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Journal of Fluorine Chemistry 103 (2000) 129–134

JOURNAL OF FLUORINE CHEMISTRY

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Lubricity of fluorinated alkyl aryl ethers

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Received 7 July 1999; received in revised form 27 September 1999; accepted 5 November 1999

Abstract

A series of fluorinated alkyl aryl ethers, composed of hydrocarbon components, fluorinated alkyl groups, and ether linkage groups, were evaluated through a variety of tests to investigate lubricating properties. The basic molecular structure with tetrafluoroethoxyphenyl groups were shown to have excellent lubricities. However, *ortho*-position substituents to ether linkage groups diminished extreme-pressure properties. Excellent lubricities were suggested to be due to strong coordination of ether oxygen atoms to metal surfaces, and formation of iron fluorides on the metal wear surfaces. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Lubricity; Metal fluoride; Fluorinated alkyl aryl ethers; Synthetic lubricants

1. Introduction

As performance and energy efficiency demands on mechanical apparatus are increasingly heightened, requirements for lubricant performance are becoming correspondingly demanding. In a previous study [1], a series of novel fluorinated alkyl aryl ethers developed as candidates for base stock of high performance lubricants were evaluated for thermal and oxidative stability. It was shown that the basic molecular structure of the fluorinated alkyl aryl ethers had excellent oxidative and thermal stability, making them and their derivatives suitable for further investigation as candidates for base stock of high performance lubricants. Due to the presence of fluorine atoms, these compounds were expected to intrinsically have excellent lubricity. In this study, lubricity of the series of fluorinated alkyl aryl ethers was investigated.

2. Experimental

2.1. Synthesis of fluorinated alkyl aryl ethers

The fluorinated alkyl aryl ethers investigated in this study were synthesized as follows.

2.1.1. Synthesis of 2,2-bis[4-(1,1,2,2-tetrafluoroethoxy)phenyl]propane (hereinafter referred to as ‘BisA-TFE’)

A solution consisting of 68.7 g of 2,2-bis(4-hydroxyphenyl)propane (hereinafter referred to simply as ‘bisphenol A’) and 6.2 g of potassium hydroxide dissolved in 120 ml of dimethyl sulfoxide was charged into a 500 ml microcylinder, which served as the reactor. The reactor was degassed, charged with N_2 gas to restore atmospheric pressure, and then heated to 60°C using an oil bath. Tetrafluoroethylene was then introduced to initiate a reaction. The reaction was carried out for about 5 h with tetrafluoroethylene fed in to maintain reactor pressure between 3 and 4 kg/cm^2.

After completion of the reaction, reaction product was obtained by distilling off dimethyl sulfoxide at 80°C under about 5 mm Hg, and 500 ml of 1,1,2-trichloro-1,2,2-trifluoroethane (hereinafter referred to simply as ‘CFC-113’) was added to the obtained reaction product. This CFC-113 phase was washed three times with 500 ml of distilled water, and CFC-113 was removed under reduced pressure. Thus, 130 g of colorless, transparent oil was obtained. The main fraction (118 g) was isolated by simple distillation, at a boiling point of about 150°C under about 0.1–0.3 mm Hg, indicating that the synthesis reaction yield was 92%.

The isolated fraction was analyzed by infrared absorption spectrometry and mass spectrometry [*m/e* 428 (M^+), 413 (M^+–CH_3)] to confirm that the fraction was BisA-TFE, having the structural formula shown in Table 1.

