions observed in the spectrum of ZnDTP on a silicon wafer were not detected on the friction surface, although fragment ions such as PS_2O^- and $C_9H_{20}O_2PS_2^-$ originating from the DTP component were detected. This result indicates that ZnDTP tribochemically reacted onto the SUS friction surface during the test. A similar result was obtained for

Table 1 Friction coefficient and detected secondary ions for each additive.

Additive	Friction coefficient	Detected ions originating from adsorbed components
ZnDTP	0.091	Zn^+, PSO_2^-, PS_2O^-, $C_9H_{20}O_2PS_2^-$
MoDTC	0.026	Mo^+, $C_{26}H_{56}N^+$, MoS_3^-,
Poly(isobutenyl) succinimde	0.082	Fragment ions from poly(isobutene) ($C_6H_{11}^+$,$C_7H_{13}^+$, etc), CNO^-
Ca-sulfonate	> 0.1	Ca^+, SO_3^-, $FeHSO_4^-$, $C_8H_7SO_3^-$, $C_{26}H_{45}SO_4^-$

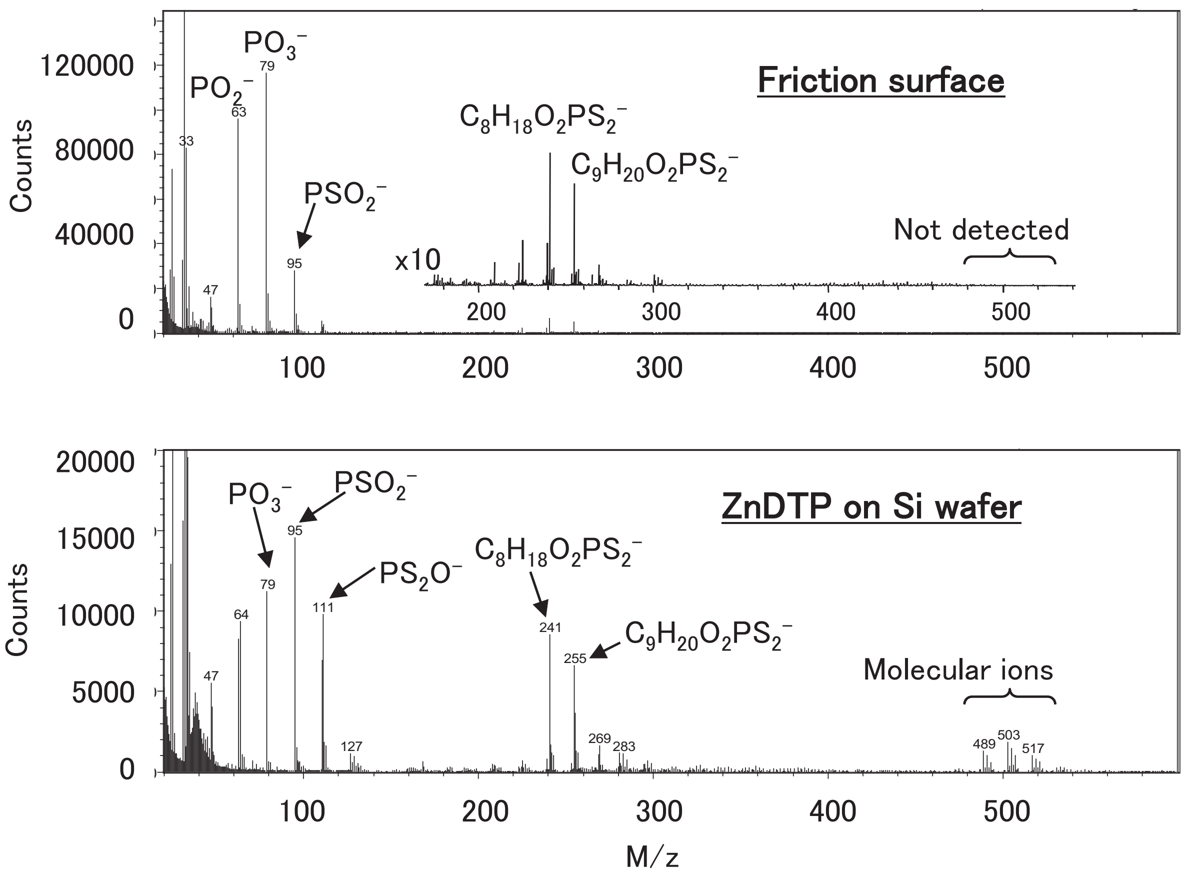

Fig. 2 Negative ion spectra of the friction surface of SUS tested in a ZnDTP simple system (upper) and for ZnDTP on a silicon wafer (lower).

