Ionic Liquid Lubricant with Ammonium Salts for Magnetic Media

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1. Introduction

Magnetic recording systems have been responsible for the widespread and inexpensive recording of sound, video, and information processing. Despite the availability of other means of storing data, such as optical recordings and semiconductor devices, magnetic recording media have the advantages of low cost, stable storage, a relatively higher data transfer rate, a relative short seek time, and high volumetric storage capacity.

1.1 Hard disk drive systems (HDDs)

In current hard disk drive (HDD) systems (Fig.1 (a)), a rigid disk is rotated by a spindle motor at a speed of 10000 revolutions per minute (rpm). Information is written and read by a magnetic head with a tiny electric current attached to the end of the slider (Fig. 1(b)). The physical spacing between the magnetic sensors and the disk is down to almost 10 nm in recent systems, and it will be necessary to be within 5-7 nm for areal densities in the Tbin^{-2} range. (Wood et al.,2002) The read/write magnetic heads are mounted in the slider and travel across the data zone during the reading and writing operations.
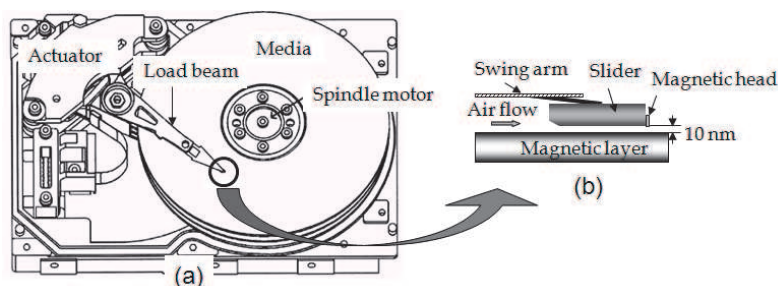

Fig. 1. Schematic drawing of a hard disk drive (a)(Kato et al., 2000) and a head-media interface (b)

However, when the drive stops, this head assembled device rests in the landing zone which is typically textured in order to reduce wear during contact-start-stop (CSS) operations. Most drives require that the static and kinetic friction forces at the head-media-interface (HMI) remain low under extreme environmental conditions and after the required number of CSS that is usually 10,000 or greater. (Jhon et al., 2001)

The rigid disk consists of an Al-Mg alloy or glass substrate, undercoat layer, a magnetic multilayer, and a carbon overcoat as illustrated in Fig. 2(a). (Maesaka and Ohmori, 2002) Nowadays, the magnetic media are perpendicular media, which consist of a Co-Cr based film. A carbon overcoat is used to enhance the wear and corrosion resistance. Finally a molecular thin lubricant, which is the topic of this chapter, is coated on the carbon layer to further reduce both the wear and friction between the HMI.
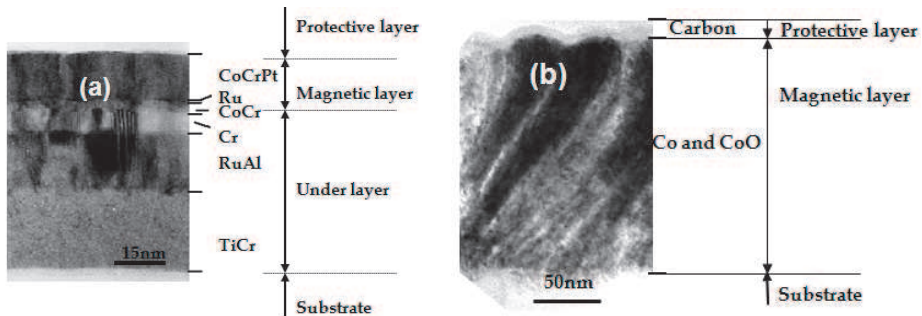

Fig. 2. Cross-sectional TEM image of magnetic layer for rigid disk (a) and magnetic tape (b).

1.2 Tape drive systems

Magnetic tape media are divided into two categories (Onodera et al., 1996a); i.e., particulate media where magnetic particles are dispersed in a polymer matrix with some additives and coated onto the polyethylene terephthalate (PET) substrate, and thin film media in which monolithic magnetic thin films are deposited onto the substrate in a vacuum, which is discussed in this chapter. For magnetic tape helical scan systems, the tape is driven by a pinch roller and a tension (0.2 – 0.5 N) is applied.
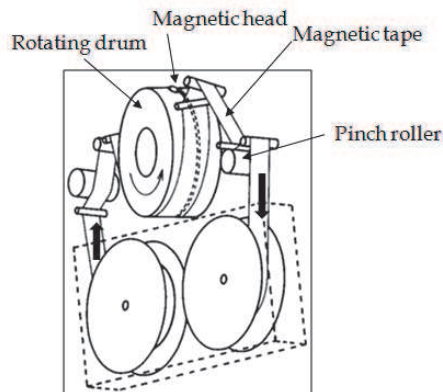

Fig. 3. Tape path for helical scan tape systems.

A video recorder uses a rotating head configuration as shown in Fig. 3. (Shiraishi et al., 1978) Much higher data transfer rates can be achieved using this rotating head drive system. (Kanota et al., 1990) The tape used is a PET substrate with an evaporated film of Co which is typically 100 nm thick. The magnetic layer fabricated with oxygen gas has obliquely aligned fine particles (Fig. 2(b)), (Ito et al., 2002) which leads to higher electromagnetic

characteristics. (Kaneda, 1997) The carbon overcoat and the lubricant layer are deposited onto the magnetic layer in a similar way to the rigid disks. (Onodera et al., 1996b)

1.3 Demand for lubricant of thin film magnetic media

In conventional magnetic recording, thin film media typically have their surfaces lubricated to reduce friction and wear resulting from contacts between the read/write magnetic head and media surface. In practice, to avoid adhesion related problems, lubrication has to be achieved with a molecularly thin lubricant film. (Homola, 1996) However, the main challenge in selecting the best lubricant for a magnetic media surface is finding a material which provides wear protection while the media surface is exposed to various environmental situations. It is important that the lubricant remain on the media surface over the life of the file without being subject to desorption, spin-off, or chemical degradation. This problem has become more difficult with the advent of a very smooth thin film surface, because thin film media do not have a mechanism for lubricant replenishment. (Klaus & Bhusha, 1985;Lin & Wu, 1990) Furthermore, lubricant adhesion to the overcoat surface is often insufficient to prevent lubricant depletion that eventually results in accelerated wear.

