THE APPLICATION OF IONIC LIQUIDS INTO SPACE LUBRICANTS

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ABSTRACT

Perfluoropolyether (PFPE) and Multiplyalkylated cyclopentane (MAC) are currently the most widely used space lubricating oils. Although PFPE can be used over wide temperature ranges, it has some issues such as the poor solubility of additives making it difficult to improve rust preventive property or friction wear characteristics and unfavourable decomposition behaviour in boundary lubrication [1, 2]. Thus PFPE is being replaced by MAC. On the other hand, MAC withstands operating temperatures of -20°C but has difficulty functioning at -40°C due to an increase in kinematic viscosity. Another issue is that some additives are effective in improving load capacity of MAC but can adversely affect the vacuum property under high vacuum.

In this study, ionic liquids were investigated as a possible base oil of next-generation space grease to solve these issues. Table 1 summarizes key properties of typical ionic liquids and currently-used space lubricants.

Table 1. Key properties of space lubricants

Base oil / Additive	Ionic liquid	Fluorine oil	Cyclopentane oil w/o additive	Cyclopentane oil w/ additive
Usability under vacuum	Good	Good	Good	NG
Friction-wear characteristics	Good	OK	OK	Good
Low temp. performance	Good~NG	Good	OK	OK
Rust preventive property	OK	OK	Good	Good

1. SELECTION OF IONIC LIQUID

Generally speaking, salt as in table salt exists in the solid state, whereas an ionic liquid is a salt in the liquid state at ordinary temperature consisting of organic ions (cation and/or anion). Since J. S. Wilkes first reported about "stable" salt based on organic ions, ionic liquids have attracted research interests [3]. Ionic liquids have potential value as used in eco-friendly reaction solvent, electrochemical device [4] and many other industries thanks to their unique characteristics including:

- High chemical stability over wide temperature ranges
- High thermal stability
- Refractoriness
- High ion conductivity

Also, the liquid state over wide temperature ranges is actively supporting their application into lubricating oils [5~10].

1.1. Desk research

There are more than 500 varieties of ionic liquid combinations available in the market. As a first step, these ion liquids were evaluated in desk research for three criteria: non-hazardousness, liquid state at -20°C and hydrophobicity. Considering that most ionic liquids are inherently soluble in water, or hygroscopic and hygroscopic leading to poor lubricating performance, hydrophobicity was considered to be an important criterion. As a result, 30 ionic liquids met these criteria.

1.2. Vacuum property

Space materials are required not to easily evaporate or not to contaminate surroundings when evaporating. The ASTM E595 outgassing test is frequently performed to determine evaporation characteristics of the materials on the basis of Total Mass Loss (TML) and Collected Volatile Condensable Materials (CVCM). ASTM defines TML as the mass loss of materials being subjected to 125°C at $<7 \times 10^{-3}$ Pa for 24 hrs and CVCM as being capable of condensing on a collector at a temperature of 25°C. As an alternative to ASTM E595, the thermo gravimetric-differential thermal analysis technique (TG-DTA) was used in this study because there was not adequate test equipment in our lab.

To begin with, TG-DTA high-temp. vapour loss measurements were carried out for five ionic liquids and a commercially available additive added MAC with a known TML and CVCM to demonstrate test conditions correlating with that of the outgassing test as shown in Figs. 1 and 2. In accordance with the NASA (National Aeronautics and Space Administration)'s specifications for TML (not exceeding 1.0%) and CVCM (not exceeding 0.1%), TG-DTA threshold criteria were set to 22% or less of mass loss at 280°C for 10 hrs.

As a result, 17 ionic liquids were kept for further evaluation of surface tension, viscosity at low and high temp. and friction-wear characteristics in air. Then, only seven ionic liquids having TFSI (bis[(TriFluoromethyl)Sulfonyl]Amide) anions achieved satisfying overall performance.