MoDTC. Meanwhile, for succinimide and Ca-sulfonate, the spectra of the friction surfaces were similar to those of the reagents on a silicon wafer.

3. 2 Friction Coefficient for Each Model Engine Oil

Table 2 shows the friction coefficients 1 hour after the start of the friction tests. These results confirm that MoDTC reduced friction in all cases, although the effects of the addition of MoDTC on the friction coefficient differed among test blocks of different materials. In the case of TiN, the effect of added MoDTC was smaller than with other materials. The presumed cause of this result is the difference in adsorbing behavior of the additives among the different materials.

Table 2 Friction coefficient for each lubrication system.

Test block	Engine oil A	Engine oil B	Base oil
SUS	0.11	0.026	0.13
CrN	0.11	0.022	0.11
TiN	0.12	0.042	0.11

3. 3 Comparison of the Friction Surfaces between Model Engine Oils A and B

Figure 3 shows typical TOF-SIMS spectra of friction surfaces tested in engine oils A and B, and **Fig. 4** shows ion images of the representative secondary ions originating from adsorbed additives on the friction surfaces. For engine oil A, Ca^+ and $C_8H_7SO_3^-$ and other secondary ions originating from Ca-sulfonate, $C_7H_7^+$ and CNO^- originating from succinimide, and

Zn^{+} and $C_9H_{20}O_2PS_2^{-}$, etc. originating from ZnDTP were detected by TOF-SIMS analysis of the friction surface. Among these, Zn^{+} was detected only from the contact area. This result indicates that ZnDTP adsorbed onto the friction surface by tribochemical reaction. For engine oil B, on the other hand, Mo^{+}, MoO_3^{-}, and MoS_3^{-} originating from the MoDTC were clearly detected, whereas sulfonate ions originating from Ca-sulfonate were not detected. Furthermore, the yields of Zn^{+} and $C_9H_{20}O_2PS_2^{-}$ originating from ZnDTP were smaller than those from engine oil A. These results suggest that MoDTC adsorbed onto the top surface of the contact area prior to the other additives, and functioned as a friction modifier.