The presence of a mobile lubricant film, an excess lubricant, is often deemed necessary to replenish itself after sliding events. Increasing the amount of a lubricant enhances the durability, but exceeding the surface roughness of the media generally leads to adhesion related problem, such as deleterious stiction. (Bhushan, 1996; Sato et al., 1999) This frictional problem cannot be solved by using the conventional functional perfluoropolyether (PFPE) as the lubricant. In order to reduce this trade-off, novel lubricants must be designed and synthesized for the smoother surface magnetic thin film media. The very large body of patents relating to the lubricity of PFPEs on thin film magnetic media shows the importance of this problem to manufacturers. (Gunsel et al., 2003; Liu et al., 2002; Ishida et al., 2005; Kondo & Uchimi, 1992; Marchon et al., 2006a)

New types of PFPE lubricants whose chemical structure are summarized in Table 1 have been reported to enhance the performance and reliability. Z-DOL has hydroxyl groups at both chain ends, which has been widely used for the rigid disk application. With the additional functional hydroxyl groups in the middle of the PFPE backbone chain, Z-tetrol multi-dentate (ZTMD) can achieve a reduced clearance, while still achieving an overall drive reliability. (Chiba et al., 2005; Marchon et al., 2006b) A20H was invented to improve the tribological performance, which can effectively block the Lewis acid sites for degradation of the PFPE chain. (Waltman et al., 2003) The backbone chain and functional group of Mono are different from the above PFPE. Mono effectively reduced the head-disk adhesive interaction during near-contact operations. (Sakae et al., 2003) Sometimes the additives, such as X1-P, are used to enhance the reliability. (Jiaa& Liu, 1999) The linear or branched PEPE physically deposited on the diamond-like carbon surface with a covalent linkage formed by thermal decomposition of the peroxide improves the stability. (Navarrini et al, 2010)

Topical lubrication of solid lubricants has not been successful because the solid lubricating layer is often found to interfere with the sensitive magnetic transducing process, and because most solid lubricants have a poor wear resistance, they tend to wear away in the tracks under the head and generate debris. (Klaus & Bhushan, 1985) Liquid lubricants have the advantage that they will creep across the surface to replenish a portion of the layer which has been removed by abrasion or head wear. However, because of their mobility, liquid lubricants may suffer the disadvantage of spinning off from the disk surfaces during operation, especially at higher operating temperatures. These lubricants may also slowly

evaporate with time at the high temperatures, thereby reducing their protection. The use of higher viscosity, low-volatility liquid lubricants may help to decrease the evaporation rate and prolong their life.
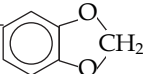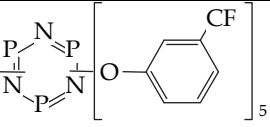
	X-CF$_2$ (OCF$_2$CF$_2$) $_n$ (OCF$_2$) $_m$ OCF$_2$ –X (0.5<n/m<1)
Z	X = - OCF$_3$
Z-DOl	X = - CH$_2$OH
Z-DIAC	X = - COOH
Z-Tetraol	X = - CH$_2$ OCH$_2$CHCH$_2$ OH $\qquad\qquad$ OH
AM2001	X = - CH$_2$OCH$_2$
A20H	HOCH$_2$CF$_2$ (OCF$_2$CF$_2$)$_n$ (OCF$_2$) $_m$OCF$_2$CH$_2$O
Mono	F-(CF$_2$CF$_2$CF$_2$O)$_l$ - CF$_2$CF$_2$CH$_2$ -N (C$_3$H$_7$)$_2$

Table 1. Molecular structure of commercial PFPE lubricants.

Based on these understandings of lubrication mechanisms, the demand for lubricants for magnetic thin film media with low friction and wear can be summarized as follows: (Klaus & Bhushan, 1985)

1. Low vapor pressure (volatility)
2. Low surface tension (replenish surface with lubricant)
3. Some affinity to the surface (with polar end group)
4. Good thermal and oxidative stability to prevent degradation during storage and use
5. Chemical inertness to met als, glasses and plastics and nondeposit formings to insure no damage to heads, guides, devices, etc.
6. No toxicity and flammability (to prevent degradation in the presence of water)
7. Good boundary lubricant (forms easily sheared chemical film during asperity contact)
8. Solubility in organic solvents

Over the past decade, ionic liquids have received a great deal of attention as a class of green solvents with a wide range of potential applications including organic and inorganic synthesis, (Sheldon, 2001) energy storage devices, (Ohno, 2005) separations, (Anderson et al., 2003; Visser et al., 2001) and catalysis. (Binnemans, 2005; Gordon, 2001; Welton, 1999) The term ionic liquid is broadly used to describe a large class of low melting fused salts that are liquids below 100°C. The most notable characteristics of many ionic liquids are their low vapor pressure, non-flammability, thermal stability, wide liquid range, and solvating properties for diverse substances. Limited results from very recent studies have shown the potential for using ionic liquids as a new class of lubricants. Friction and wear reductions have been reported on met allic and ceramic surfaces lubricated by selected ionic liquids compared to the conventional hydrocarbon lubricants.(Liu et al., 2002; Ye et al., 2001) Some fluoroalkyl-substituted immidazolium and a new series of imidazolium cation-based ionic liquids have been successfully prepared.(Singh et al., 2002; Branco et al., 2002) Alkylimidazolium tetrafluoroborates and hexafluoro-phosphate exhibit good tribological

performances for steel, aluminum, copper, single crystal SiO$_2$ and Si, and sialon (Si-Al-O-N) ceramics as compared to phosphazene (X-1P) and PFPE.(Liu et al., 2002; Mu et al., 2004; Mu et al., 2005; Ye et al., 2001; Ye et al., 2002) Ammonium-based ionic liquids provide friction reduction from elastohydrodynamic to boundary lubrication regimes compared to the fully-formulated base oil. (Qu et al., 2006) Ionic liquids have also been studied to determine their effectiveness as additives for base oil and water and the chemical and tribochemical reactions have been evaluated to understand the lubrication mechanisms. (Iglesias et al., 2004; Omotowa et al., 2004; Philips & Rabinski, 2004; Reich et al., 2003)

Protic ionic liquids are a subset of ionic liquids formed by the stoichiometric (equimolar) combination of a Bronsted acid with a Bronsted base.(Greaves et al., 2006; Greaves & Drummond, 2008; Xu & Angel, 2003;Yoshizawa et al., 2003) Relevant investigations into the molecular interactions of carboxylic acids and amines were conducted by Kohler et al., and the complexes of acid and amine with the molecular ratio of 1:1 can be found. (Kohler, 1981a, 1981b) Ionic liquids, which possess an octadecyl ammonium salt with pentadecafluoro octanate, significantly reduce the friction compared to the corresponding amide and Z-DOL. (Kondo, 1987a,b, 1997; Kondo et al., 1989, 1990, 1993a,b, 1994a,b) The modified PFPEs having the same hydrophilic group have also been synthesized and also show better frictional properties, which have been used as a lubricant for magnetic thin film media for a long time. (Kondo et al., 1996, 1994; Kondo, 2008) In this chapter, a series of ionic lubricants having the same hydrophilic group stated above are deposited on the magnetic thin film media and the effect of their molecular structures on the frictional properties is systematically investigated.

The lubricant is required to be very thin on the order of a mono-molecular layer. Therefore, the frictional properties depend not only on the molecular structure, but also on the microscopic structure of the lubricant film.(Seki & Kondo, 1991; Kondo & Seki, 1993a; Kondo et al., 1996; Kondo, 2008) Microscopic coverage of this alkylammonium-based protic ion liquid film on the medium surface is also examined using FTIR and X-ray photoelectron spectroscopy (XPS) and related to the spectra to the frictional properties.
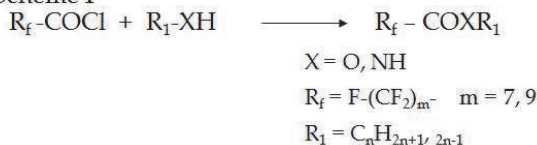
2. Materials

Three types of lubricants which possess both the perfluoroalkyl group and hydrocarbon long chain, that is an ester, amide, and carboxylic acid amine salt, were synthesized by the following Scheme 1 in Fig.4. The ester and the amide were prepared by the addition of carboxylic acid chloride to the hexane solution of the corresponding alcohol and amine in the presence of a base agent. The perfluorocarboxylic acid and the carboxylic acid ammonium salts are prepared by warming the mixture of the perfluorocarboxylic acid and the amine to 80°C until the complete dissolution was obtained (Scheme 2).(Kondo et al., 1989, 1994)