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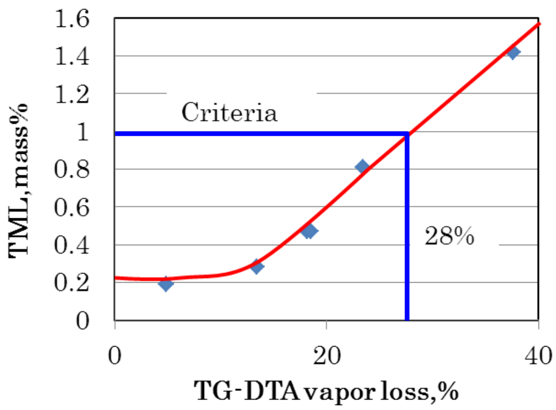


Figure 1. Correlation between TML and TG-DTA

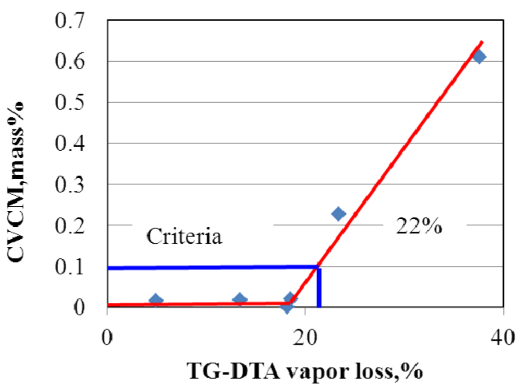
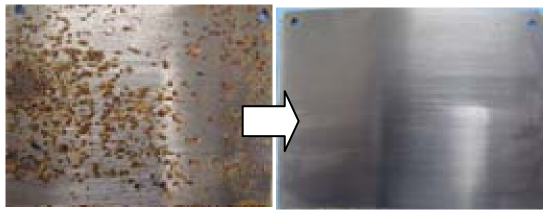


Figure 2. Correlation between CVCM and TG-DTA

1.3. Rust preventive property

Spacecraft and satellites need to be rust-resistant as they are stored in the atmosphere for 1~5 years before launching. Humidity cabinet tests were carried out using test plates made of common spacecraft steel SUS440C. Figure 3(a) shows a typical plate with ionic liquid after testing which was rated as E (50% rust or more). It is known that ionic liquids are unlikely to provide sufficient rust prevention. Accordingly, several rust inhibitors of varying chemical classifications and action mechanisms were examined. Only an absorption film type rust inhibitor was effective to improve the rust preventive property of a TFSA-type ionic liquid as shown in Figure 3(b)



(a) Ranked as E w/o rust inhibitor (b) Ranked as A w/ rust inhibitor

Figure 3. Humidity cabinet test

(JIS K2220.21.compliant) : Temp. 49°C, humidity 95%RH, testing time14days, SUS440C

2. PREPARATION OF GREASE

The ionic liquid selected through the above-mentioned examinations was thickened by common thickeners including Li-soap, urea series, organic clay, silica, polytetra-fluoroethylene (PTFE) and carbon black to formulate trial greases. Table 2 shows penetration, oil separation and rust preventive property of the trial greases. Long-chain aliphatic diurea and organic clay showed unfavorable oil separation, and silica caused rust. Aromatic diurea, PTFE and carbon black met all the criteria. Finally, aromatic diurea was selected as the most appropriate thickener as it outperformed PTFE and carbon black in subsequent outgassing measurements and other performance evaluations.

With an ionic liquid as base oil, aromatic diurea having aromatic end group showed a greater thickening effect

Table 2. Evaluation results of each thickener

Thickener / Type	Target	Li-St	Li-12OHSt	Aliphatic Diurea (short-chain)
mass%		15	15	10
Penetration (worked)	250~300	Failed to formulate grease		440<
Oil separation mass% (100℃×24h)	5 or less	—	—	—
Rust prevention	A	—	—	—

Thickener / Type	Target	Aliphatic Diurea (long-chain)	Aromatic Diurea	PTFE
mass%		24	16	30
Penetration (worked)	250~300	278	273	296
Oil separation mass% (100℃×24h)	5 or less	19.6	3.7	3
Rust prevention	A	A	A、A	A、A

