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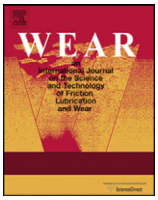

Effect of sulfur-containing additive on the decomposition of multialkylated cyclopentane oil on the nascent steel surface

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ABSTRACT

The role of di-tert-dodecyl disulfide as an additive in the decomposition process of hydrocarbon oil on the nascent surface of bearing steel 52100 was investigated by a ball-on-disk friction tester in a vacuum chamber with a quadrupole mass spectrometer (Q-MS). After the formation of a nascent surface, hydrogen and gaseous hydrocarbons desorbed as tribochemical reaction products. The desorption rate of gaseous hydrocarbons decreased significantly when the additive was introduced. The additive prolonged the induction period of the decomposition. XPS and ToF-SIMS analysis revealed that additive molecules and lubricant molecules competitively chemisorbed on the nascent surface and reaction occurred by the formation of iron sulfide, which poisoned the catalytic activity of active sites leading to deactivation. As a result, decomposition of hydrocarbon oil decreased significantly.

1. Introduction

With the rapid progress of high technology fields such as spacecraft mechanisms, semiconductor production and microelectromechanical systems (MEMS), new hydrocarbon oils and greases with good properties have been developed. Synthetic multialkylated cyclopentane oils (MACs) are one of the candidates which have been gaining wide acceptance in spacecraft mechanisms [1–6]. MACs have excellent viscosity properties, high thermal and chemical stability, especially very low vapor pressure, which supplies adequate lubricants in systems where it is impossible to replenish the lubricant during the life of the instruments [7].

Tribochemistry is one of the most important aspects influencing the tribological properties of the systems. Under boundary lubrication conditions, the surface layers on solids such as metal oxides and organic contaminants are removed by mechanical stimulation, resulting in the formation of nascent surfaces. There are many kinds of active sites on the nascent surfaces like kinks, steps and terraces [8–10]. The nascent surface has high activity to catalyze and accelerate the decomposition of organic compounds [11–15]. Although the chemical stability of MACs is very high, under friction conditions and in contact with metals, MACs partially decompose, forming low molecular weight products, such as hydrogen, methane and ethane [2,16]. The produced hydrogen interacts with steel to induce subcritical crack growth leading to ductility diminution and causes hydrogen embrittlement [17,18]. Hydrogen embrittlement of steels will cause trouble in the gas and oil industry where high concentrations of hydrogen are present. Moreover contamination of low molecular weight products will be harmful to the vacuum systems. Lubricant loss through decomposition reaction leads to MACs film disruption and surface damage.

The decrease of MACs' stability under tribological conditions compared to their high thermal and chemical stability, is very complex because it may involve catalytic effects of nascent surface, mechanical degradation induced by shearing forces and the temperature increase at the contacts. The advantage of MACs over more traditional lubricants for vacuum such as perfluoropolyether (PFPE) is their compatibility with currently available hydrocarbon-based additives [19]. It is important to study the tribological mechanisms through which the oil and additive function will be understood.

Organic sulfides have been shown to react with nascent surface and metal sulfides were formed on the surface, which possibly caused the catalyst poison of active sites [20]. The objective of the present work is to study the contribution of di-tert-dodecyl disulfide as the deactivator to the decomposition of MAC oil on the nascent steel surface. In addition X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) were applied to make clear the decomposition mechanism.

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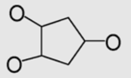
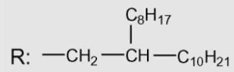
Table 1
Properties of sample oil.

Chemical structure		 R: $-CH_2-CH(C_8H_{17})-C_{10}H_{21}$
Kinematic viscosity (cSt)	100 °C 40 °C −40 °C	14.6 108 80, 500
Viscosity index	137	
Vapor pressure	25 °C, 3.999 × 10^{-9} Pa	
Evaporation	100 °C, 24 h, none	

2. Experimental

The oil used in the experiments was synthetic multialkylated cyclopentane, 1,2,4-tris (2-octyl-dodecyl) cyclopentane, produced by Nye Lubricants, Inc. and was used without further processing. A summary of the physical properties of the oil is shown in Table 1. Additive-free MAC oil, MAC oil mixed with 1 wt.% of di-tert-dodecyl disulfide were examined in this study. A thin lubricant film was formed on the disk surface with the average thickness of 10 μm.

Schematic diagram of the test apparatus used in this study is illustrated in Fig. 1. A ball-on-disk type sliding tester was installed in a high vacuum chamber with a base pressure less than 2 × 10^{-4} Pa. Ball and disk specimens were made of bearing steel 52100. The ball was 6.35 mm in diameter. The disk was 24 mm in diameter and 7 mm in thickness. The disk was mirror polished to an average roughness of Ra 0.02 μm. The specimens were thoroughly cleaned for 10 min in an ultrasonic bath with petroleum ether and hexane respectively before the sliding test. After the friction test, the test disk was cleaned with hexane in order to remove the excess lubricant that did not react with the steel surface and the chemical analysis of the wear scar was carried out. During the rubbing test, the pressure in vacuum chamber was measured by a Bayard–Alpert ion gauge, and intensities of the molecular and fragment ions coming from reaction products were monitored by a quadrupole mass spectrometer (Q-MS). All the tests were carried out on the same friction track by using the same ball at the room temperature. Tests were performed at the sliding velocities of 0.02, 0.03, 0.04, 0.05 and 0.06 m/s. The load was set at 2, 4, 8, 12 and 16 N at each of the constant sliding velocities as mentioned above.