Three different types of PFPEs, which possess a carboxylic acid group as the end group, were used as the raw materials. K-lube is a homopolymer of perfluoro-isopropylene oxide, and D-lube is a homopolymer of perfluoro-n-propylene oxide. K-lube and D-lube have one end group. Z-lube is a random copolymer of the perfluoro oxymethylene and oxyethylene oxide monomers, which have two identical end groups. The average molecular weight of the PFPEs is about 2000.
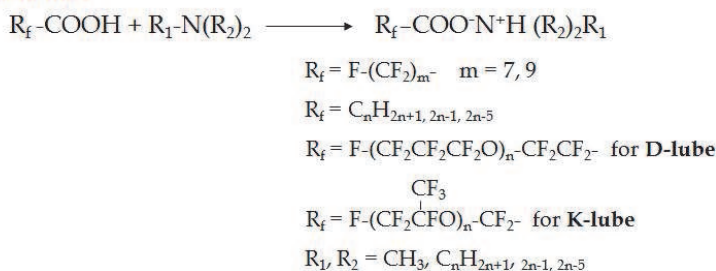
The ammonium salts with PFPE carboxylate lubricants were synthesized according to Scheme 2 and Scheme 3 in Fig. 4 in the same manner. (Kondo & Kaneda, 1994; Kondo, 2008) The chemical structure is determined by its infrared spectra: 3200-2800cm^{-1}(N$^+$H$_3$

stretching), 2918 cm^{-1} and 2958 cm^{-1} (CH$_2$ stretching), 1674 cm^{-1} (CO stretching), 1280-1110 cm^{-1} (CF stretching). The CO stretching moved from 1800 cm^{-1} to 1674 cm^{-1}, and the N$^+$H$_3$ stretching at 3200-2800 cm^{-1} appears, thus identifying the ammonium salt with a carboxylate structure. The synthesized lubricants are summarized in Table 2.

Scheme 1
$$R_f\text{-COCl} + R_1\text{-XH} \longrightarrow R_f - COXR_1$$

$$X = O, NH$$
$$R_f = F\text{-}(CF_2)_m\text{-} \quad m = 7, 9$$
$$R_1 = C_nH_{2n+1,\ 2n-1}$$

Scheme 2
$$R_f\text{-COOH} + R_1\text{-N}(R_2)_2 \longrightarrow R_f\text{-COO}^-N^+H (R_2)_2R_1$$

$$R_f = F\text{-}(CF_2)_m\text{-} \quad m = 7, 9$$
$$R_f = C_nH_{2n+1,\ 2n-1,\ 2n-5}$$
$$R_f = F\text{-}(CF_2CF_2CF_2O)_n\text{-}CF_2CF_2\text{-} \text{ for } \textbf{D-lube}$$
$$\hspace{5cm} CF_3$$
$$\hspace{4cm} |$$
$$R_f = F\text{-}(CF_2CFO)_n\text{-}CF_2\text{-} \text{ for } \textbf{K-lube}$$
$$R_1, R_2 = CH_3, C_nH_{2n+1,\ 2n-1,\ 2n-5}$$

Scheme 3
$$HOCO\text{-}R_f\text{-COOH} + R_1\text{-N}(R_2)_2 \longrightarrow (R_2)_2R_1N^+HO^-COR_f\text{-COO}^-NH^+(R_2)_2R_1$$

$$R_f = \text{-}CF_2O\text{-}(CF_2O)_m\text{-}(CF_2CF_2O)_n\text{-}CF_2O\text{-}CF_2\text{-} \text{ for } \textbf{Z-lube}$$
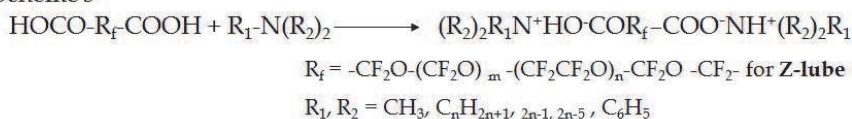$$R_1, R_2 = CH_3, C_nH_{2n+1,\ 2n-1,\ 2n-5}, C_6H_5$$

Fig. 4. Synthetic scheme for the new ionic liquid lubricant and the reference compound

3. Friction properties of novel lubricants

3.1 Friction measurement apparatus

The apparatus shown in Fig.5 was used to measure the CSS friction characteristics of the rigid disks. Friction at the head slider was measured by a strain gauge for each CSS operation during the starting of the spindle motor with a 10g load at 25°C, 50% relative humidity.
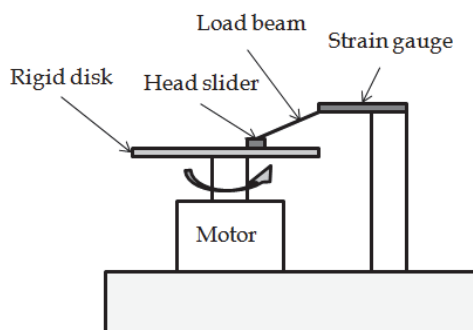

Fig. 5. Friction measuring apparatus for rigid disk.

R_F-CO-Y-R

Number	R_F	Y	R	mp /°C
1	C_7F_{15}	O	$C_{18}H_{37}$	29
2	C_7F_{15}	O	$C_{18}H_{31}$	<20
3	C_7F_{15}	NH	$C_{18}H_{37}$	91
4	C_7F_{15}	NH	$C_{18}H_{31}$	48
5	C_7F_{15}	$O^-H_3N^+$	$C_{18}H_{37}$	55
6	C_7F_{15}	$O^-H_3N^+$	$C_{18}H_{31}$	<20
7	C_9F_{19}	$O^-H_3N^+$	$C_{12}H_{25}$	61
8	C_9F_{19}	$O^-H_3N^+$	$C_{14}H_{29}$	65
9	C_9F_{19}	$O^-H_3N^+$	$C_{18}H_{37}$	71
10	C_9F_{19}	$O^-H_3N^+$	$C_{24}H_{49}$	85
11	$-CF_2O-(CF_2O)_m-(CF_2CF_2O)_n-CF_2O-$	$O^-H_3N^+$	$C_{18}H_{37}$	38-40
12	$-CF_2O-(CF_2O)_m-(CF_2CF_2O)_n-CF_2O-$	$O^-H_3N^+$	$C_{18}H_{35}$	< 30
13	$-CF_2O-(CF_2O)_m-(CF_2CF_2O)_n-CF_2O-$	$O^-H_3N^+$	$C_{18}H_{31}$	< 30
14	$-CF_2O-(CF_2O)_m-(CF_2CF_2O)_n-CF_2O-$	$O^-H_2N(CH_3)^+$	$C_{18}H_{37}$	79-82
15	$-CF_2O-(CF_2O)_m-(CF_2CF_2O)_n-CF_2O-$	$O^-HN(CH_3)_2^+$	$C_{18}H_{37}$	55-57
16	$-CF_2O-(CF_2O)_m-(CF_2CF_2O)_n-CF_2O-$	$O^-H_2N(C_{18}H_{37})^+$	$C_{18}H_{37}$	51-55
17	$-CF_2O-(CF_2O)_m-(CF_2CF_2O)_n-CF_2O-$	$O^-H_2N(C_6H_5)^+$	$C_{18}H_{37}$	31-33
18	$F-(CF_2CF_2CF_2O)_n-CF_2CF_2-$	$O^-H_3N^+$	$C_{18}H_{37}$	< 30
19	$F-(CF_2CFO)_n-CF_2-$ with CF_3 branch	$O^-H_3N^+$	$C_{18}H_{37}$	

Table 2. Molecular structure and melting point of ionic liquid lubricants.