Thickener / Type	Target	Organic bentonite	Silica (hydro-phobized)	Carbon black
mass%		20	6	4
Penetration (worked)	250~300	288	267	298
Oil separation mass% (100℃×24h)	5 or less	33	2	4
Rust prevention	A	—	A、C	A、A

Failed

than thickeners having alkyl end group such as Li-soap and aliphatic diurea. Thickeners having alkyl end group are known to be effective against less polar base oils. Meanwhile, highly-polar ionic liquids presumably prevent these thickeners from forming 3D network to hold the oil.

3. VERIFICATION OF IONIC LIQUID-BASED GREASE

Table 3 shows general properties of a grease formulated with an ionic liquid base oil and aromatic diurea thickener to have a worked penetration of 280, which was referred to as IU. Representative space greases actually used in practice, FF, MU and MN were evaluated for comparison. FF was based on straight chain PFPE. Whereas, MU and MN were based on MAC oil (Tris (2-octyldodecyl)Cyclopentane).

Figure 4 shows low temp. kinematic viscosities of each grease. Although MAC had an increase in viscosity at -40°C, the ionic liquid had a low viscosity at the same level as PFPE indicating that it can be effectively used in the low temperature-range where only PFPE was used.

Table 3. General properties of space greases

Grease name			Criteria	IU	FF	MU	MN
Base oil	Type			Ionic liquid (TFSA)	PFPE	MAC	
	Kinematic visc. mm^2/s	40℃	-	20	144	104	
		-40℃	10000 or less	5000	5500	89000	
Thickener			-	Urea	PTFE	Urea	Na series
Additive			-	Rust inhibitor	-	-	EP additive etc.
Worked penetration			250~300	280	280	300	276

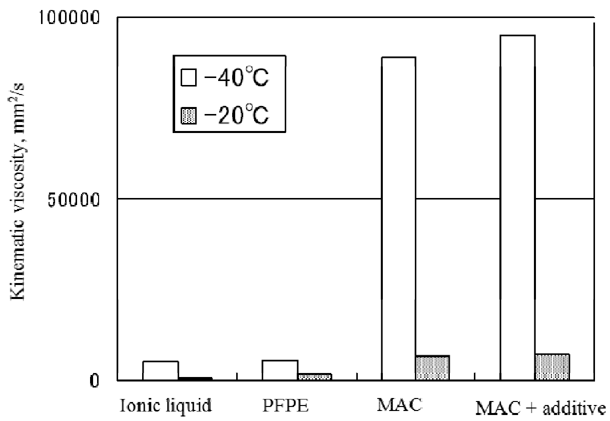


Figure 4. Low temp. kinematic viscosity of ionic liquid and space lubricating oils

3.1. Outgassing property under vacuum

Outgassing measurements were carried out to evaluate vacuum property of IU. As shown in Table 4, IU met the NASA specifications for TML and CVCM.

Table 4. Result of outgassing test

	IU	NASA specification
TML, mass%	0.881±0.004	1.0 or less
CVCM, mass%	0.096±0.004	0.1 or less

3.2. Friction and wear characteristics under vacuum

As for space machine elements including a solar cell paddle drive mechanism, antenna positioning mechanism and bearings and reducers for various scanners, lubricating oils, greases and solid lubricants are selectively used depending on component's own situation. When lubricated with lubricating oil or grease, these machine elements under low-speed condition (<100rpm) are often operated in the mixed- or partial-EHL~boundary lubrication regimes [10].

Figs. 5 and 6 show wear and friction characteristics of each grease under vacuum, respectively. Compared to other greases, IU and its base oil had a lower wear rate and a lower coefficient of friction down to about 0.10 with small variations. IU exceled conventional PFPE and MAC oil-based lubricating oils and greases at friction characteristics.