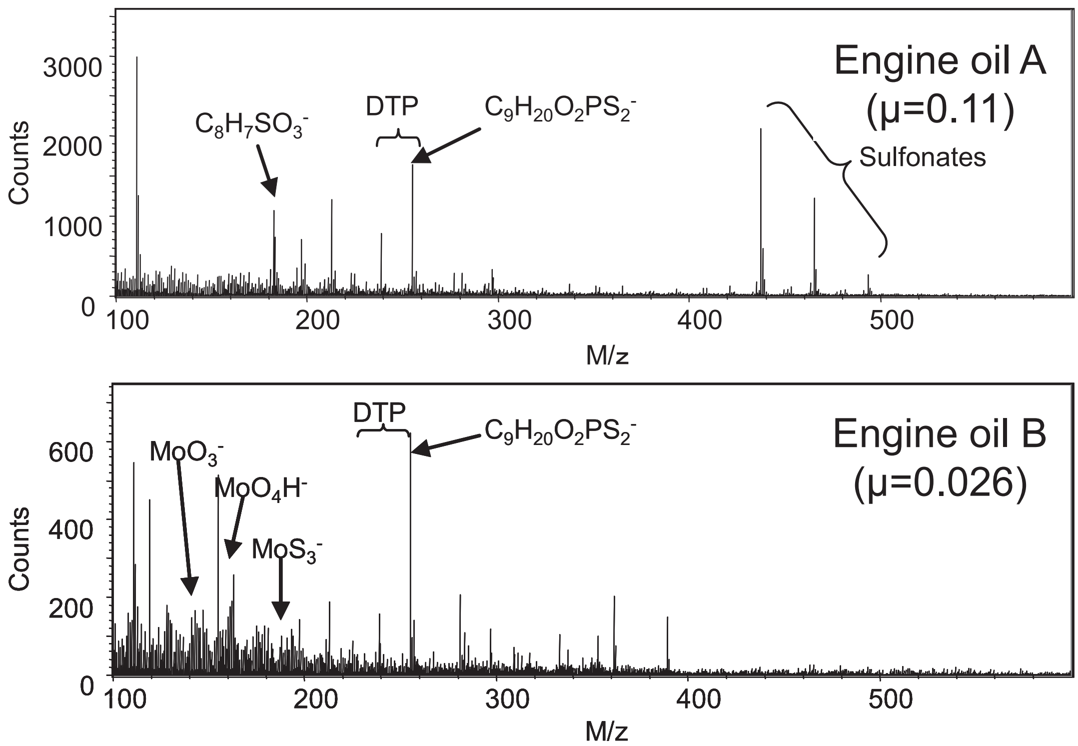

Fig. 3 Negative ion spectra of the friction surfaces of SUS test blocks, tested in engine oils A and B.

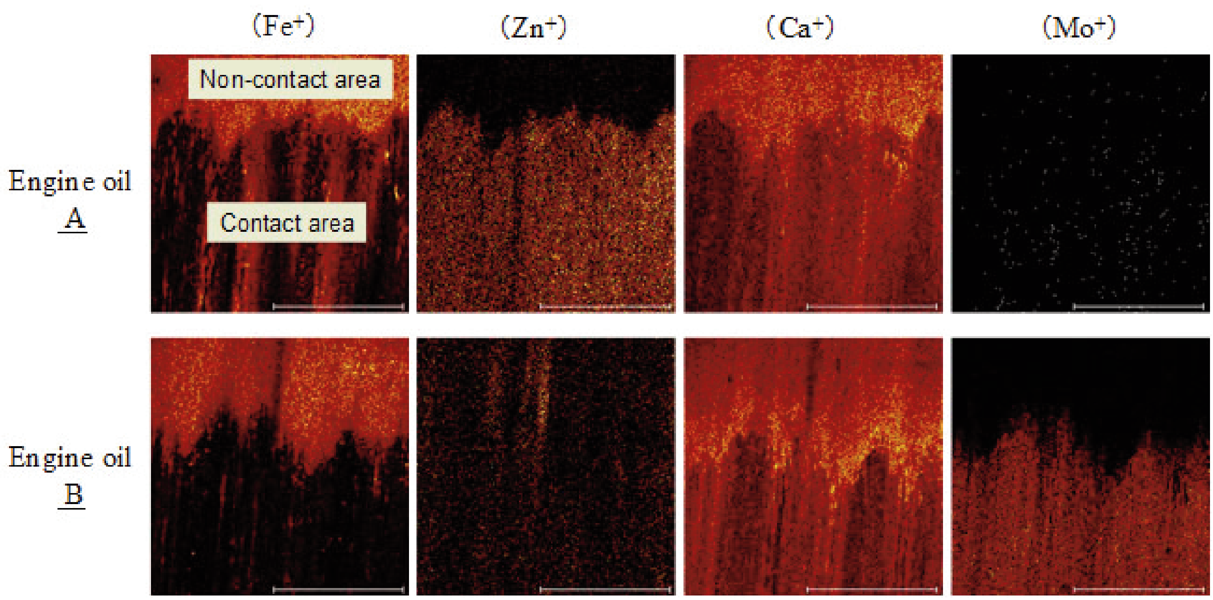

Fig. 4 Positive ion images of the friction surfaces of SUS test blocks tested in engine oils A and B. The field of view is 200 square microns.

3. 4 Comparison of Three Different Test Blocks

In the lubrication tests in engine oil B, as shown in Table 2, the friction coefficient of TiN was higher than that of the other test blocks. On the basis of the TOF-SIMS spectra of the friction surfaces shown in **Fig. 5**, the yield of Mo^+ and S^- from the TiN surface was found to be smaller than that from other materials. **Figure 6** shows positive ion images of the friction surfaces of three types of test blocks. As seen in these images, the distribution of Ca^+ and Mo^+ on the friction surface of TiN was different from that of SUS or CrN. On the SUS and CrN surfaces, Mo^+ was distributed only at the contact area and the distribution was rather homogeneous, and the Ca^+ yield at the contact area was smaller than that at the non-contact area. This result suggests that Mo compounds originating from MoDTC adsorbed onto the friction surfaces by tribochemical reaction prior to Ca compounds originating from Ca-sulfonate, and acted as a friction modifier. In the case of the TiN surface, on the other hand, Mo^+ was distributed only in the contact area as on CrN and SUS surfaces, but this distribution was not homogeneous. Moreover, the Ca^+ yield at the contact