A schematic diagram of the friction measurement apparatus for the magnetic tapes is shown in Fig.6. The coefficients of kinetic friction are measured for 8-mm wide tapes sliding around a quadrant of a 4-mm diameter polished stainless steel (SUS 304) cylinder. The friction coefficient was calculated from the change in the sliding of the tension (T_1) exerted by a 20-g

weight (T_2) hanging from the tape sliding on the cylinder. A 50-mm section of the tape is made to slide against the cylinder at a speed of 5 mms^{-1} in a reciprocating motion at 25°C, 60% relative humidity.
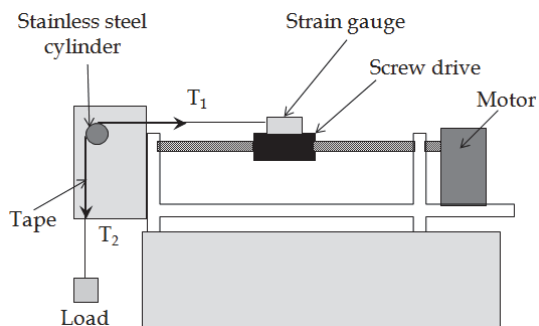

Fig. 6. Schematic diagram of the friction measurement apparatus for ME tapes.

3.2 Frictional performance of the newly synthesized ionic liquid lubricant with ammonium salt for magnetic media

The new lubricants exhibited a good CSS friction properties for the rigid disks compared to the PFPE (Z-DOL) as shown in Fig.7. The relationship between the CSS durability and the molecular structure of the lubricant in terms of the polar group, chain length, and chain symmetry was investigated.

The frictional characteristic of the carboxylic acid ammonium salt coated on the magnetic tape by dip-coating is shown in Fig.8. The friction coefficient is shown as a function of the number of cycles of reciprocating motion over the cylinder. The frictional characteristic of a conventional PFPE (Z-DOL) is shown for comparison. For the ammonium salt, the friction coefficient is low and remains at 0.18 even after 100 cycles of reciprocating motions, but it is more than 0.30 for the PFPE.
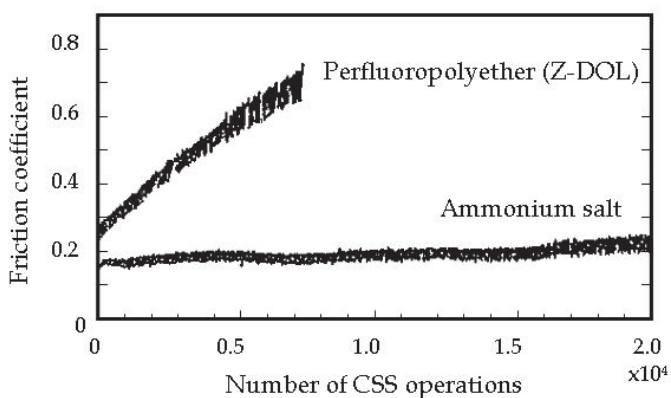

Fig. 7. Frictional coefficient of disk coated with lubricant (10) versus number of CSS operations. The functional PFPE (Z-DOL) shown for comparison.
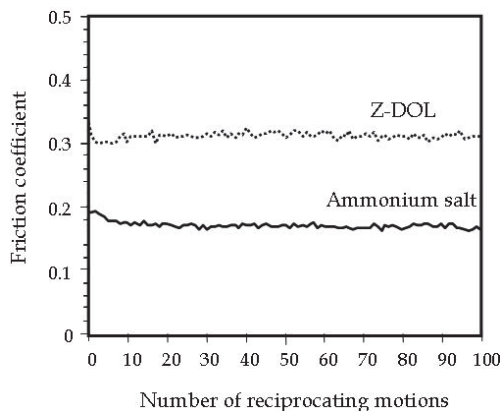
Fig. 8. Friction coefficient of the carboxylic acid ammonium salt (Lubricant 9) and Z-DOL during friction test at 25°C and relative humidity of 60%.

4. Effect of molecular structure on friction

4.1 Hydrophilic group
4.1.1 Effect of hydrophilic group on CSS friction of HDD

The CSS friction properties of three types of lubricants, i.e., ester (Lubricant 1), amide (Lubricant 3), and carboxylic acid ammonium salt (Lubricant 5) are shown in Fig.9. These friction measurements of the synthesized lubricants revealed that the ester and the amide are far less durable than the comparable salt type. For the ester and amide lubricants, the friction coefficients (μ) were around 0.25 for the first ten CSS operations, but rose with the increasing number of CSS operations (n). Especially, for the ester lubricant, μ steeply increased after 20 operations, and the carbon protective layer got damaged when the μ became over 0.90 at n = 138. For the amide lubricant, the slope of Δμ per Δn decreased compared to the ester, however, a wear scar occurred at n = 3279. For the carboxylic acid ammonium salt lubricant, the μ value remained nearly constant at around 0.25 throughout the 10^4 CSS operations and the medium was scarcely damaged. The low initial value of μ, 0.2-0.3, indicates that there is sufficient lubricant film to protect the rubbing surface.
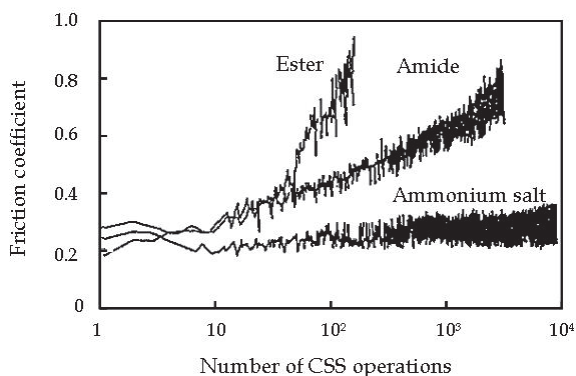

Fig. 9. Friction coefficient of disk coated with ester lubricant (Lubricant 1), amide (Lubricant 3), and carboxylic acid ammonium salt (Lubricant 5) versus number of CSS operations.

4.1.2 Frictional tests for magnetic tapes

Fig. 10 shows the friction coefficient variation vs. the reciprocating cycles for the salt and for the amide. For the salt, the friction coefficient value remained low and steady at approximately 0.23 throughout the 100 reciprocating cycles. The friction coefficient with the amide increased with the number of cycles.

Fig. 10. Comparison of frictional properties of ammonium carboxylate ionic liquid and the corresponding amide during a friction test.

4.2 Hydrophobic group

The hydrocarbon chain length of the salt type lubricant were changed and the CSS durability measured (Fig. 11). As the number of carbon atoms in the amine molecule (n) increased, μ decreased until a nearly constant value of 0.24 was attained. The shorter homologues showed an increase in μ as a result of the breakdown of their film. (Beltzer & Jahanmir, 1987)

Fig. 11. Friction coefficients of the salt type lubricants after 20,000 CSS operations.