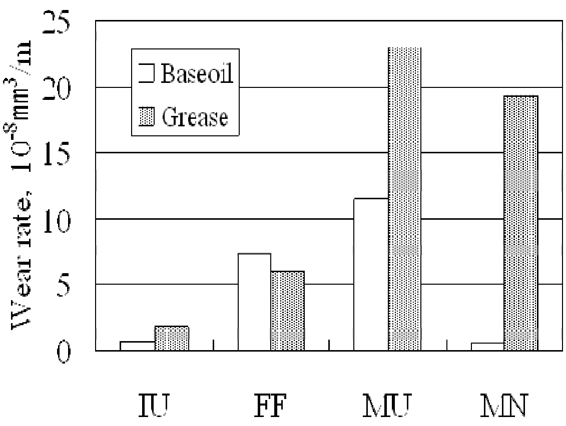


Figure 5. Wear characteristics under vacuum (Apparatus : Ball on disk, sliding speed 20mm/s, max. contact pressure 2.8GPa, vacuum <10^{-4}Pa, testing time 3h, ball and disk material SUS440C)

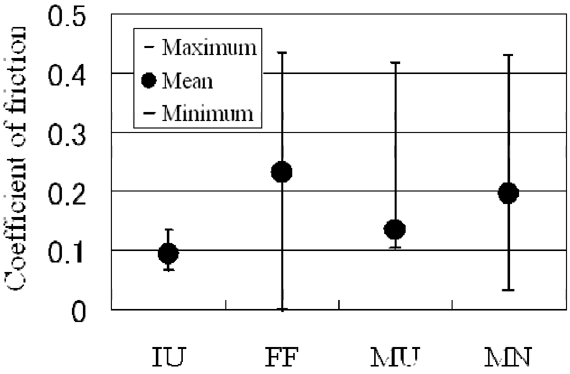


Figure 6. Friction characteristics under vacuum

3.3. Radiation resistance

In geostationary orbit, γ rays having strong penetrating power transmit through even an aluminium film of 1mm thickness allowing machine elements to be subjected to γ rays of about 10^5Gy in 10 years. To cope with this situation, space materials are required to be highly radiation resistant.

Figure 7 shows results of the unworked penetration measurements performed by Japan Atomic Energy Agency for each grease subjected to ^{60}Co- γ rays. The measurements were conducted by delivering a 10^4 Gy/h of radiation at certain periods of time (1h, 10h and 100h) under nearly-sealed condition so that the influence of oxygen was eliminated. IU exhibited high radiation resistance and maintained the initial level of unworked penetration after radiation of 10^6 Gy.

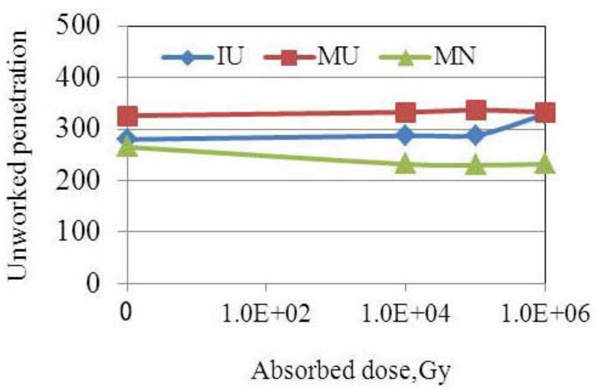


Figure 7. Unworked penetration after γ ray radiation

4. CONCLUSIONS

This report presented a case study where ionic liquids were investigated and applied as a base oil to formulate a space grease satisfying the various demanding requirements.

IU, the ionic liquid-based space grease developed through this study was found to have excellent properties as follows:

(1) Has a low base oil viscosity at -40°C providing sufficient lubrication at low temperatures where before only PFPE greases could be used.
(2) Satisfies the NASA's specification for the universal space equipment standards, TML and CVCM.
(3) Has superior friction and wear characteristics under vacuum below 10^{-4} Pa.
(4) Shows good resistance to γ ray radiation and so is compatible with the space environment.

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