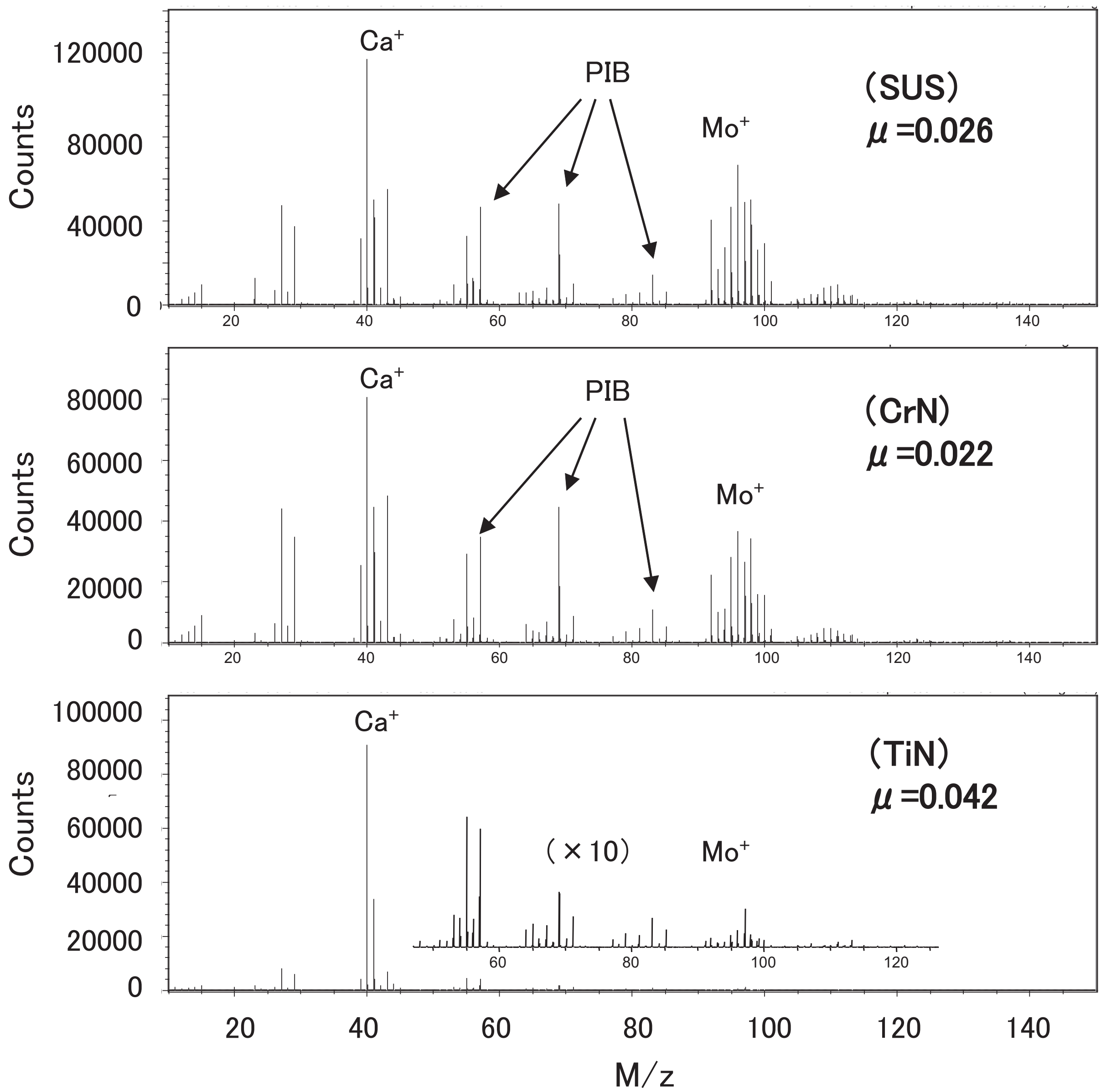

Fig. 5 Positive ion spectra of the friction surfaces of three types of test blocks tested in engine oil B.

area was higher than that of the non-contact area. These results suggest that Ca compounds adsorbed onto the TiN surface prior to Mo compounds, and partially inhibited the performance of MoDTC as a friction modifier.