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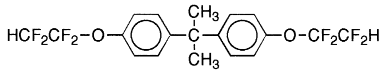
PII: S0022-1139(99)00293-6

Table 1
Lubricity of basic fluorinated alkyl aryl ether and conventional high performance lubricants

BisA-TFE



Sample	Viscosity[a] (cSt at 40°C)	Coefficient of friction[b]	Four-ball test[c] Fail load (kg/cm^2)	Falex test[d]	
				Fail load (kgf)	Wear (mg)
BisA-TFE	26	0.13	9.0	>680	14.2[e]
Naphthene mineral oil[f]	30	0.15	5.0	180	40[g]
Ester oil[h]	20	0.14	5.0	–	–
Turbine oil[i]	32	0.15	4.5	–	–

[a] Measured with E-type rotational viscometer manufactured by Tokyo Keiki K.K.
[b] Measured with pendulum-style friction tester manufactured by Shinko Engineering.
[c] Measured with Soda four-ball test machine manufactured by Shinko Engineering.
[d] Measured with Falex pin and vee-block test machine manufactured by Shinko Engineering.
[e] Measured under blowing of HFC-134a.
[f] Suniso 3GS, manufactured by Nippon Sun Oil Company.
[g] Measured under blowing of CFC-12.
[h] Unistar H334R, manufactured by Nippon Oil Fats.
[i] Tellus Oil 32, manufactured by Showa Shell Sekivu K.K. (containing additives).

2.1.2. Synthesis of 1,1,3,3-tetramethyl-4-(1,1,2,2-tetrafluoroethoxy)phenylbutane (hereinafter referred to as 'PTOP-TFE')

PTOP-TFE was prepared in substantially the same manner as BisA-TFE except that *p-tert*-octylphenol (obtained from Tokyo Kasei Kogyo) was used in place of bisphenol A. The synthesis reaction yield was 94%. Infrared absorption spectrometry and mass spectrometry [*m/e* 306 (M^+)] confirmed that the obtained product was PTOP-TFE, having the structural formula shown in Table 2.

2.1.3. Synthesis of 2,2-bis[4-(1,1,2,2-tetrafluoroethoxy)phenyl]-4-methylpentane (hereinafter referred to as 'MIBK-Bis-TFE')

MIBK-Bis-TFE was prepared in substantially the same manner as BisA-TFE except that 2,2-bis(4-hydroxyphenyl)-4-methylpentane (obtained from Honshu Chemical Industry) was used in place of bisphenol A. The synthesis reaction yield was 95%. Infrared absorption spectrometry and mass spectrometry [*m/e* 470 (M^+)] confirmed that the obtained product was MIBK-Bis-TFE, having the structural formula shown in Table 2.

2.1.4. Synthesis of BisP-OT-TFE, BisP-IOTD-TFE, BisC-TFE and BisOSBP-A-TFE

These compounds were prepared in substantially the same manner as BisA-TFE, except that 2,2-bis(4-hidroxyphenyl)octane, 1,1-bis(4-hydroxyphenyl)-2-ethylhexane, 2,2-bis(3-methyl-4-hydroxyphenyl)propane, and 2,2-bis(3-*sec*-butyl-4-hydroxyphenyl)propane, respectively, were used in place of bisphenol A. Each of these materials were obtained from Honshu Chemical Industry. Synthesis reaction yields were 90, 88, 90, and 94%, respectively. Infrared absorption spectrometry and mass spectrometry confirmed that the products were compounds having the structural formulas shown in Table 2.

2.2. Conventional lubricants

Commercially available lubricants were used in this study to provide reference data. Naphthene mineral oil (Suniso 3GS) was obtained from Nippon Sun Oil Company, ester oil (Unistar H334R) was obtained from Nippon Oil Fats and turbine oil (Tellus Oil 32) was obtained from Showa Shell Sekiyu K.K. Three types of perfluoropolyether oils, as below, were also studied.

Fluid K: $C_3F_7O[CF(CF_3)CF_2O]_xC_2F_5$
Fluid F: $CF_3O[CF(CF_3)CF_2O]_m(CF_2O)_nCF_3$
Fluid D: $C_3F_7O(CF_2CF_2CF_2O)_xC_2F_5$

Fluid K was obtained from Du Pont (Krytox 143AB), Fluid F was obtained from Montefluos (Fomblin Y25A) and Fluid D was obtained from Daikin Industries (Demnum S-65).