For the given polar group, one of the key properties required for friction reduction is a high intermolecular cohesion energy (due to dispersive or van der Waal's interactions) between

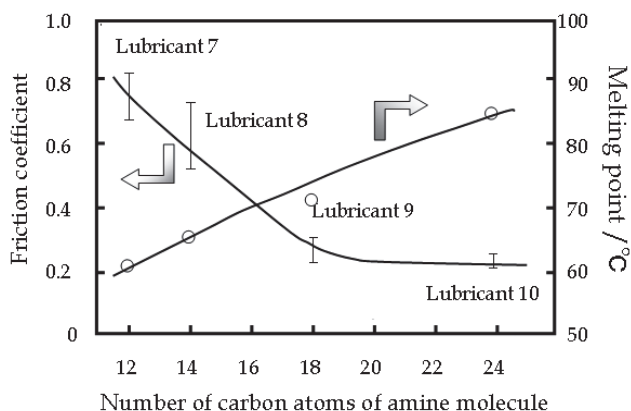the hydrocarbon chains. Melting of the lubricant materials by heating involves disruption of the dispersive interactions between the hydrocarbon chains, (Markley, 1968) therefore, the melting point of the lubricant should be related to the dispersive interactions of the hydrocarbon chain. (Beltzer & Jahanmir, 1987) The melting point becomes higher with the increasing hydrocarbon chain length and μ decreases. Not only the polar group but also the chain length due to dispersive interactions determined the durability.

4.3 Frictional properties of modified PFPEs on magnetic tapes
4.3.1 Frictional properties of new lubricant

The good viscosity characteristics, low melting point, low surface energy, low volatility, and good thermal stability of PFPE are among the important criteria for selecting a lubricant. By changing the perfluorocarboxylic acid with PFPE carboxylic acid, that is Z-lube in Scheme 3 and D- and K-lubes in Scheme 2 of Fig. 4, the modified PFPEs are expected to have lower melting point and improved thermal properties compared to the corresponding perfluorocarboxylic acid homologue.

The frictional characteristics of the three types of modified PFPEs of the ammonium salt with carboxylate are shown in Fig.12. For the ammonium salt, it is low and approximately 0.17 even after 100 cycles of reciprocating motion, and is not dependent on the chain structure of the PFPE. However, it is over 0.30 for the conventional PFPE, and other types of end groups, such as the other hydroxyl(Z-Tetraol) and piperonyl(AM2001), have a similar frictional coefficient of approximately equal to or greater than 0.30 (data not shown).

Fig. 12. Frictional properties of the three types of the modified PFPEs using stearyl amine. The conventional Z-DOL is shown for comparison.

Fig. 13 shows the dynamic friction coefficient during the reciprocating operation for each PFPE. The amplitude of the saw tooth pattern in the friction curve is significantly high for the Z-DOL tapes; these fluctuations in sliding resulted from the stick-slip process and are associated with squeal and chatter. However, the dynamic friction coefficient was relatively constant and the stick-slip phenomenon is only slightly observed for the ammonium salt tapes (Lubricant 11).

(a) Ammonium salt   (b) Z-DOL

Fig. 13. Change in dynamic friction coefficient during the reciprocating operation for the different PFPE.

4.3.2 Effect of molecular structure of amine

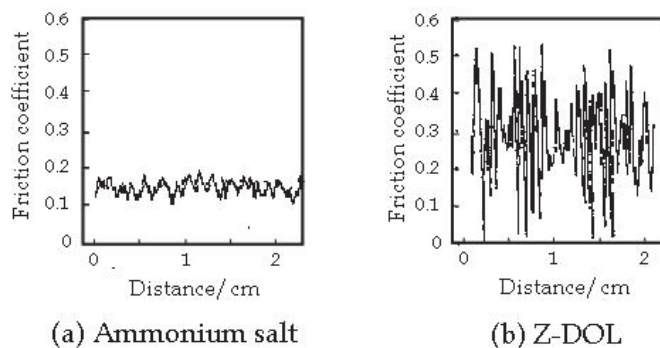Secondly, the molecular structure of the amine is changed using stearyl amine derivatives in order to fix the chain length of the longest substituent. The frictional results of the PFPE ammonium salts after 100 reciprocating motions and their melting points are summarized in Table 3. The introduction of a double bond into the hydrocarbon long chain, an oleyl with one double bond and a linoleyl with three, also makes the friction coefficient increase.

Lubricant number	Structure of lubricant	Friction coefficient	Melting point /°C
11 (stearyl)	$C_{18}H_{37}NH_2$	0.17	38-40
12 (oleyl)	$C_{18}H_{35}NH_2$	0.20	<30
13 (linolenyl)	$C_{18}H_{31}NH_2$	0.25	<30
14 (methyl stearyl)	$C_{18}H_{37}NHCH_3$	0.19	79-82
15 (dimethyl stearyl)	$C_{18}H_{37}N(CH_3)_2$	0.20	55-57
16 (distearyl)	$(C_{18}H_{37})_2NH$	0.21	51-55
17 (phenyl stearyl)	$C_{18}H_{37}NHC_6H_5$	0.30	31-33

Table 3. Fiction coefficients and melting points of the lubricants with the molecular structure of the amine having 18 carbon derivatives.

By replacing the hydrogen atoms of the amine group with alkyl and phenyl groups, a different series of salts would be obtained. This trend strongly suggests that replacing the hydrogen atom of the amine with an electron donating alkyl group increases the electrostatic interactions (including possible hydrogen bonding) between the cation and anion in the salts, which, in turn, raises the melting point. The alkyl substituted ammonium salt, e.g., by methyl and stearyl groups, have higher melting points than the non-substituted stearyl amine salt, nevertheless, the friction coefficient was somewhat inferior to the stearyl amine. Exchanging the amine of the salts for the larger phenyl substituent generally produced a further decrease in the melting point. As a general trend, for each anion, the salts with cations of lower symmetry show a lower melting point than those with cations of higher symmetry. Also, adding the bulky phenyl group significantly increased the friction. These magnitudes of increase in the friction suggest a blocking effect by the large

substituent attached to the amine nitrogen, which hinders adsorption of the polar group on the media surface. Steric hindrance by the polar group caused the high friction.

The cohesive energy density is normally lower for the fluorocarbon and ether group compared to the hydrocarbon. Cong et al. indicated that the film strength controlled by intermolecular attractive forces is an important factor that affects the frictional properties of the monolayers, which are associated with a higher load-capacity. (Cong et al., 2000) The attractive forces between the fluorocarbon chains are lower than those between the hydrocarbon chains and the presence of oxygen atoms in the PFPE backbone decreases the intermolecular attractive force. For the ammonium salts of the PFPEs, the reason for the lower friction might be the incorporation of a hydrocarbon into the molecules. Therefore, it is expedient to increase the dispersive interaction by introduction of a hydrocarbon chain into a PFPE molecule without steric hindrance between the polar group of the lubricant and media surface. To be precise, a saturated straight long chain ammonium salt is the best selection.

The use of a conventional PFPE is limited by the solvent. However, since the modified PFPEs contain a hydrocarbon moiety and ammonium salt moiety, it is soluble in alcohols, and other conventional fluorinated solvents, which makes its practical use convenient. Fig. 14 shows the consequences for friction of the stearyl ammonium salt of Z-lube by changing to a thinner dip-coating. In this case, ethanol, n-hexane-20%wt.ethanol, and a fluorinated solvent were used. It is evident that the frictional properties are independent of the dip-coating solvent.
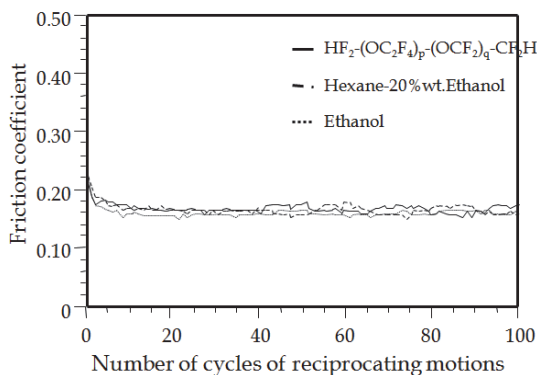

Fig. 14. Influence of changing to a thinner lubricant on the friction coefficient.

