ABSTRACT
In order to clarify the degradation mechanisms of the PFPE fluid under a head/disk sliding contact, decomposition reactions of z-dol fluids were investigated under triboplasma generation and in the atmospheres of oxygen, nitrogen and air in gas-discharge-plasma. The results showed that the PFPE degradation proceeds through intermolecular reactions with ambient air molecules by the tribomicroplasma.

INTRODUCTION
Some mechanisms of the PFPE decomposition mechanism have been proposed under head/disk sliding contact. These are mechanical shearing, thermal decomposition, catalytic decompositions [1] and electron induced decompositions [2], and so on. However, the mechanisms do not explain fully the PFPE decompositions. On the other hands, recently it was observed that triboplasma was generated in the gap of a sliding contact [3]. The triboemission characteristics in the simulation tribosystem of the head slider on the diamond like carbon (DLC) film overcoat showed the generation of the plasma in HDD [4]. Further, it was verified that the triboplasma decomposes the PFPE fluids under sliding contact, suggesting that the decomposition proceeds through intermolecular reactions with air molecules [5].

The purpose of the present study is to investigate the intermolecular decomposition mechanism of Z-dol with ambient air due to tribomicroplasma. The z-dol decomposition is studied in the gas discharge plasma in air, oxygen and nitrogen gas atmospheres.

EXPERIMENTAL PROCEDURES
Figure 1 shows the triboplasma reaction measuring apparatus (left) and gas-discharge reaction measuring apparatus (right). In the triboplasma reaction apparatus, three diamond pins with a radius of 1 mm was slid on the sapphire disk coated with z-dol, the average molecular weight of which was 2,0000, under a normal force 84 mN/(3 pin) and a sliding velocity of 13 cm/s. During the sliding experiment, the volatile products evolved from the sliding contact were collected by the adsorbents packed in a tube for 30 days. In the gas-discharge-plasma reaction, volatile products evolved from the decomposition of the Z-dol coated on one of the parallel Au electrodes in the plasma under an voltage of 400 volts and electric current of 6 mA and gas pressure of $1.33 \times 10^{-2}$ Pa was collected by the adsorbents packed in a tube for 2 min. The collected volatile products in the tube was then desorbed using a thermal desorption system (TD), fed into a gas chromatograph (GC) and identified by a Quadrupole mass spectrometer (QMS).
RESULTS AND DISCUSSION

Figure 2 shows a GC spectrum evolved from the decomposition of the Z-dol under lubrication in dry air atmosphere. As seen in Fig. 2, CF₃COOH was detected at a retention time of 7.53min.

Figure 2. GC spectrum of volatile products evolved from z-dol lubricated contact

Figure 3 show GC spectrum of the volatile products evolved by gas-discharge-plasma degradation of Z-dol coated on the Au cathode electrode surface in air, in O₂ and in N₂. In air, CF₃CONH₂ and CF₃COOH were detected at the retention time of 5.61 min and 7.51 min, respectively. In O₂, no volatile product was detected by GC. While in N₂, CF₃CONH₂ and CF₃CF₂CONH₂ were detected. These products were identified with their mass spectrum. These results demonstrate that nitrogen is deeply concerned with the decomposition of Z-dol to produce at the decomposition products having -CONH₂ group. As CF₃COOH is produced in air, but not in O₂, CF₃C=O can be produced under co-existence of O₂ and N₂ in the atmosphere.

Figure 3. GC spectrum of volatile products evolved from decomposition of z-dol fluid by gas-discharge-plasma

Figure 4 shows a reflective Vacuum FTIR spectrum on cathode surface coated with Z-dol before and after gas discharging in air, O₂ and N₂. It is seen that OH group of Z-dol was removed by the attack of plasma and C=O and NH₂ groups were produced in air. As the CF₃COOH with the boiling point of 72.4 °C must be evaporated in the vacuum FTIR, the -C=O group detected in air is not came from that of CF₃COOH. While CF₃CONH₂ is a solid with melting point 65 °C and boiling point of 162.5 °C, so that the -C=O and -NH₂ groups would be those of -CONH₂. From these results, it is clear that Z-dol is decomposed not only by the uni-molecular decomposition but also through the reactions with O₂ and N₂ in air as in the following reaction in the triboplasma.

\[
\text{HOCH}_2\text{CF}_2-(\text{CF}_2\text{CF}_2\text{O})_m-(\text{CF}_2\text{O})_n-\text{CF}_2\text{CH}_2\text{OH} + \text{O}_2 + \text{N}_2 \rightarrow \text{(denatured Z-dol)} + \text{CF}_3\text{CONH}_2 + \text{CF}_3\text{C}_2\text{CONH}_2 + \text{CF}_3\text{COOH}
\]

CONCLUSION

Z-dol molecules are decomposed with the reaction of oxygen and nitrogen molecules in ambient air under triboplasma generation.

ACKNOWLEDGMENTS

This study is supported by Grants-in-Aid through the Ministry of Education, Culture, Sports, Science, and Technology of Japan. The author would like to express his thanks to Shamim Md. Mirza for his help to do experiment.

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