The chemical composition of the wear scar was analyzed by small area XPS. The X-ray source was a beam of monochromated Al Kα (1486.6 eV). The diameter of the analysis area was 120 μm. The binding energy reference was taken as the main component of the C 1s peak at 284.5 eV for adventitious carbon.

ToF-SIMS was also used for chemical identification and mapping of products formed on the sliding surfaces. The conditions were: analysis area of 120 μm × 120 μm with a primary-ion accelerating voltage of 15 kV, a secondary ion accelerating voltage of 3 kV, and mass number range of 0–3000 amu. The analyzed area covers both the worn surface and outside of the wear track. The relative concentrations of compounds were estimated by comparing the intensity of individual fragments detected both in and outside of the wear track. Depth profile analysis of main fragments was also performed.

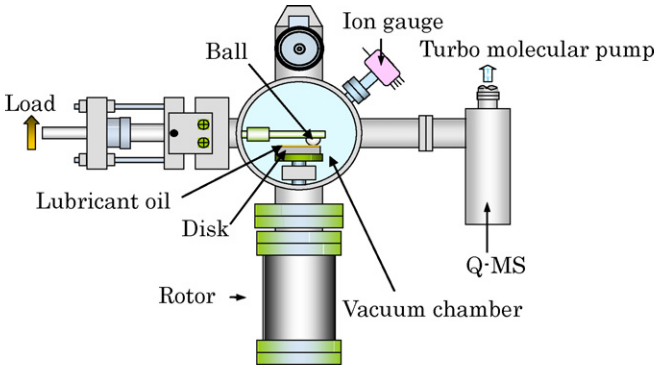


Fig. 1. Schematic diagram of the test apparatus for investigation of the chemical nature of a nascent surface.

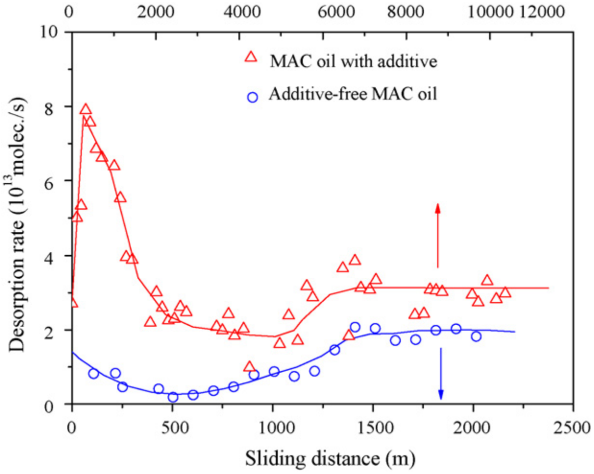


Fig. 2. Desorption of hydrogen during surface contamination removal (sliding velocity: 0.02 m/s; load: 8 N).

3. Results and discussion

3.1. *Desorption of hydrogen during sliding process*

The surface of the steel disk was covered with layers composed of oxides, chemisorbed water and organic contaminants, which were less active than the nascent surface. In order to obtain the nascent surface to study the decomposition mechanism, the contamination layers should be removed. Fig. 2 shows desorption of hydrogen as a decomposition product from additive-free MAC oil and MAC oil with the additive during the removal of the surface layers. It took about 1500 m of friction to obtain the nascent surface for additive-free MAC oil, while 6000 m was necessary for MAC oil with the additive. The results indicated that the additive prolonged the induction period of the decomposition.

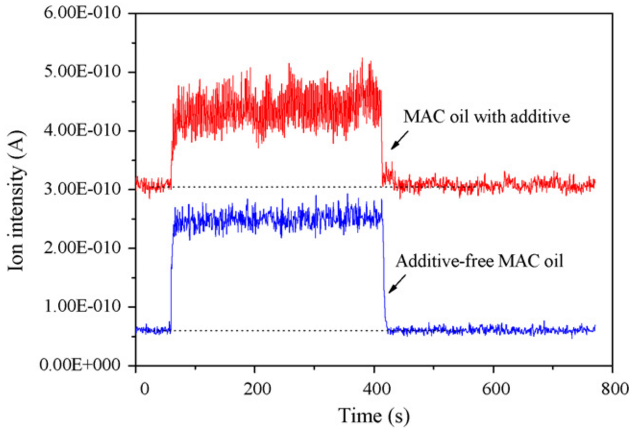


Fig. 3. The ion intensity of methane generated from additive-free MAC oil and MAC oil with the additive obtained by mass spectrometer.