5. Langmuir-Blodgett (LB) films of the salt type lubricant

In order to elucidate the molecular level structure of the spontaneously adsorbed layers, a comparative structural study with films prepared by the Langmuir-Blodgett (LB) method is useful. Langmuir films (L films, i.e., monolayer on the water surface) and Langmuir-Blodgett films (LB films) of the lubricants were prepared and studied using a Jpyce-Loebl.

5.1 Basic properties of the L films and LB films

The ammonium salt with perfluorocarbxylate (Lubricant 5), and the corresponding ester (Lubricant 1) and the amide (Lubricant 3) are compared. The salt forms a much more stable monolayer on the water surface than the other two ester and amide lubricants. Fig.15 shows

the area decay curve of the L films of the salt and the amide on the water surface when they are held at a surface pressure of 25mNm^{-1}. The curve for the ester is unstable such that it collapsed as it was compressed. The area decay over 1 hour was less than 5% for the salt, whereas for the amide it was 45%, indicating a good stability for the salt monolayer. This result suggests a good balance between the polar and hydrophobic nature of the salt molecule, which is a necessary condition for producing a stable monolayer on the water surface.

Furthermore, the isotherm of the salt shown in Fig.16 suggests that the molecules of the salt were closely packed in the L film. From Fig. 16, the area per molecule at 25 mNm^{-1} is about 0.6nm^2. The areas occupied by an alkyl chain and a perfluoroalkyl chain are about 0.2 nm^2 and 0.4 nm^2, respectively, when their chain axes are perpendicular to the water surface. Therefore, it is suggested that the alkyl chains and perfluoroalkyl chains of the salt molecules are highly ordered and closely packed with their chain axes perpendicular to the water surface in the L film.

The closely packed monolayer is transferred onto the surface of the magnetic layer at 25 mNm^{-1} with a dipping speed of 5 mmmin^{-1} upon withdrawal from the water. The deposition trace suggested that there is an even deposition and the transfer ratio is about 0.75. Therefore, in the LB film monolayer, the area occupied by one salt molecule is calculated to be about 0.8 nm^2. The difference in occupied area per molecule indicates that the chain leans slightly to the surface normal. The tilt of the chains in the LB monolayer is induced by the deposition process.
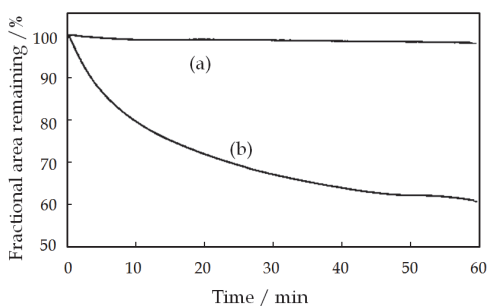

Fig. 15. Area decay curve of the L films of the salt (a) and the amide (b) at a surface pressure of 25mNm^{-1}.
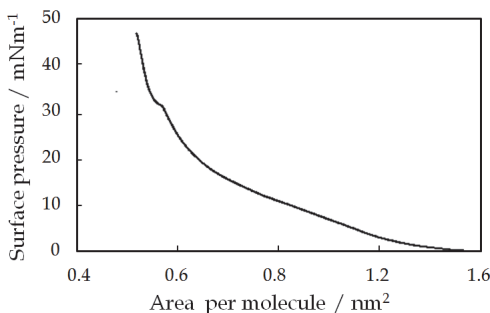

Fig. 16. Isotherm of the salt.

5.2 FTIR study for LB films

The friction properties may be enhanced by a microscopically smooth coverage of the lubricant film over the media surface. In the FTIR-RAS spectra, the components of the vibrational moments of the chemical bonds, which are parallel to the substrate normal, selectively appear. Therefore, the FTIR-RAS spectra are useful for investigating the molecular orientation of a lubricant film on a substrate.

The salt-type lubricant films, which are prepared by the LB method and the spontaneous adsorption from the lubricant solution, are compared in Fig.17. The bands in the 3000-2800 cm^{-1} and 1370-1100 cm^{-1} regions are assigned to the CH and the CF stretching vibrations, respectively. The band at around 1674cm^{-1} is assigned to the COO$^-$ anti-symmetric vibration. The absolute intensities of these bands are very similar in both spectra, which suggest that the adsorbed layer of the salt is in fact a monolayer and that the degree of orientation and packing of the alkyl and perfluoroalkyl chains closely resembles that in the LB monolayer. Therefore, the area occupied by one salt molecule in the adsorbed layer is approximately 0.8nm^2.
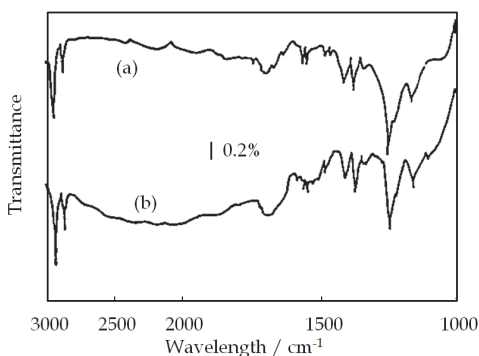

Fig. 17. FTIR reflection adsorption spectra of the novel lubricant films prepared by (a) spontaneous adsorption method and (b) LB method on the surface of the magnetic layer.

6. Spectroscopy of lubricant film

6.1 FTIR study for lubricant film of different hydrophilic groups

Figs. 18 and 19 compare the RAS of the lubricant film and transmission spectra of the bulk material for the salt and the amide, respectively. The mode assignment and peak positions for the RAS and for the transmission spectra are summarized in Table 4.

For the salt, the differences in the spectra between the RAS of the adsorbed lubricant film on the substrate (a) and the transmission spectra of the bulk materials (c) are described as follows:

1. In the RAS spectrum of the adsorbed film, the bond assigned to the COO$^-$ asymmetric stretching vibration at 1674 cm^{-1} is much weaker than in the spectrum of the bulk material.
2. The relative intensity in wavenumber of the CF$_2$ stretching vibrations in the 1250-1140 cm^{-1} region is changed and shifted to a higher frequency in the RAS spectrum.
3. The band assigned to the CH$_2$ stretching vibration in the RAS spectrum in the vicinity of 2900 cm^{-1} is also shifted to a higher frequency than that in the spectrum of the bulk.

The weakness of the band at 1674 cm^{-1} suggests that asymmetric stretching of the COO$^-$ (hydrophilic) group is almost parallel to the substrate surface in the adsorbed film. The changes in the relative intensity and the higher frequency shift in the 1250 to 1140 cm^{-1} region are similar to those reported for a monolayer of perfluorocarboxylic acid. (Chau & Porter, 1990) These changes have been attributed to adsorption of the molecules with preferential orientation and perfluoroalkyl chains tilted in the adsorbed layer.