Although the reason for the differences in adsorbing behavior among the materials has not been completely clarified, the adsorbing behaviors are thought to be affected by affinities between the additives and materials.

4. Conclusions

(1) The friction reducing effect and the adsorbing behavior of typical lubricant additives in engine oil were clarified by friction tests and TOF-SIMS analysis of friction surfaces.

(2) It was found that MoDTC adsorbed onto the top surface of the contact area, forming MoS_2 prior to other additives such as ZnDTP, reducing the friction coefficient. However, the effects of the addition of MoDTC on the friction coefficient differed among the examined test block materials.

(3) The friction reducing effect was found to be correlative with the amount of MoDTC adsorbed on the friction surface. The amount of adsorbed MoDTC on the friction surfaces of SUS and CrN, which showed smaller friction coefficients, were larger than that on the friction surface of TiN.

(4) From above results, it was confirmed that TOF-SIMS is a powerful tool for the analysis of real-world lubrication phenomena occurring on friction surfaces lubricated with engine oils.

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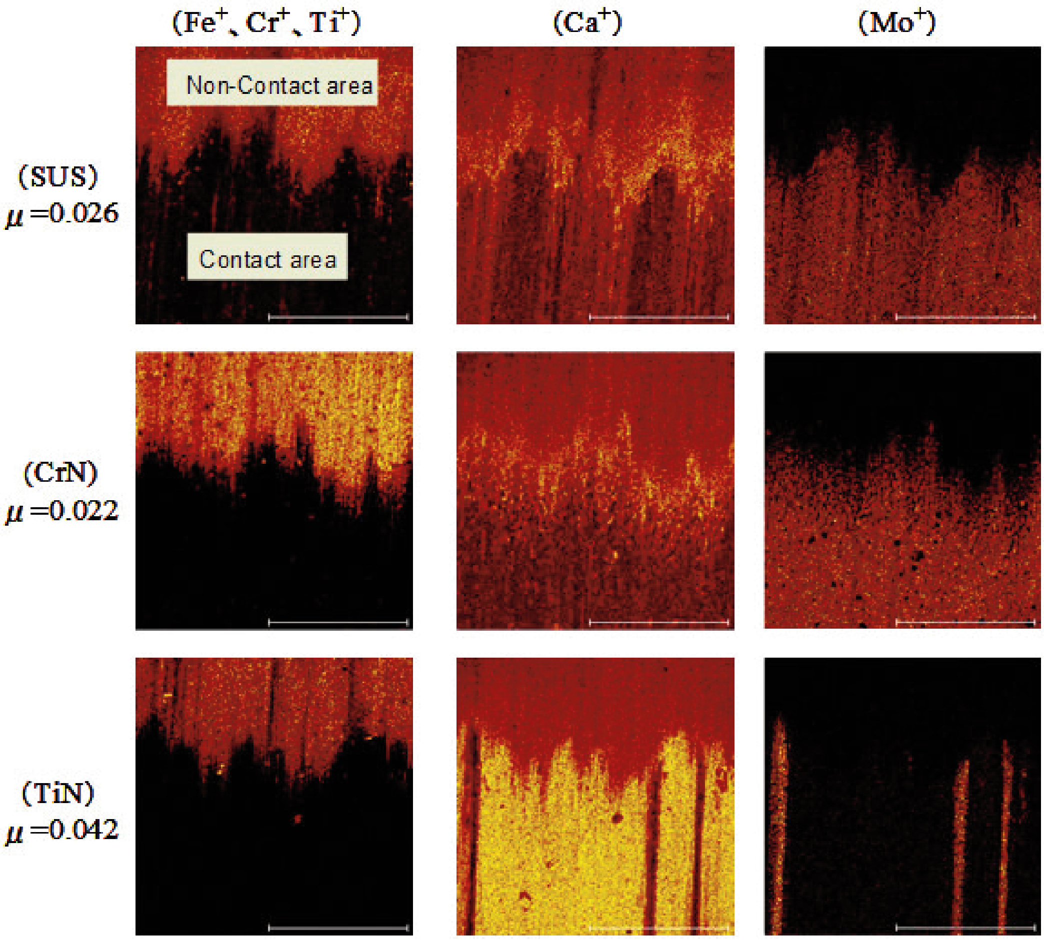

Fig. 6 Positive ion images of the friction surfaces of three types of test blocks tested in engine oil B. The field of view is 200 square microns.

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