The higher frequency shift of the CH$_2$ stretching vibrations is often observed when the alkyl chains are in a liquid phase or in a solution, where the cohesive interaction between them is weak. (Asher & Levin 1977) A probable cause of the higher frequency shift in the RAS spectrum is that the perfluoroalkyl chains hinder a cohesive interaction between the alkyl chains in the monolayer.
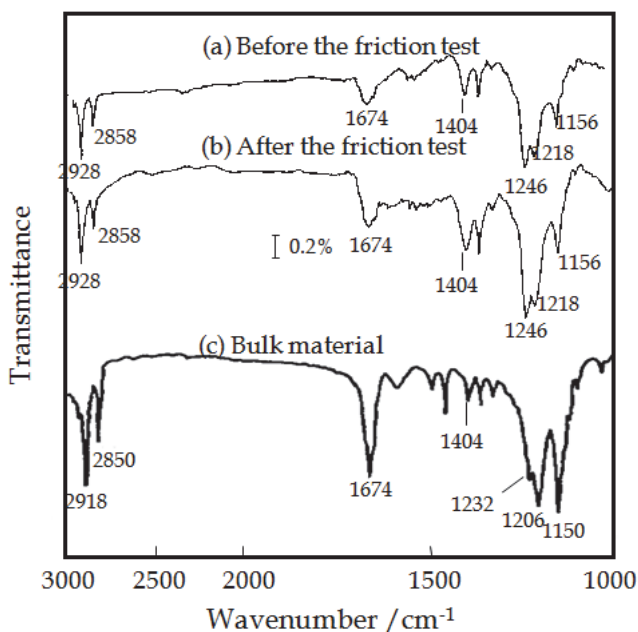

Fig. 18. FTIR spectra of ammonium, C$_9$F$_{19}$ -COO$^-$H$_3$N$^+$-C$_{18}$F$_{37.}$ (a)RAS spectra of adsorbed film; (b)RAS spectra of adsorbed film after friction test; (c) Transmission spectrum of bulk material.
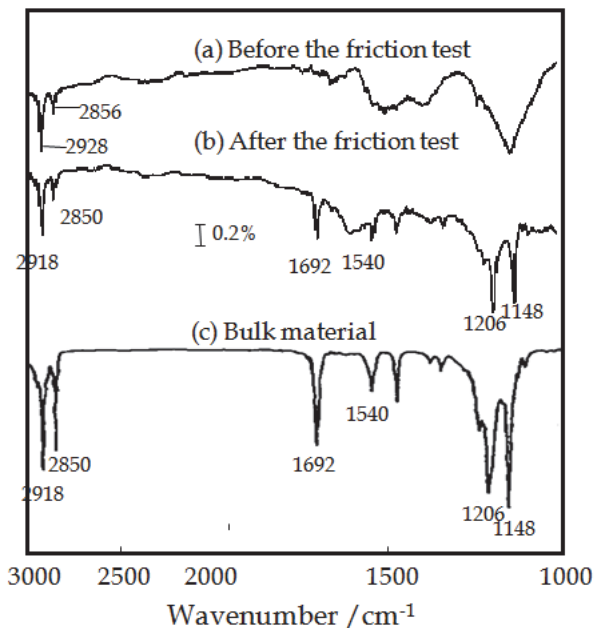
Fig. 19. FTIR spectra of amide, C_9F_{19} -CONH-$C_{18}F_{37}$. (a)RAS spectra of adsorbed film; (b)RAS spectra of adsorbed film after friction test; (c)Transmission spectrum of bulk material.

For the amide, the spectral pattern of the film in the region of the CF_2 and CF_3 stretching vibrations, 1250 to 1140 cm^{-1}, is different from that of the salt. However, the decrease in intensity of the stretching vibrations for C=O at 1692 cm^{-1} and the high frequency shift of the CH_2 stretching mode behaves similar to the carbonyl stretch and high frequency CH_2 shift for the salt.

The FTIR-RAS spectra of the lubricant film after the friction test are also shown in Figs. 18(b) and 19(b). The absolute intensity of the CH_2 stretching region is similar in the spectra both before and after the friction test, indicating that sliding causes no substantial change in the surface concentration of the alkyl groups. For the salt, the spectra both before and after the test are similar, therefore, the rubbing motion caused no change in the microscopic structure of the lubricant film. On the other hand, there are several differences in the RAS spectrum of the adsorbed film of the amide before and after the test. These results are summarized as follows:

1. The bands at approximately 1692 cm^{-1} and 1540 cm^{-1}, which are assigned to the C=O stretching vibration and the NH bending vibration, respectively, appear after the test.
2. The pattern of the CF_2 and CF_3 stretching vibrations at 1250 cm^{-1} and 1140 cm^{-1} changes.
3. The band of the CH_2 antisymmetrical and symmetrical stretching vibrations in the 3000 to 2800 cm^{-1} region shifts to a lower frequency.

Thus, the spectrum of the adsorbed amide film approachs the spectrum of the bulk material with sliding. This suggests rearrangement of the amide monolayer by the sliding process, perhaps into three-dimensional crystals or amorphous piles.

These results show that the layers of the amide were composed of orientated molecules, although they produced a higher friction coefficient than those of the salt. A possible cause

for the higher friction coefficient is that a layer structure with a high degree of molecular orientation is less stable for the amide compared to the salt. This is demonstrated by the decay curve on the water surface in Fig.15.

The FTIR-RAS spectra showed that the polar group of both lubricants interacted with the magnetic surface before the friction test. For the ammonium salt, the friction coefficient is low and constant throughout the 100 reciprocating cycles (Fig. 10). From a spectroscopic point of view, before and after the spectra of the friction test are similar, suggesting no change in the structure of the lubricant film. In contrast, for the amide, the friction increases with the number of cycles, thus the adsorbed lubricant was changed into bulk-like aggregates, which brings about the bare contact and leads to a higher friction.

Peak position /cm^{-1}				Vibration mode
Amide		Ammonium salt		
Bulk material	Film	Balk material	Film	
2918	2928	2918	2928	CH$_2$ asymmetric stretching
2850	2856	2850	2858	CH$_2$ symmetric stretching
		1674	1674	COO$^-$ asymmetric stretching
		1404	1404	COO$^-$ symmetric stretching
1692				CO stretching
1232		1232	1246	CF$_2$ asymmetric stretching (E$_1$ symmetry)
1206		1206	1218	CF$_2$ asymmetric stretching (A$_2$ symmetry) + CF$_3$ stretching
1148		1150	1156	CF$_2$ symmetric stretching (E$_1$ symmetry)

Table 4. Mode assignment and peak positions for the ammonium salt and amide in KBr and as adsorbed on a magnetic layer.

6.2 Angle resolved X-ray photoelectron spectroscopy (ARXPS) study for microscopic coverage of modified PFPE

The uniformity of the monolayer level lubricant on the magnetic thin film media has been investigated using ARXPS with the finding that the PFPE is a discontinuous film. (Kondo et al., 1996;Moulder et al., 1986) Kimachi et al. proposed an island model to describe the coverage of conventional PFPEs on the magnetic recording media. (Kimachi et al., 1987) On the other hand, the modified PFPE has a good lubricity compared to the conventional ones, which implies a different film formation. In order to gain insight into this effect, microscopic coverage of the lubricant on the surface is investigated by ARXPS. The Z-lubes with and without modification are deposited under the same conditions.

A lubricant layer completely covers the surface with a constant thickness of d in the uniform model. In the island model, the surface is discretely covered with lubricant islands having the average thickness of d (Fig. 20). It is assumed in these models that the surface is flat and that elemental atoms are homogeneously distributed in the lubricant layer. (Fadley, 1974) Based on these assumptions, the photo-electron intensity ratio, I_{lub}/I_{sub} is expressed as a function of the take-off angle, φ, and the lubricant coverage ratio, Θ, on the surface of the

magnetic layer. I_{lub} is the intensity of the photoelectron detected from the lubricant layer and, I_{sub} is the intensity from the under layer.

In Fig. 21, I_{lub}/I_{sub} is plotted as a function of $\sin \varphi$, and the calculated model curves of Θ using the island model are also shown. Because the I_F of the modified PFPE is somewhat low, I_{lub}/I_{sub} is normalized in such a way that the I_{lub}/I_{sub} at 90 degrees is 1.

The coverage of the modified PFPE is greater than the conventional lube, despite the fact that the amount of lube on the surface is somewhat lower. The higher coverage reduces the dry contacts at the rubbing surface and minimizes friction.
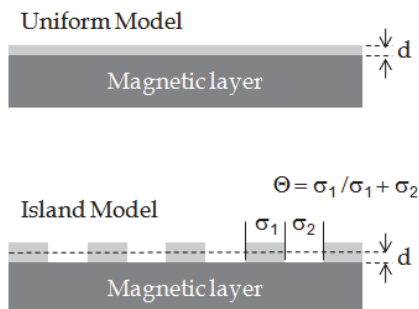
Fig. 20. Lubricant coverage models. Θ is the lubricant coverage ratio in island model and d is the average thickness.

It can be considered that two factors determine low friction, namely, better coverage and a strong interaction between the lubricant and the media surface. Better coverage is ascribed to the balance of the hydrophobic and hydrophilic properties of the lubricant. It is well-balanced when the hydrocarbon chain is introduced. The polar group of the ammonium salt without steric hindrance has strong interactions at the surface.

6.3 Heat of the preferential adsorption

These three types of lubricants, the salt (lubricant 5), the amide (Lubricant 3), and the ester (Lubricant 1), have the same hydrophobic groups, but have different friction coefficients, which are related to the polar group of the lubricant molecule. A plausible explanation is that the salt-type lubricant leads to greater adhesion than the ester and amide. As the surface of the sputtered carbon protective layer is classified as rather polar because it contains 5 and 7atom% hydroxyl and carbonyl groups, respectively, a source of the attractive force at the surface may be the interactions between these polar groups. (Kondo & Nishida, 2007) In order to gain insight into this effect on the friction properties, the dielectric loss measurements are conducted.

The relative dielectric constant (ε) of the lubricants is measured at 3MHz and summarized in Table 6. The relative dielectric constant, which is a parameter of the dipole moment, is 2.01 and 2.36 for the ester and the amide, respectively, but 2.66 for the salt-type. The higher the dielectric constant, the more strongly the lubricant seems to adsorb on the medium.

The formation of the lubricant film is a spontaneous process caused by a decrease in the free energy of the solid surfaces and lubricant molecule adsorption. The heat of adsorption of lubricants on a rubbing surface can be taken as a measure of the strength of attachment of the lubricant molecules to the surfaces and are also shown in Table 6.
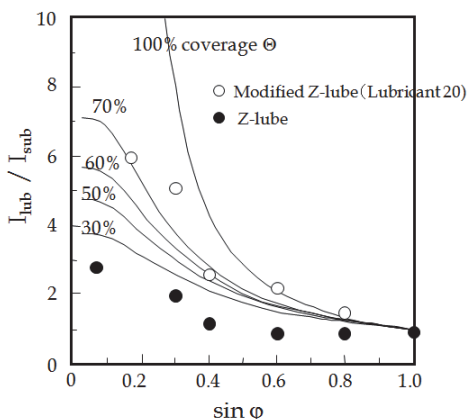
Fig. 21. Coverage of the media surface with lubricant by ARXPS and the calculated curves using island model shown for comparison.

For the ester and the amide type, the heat of adsorption is small, and the heat of desorption is partially observed. However, for the salt-type, the heat of adsorption was very high compared to the ester and amide, and the heat of desorption could not be detected. These results confirm that the ester and amide were held by weak interactions on the carbon surface, whereas irreversible adsorption had taken place for the salt-type. The high heat of adsorption of the salt-type on the carbon surface results from these strong interactions and accounts for its low and steady friction. The low heat of adsorption for the ester and the amide, by contrast, apparently produces a film which is easily disrupted by sliding to give a rising friction coefficient with sliding.

Structure and lubricant number	Dielectric constant**	Heat of adsorption /erg cm^{-2}	Heat of desorption /erg cm^{-2}
(2)$C_7F_{15}CO\ O\ C_{18}H_{31}$	2.01	2.1	1.0
(4)$C_7F_{15}CO\ NH\ C_{18}H_{31}$ *	2.36	2.7	1.9
(6)$C_7F_{15}\ O^-H_3N^+C_{18}H_{31}$	2.66	18.9	Not detected

* Stearyl amide is slightly soluble in the solvent, therefore, the double bonded lubricants are used.
**Dielectric constant is measured at 3 MHz.

Table 6. Heat of adsorption and desorption of the lubricants on the surface.

7. Conclusions

The frictional properties of newly synthesized ionic liquid lubricants for magnetic media have been investigated. A novel ionic liquid, which has an ammonium salt with a carboxylate as a hydrophilic group, has a lower frictional coefficient than the other conventional PFPE. It can be considered that two factors determined the low friction, namely, better coverage and strong interaction between the lubricant and the media surface. These ionic liquid lubricants invented around 1987 (Haga & Kondo, 1987;Kondo, 1987, 1992; Kondo & Haga, 1987; Kondo & Uchimi, 1992) have been used for magnetic tapes of 8mm video, digital video cassette, the AIT system, and the broadcast application for about a

quarter century because of their good lubricity and also from an environmental point of view.

The effects of the molecular structure of the modified PFPE on the frictional properties are summarized as follows:

1. Stronger adsorption due to the adhesive interaction of the polar group, thus the novel carboxylic acid ammonium salt has a lower and more stable friction coefficient.
2. Sufficient length and symmetry of the hydrocarbon chain cause the extensive cohesive interactions, and these dispersive interactions compensate for the friction reduction.
3. On the contrary, for the olefinic lubricant, the friction coefficient increased with the increasing number of reciprocating cycles because of the weaker cohesive interactions.
4. The ammonium salt polar group can be introduced to the commercial PFPE, and the frictional coefficient is independent of the molecular structure of the PFPE backbone polymer and of the thinner dip-coating, which makes practical use convenient without any environmental problems.

From a microscopic point of view, the lubricant film coverage was also investigated as follows:

1. A layer of the carboxylic acid ammonium salt lubricant film prepared by the spontaneous adsorption is highly ordered and closely packed as in the LB monolayer.
2. The polar COO- groups of the salt are adsorbed almost parallel to the surface, and the sliding scarcely changes the salt-type lubricant film, while the arrangement of the amide film into a bulk phase occurs due to the sliding process.
3. The modified PFPE uniformly covers the magnetic surfaces; this is why it minimizes the friction.

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This volume, of a two volume set on ionic liquids, focuses on the applications of ionic liquids in a growing range of areas. Throughout the 1990s, it seemed that most of the attention in the area of ionic liquids applications was directed toward their use as solvents for organic and transition-metal-catalyzed reactions. Certainly, this interest continues on to the present date, but the most innovative uses of ionic liquids span a much more diverse field than just synthesis. Some of the main topics of coverage include the application of RTILs in various electronic applications (batteries, capacitors, and light-emitting materials), polymers (synthesis and functionalization), nanomaterials (synthesis and stabilization), and separations. More unusual applications can be noted in the fields of biomass utilization, spectroscopy, optics, lubricants, fuels, and refrigerants. It is hoped that the diversity of this volume will serve as an inspiration for even further advances in the use of RTILs.

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