2.3. Evaluation of lubricating properties

Coefficient of friction was measured using a pendulum-style friction tester manufactured by Shinko Engineering with an initial oil temperature of 20°C. Four-ball test fail load was measured using a Soda four-ball test machine manufactured by Shinko Engineering at 200 rpm. Load oil pressure was increased by 0.5 kgf/cm^2/min, and fail load was determined as the oil pressure at seizure.

Falex test fail load[1] was measured using a Falex pin and vee-block test machine manufactured by Shinko Engineer-

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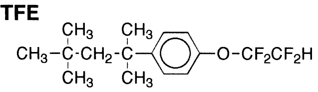
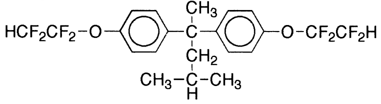
[1] ASTM Designation D3233-86.

Table 2
Lubricity of substituted fluorinated alkyl aryl ethers

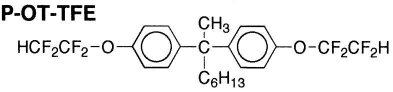
PTOP-TFE



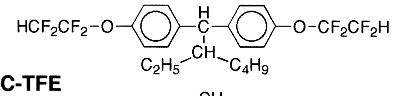
MIBK-Bis-TFE



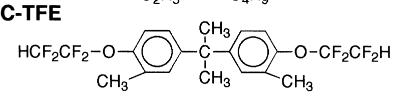
BisP-OT-TFE



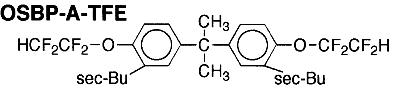
BisP-IOTD-TFE



BisC-TFE



BisOSBP-A-TFE



Compound	Viscosity (cSt at 40°C)[a]	Falex test[b]	
		Fail load (kgf)	Wear (mg)
PTOP-TFE	6	360	10.0[c]
MIBK-Bis-TFE	109	>680	17.7[c]
BisP-OT-TFE	112	>680	12.8[c]
BisP-IOTD-TFE	250	460	14.2[c]
BisC-TFE	115	480	–
BisOSBP-A-TFE	91	440	14.7[c]
cf. BisA-TFE	26	>680	14.2[c]
cf. Naphthene mineral oil[d]	30	180	40.0[e]

[a] Measured with E-type rotational viscometer manufactured by Tokyo Keiki K.K.
[b] Measured with Falex pin and vee-block test machine manufactured by Shinko Engineering.
[c] Measured under blowing HFC134a.
[d] Suniso 3GS, manufactured by Nippon Sun Oil Company.
[e] Measured under blowing CFC-12.

ing. The tester was driven for 3 min at a load of 136 kgf, then load was increased continuously until failure.

Wear was measured using a Falex pin and vee-block test machine[2]. Refrigerant gas (CFC-12 or HFC-134a) was blown into sample oil at a blow rate of approximately 150 ml/min for about 30 min. A load of 90 kgf was applied, and the Falex tester was driven for 5 min with continuous gas blowing. Load was then increased to 230 kgf, and the tester was driven for 2 h under constant 230 kgf load. The weight of the vee-block and pin was measured before and after each test run, and 'wear' was defined as the difference between these weight measurements.

Four-ball extreme-pressure tests[3] were carried out using a tester manufactured by Falex. A series of tests of 60 s duration were conducted at 1500 rpm with increasing load (20, 32, 40, 50, 63, 80, 100, 160, and 200 kgf) until welding occurred. The scar diameters of the stationary test balls were measured, and the 'last non-seizure load' was defined as the lowest applied load at which the measured scar diameters were not more than 5% above the reference scar diameter as calculated to compensate for dynamic conditions specific to the test apparatus.

2.4. XPS measurement

Journals from Falex wear tests were rinsed with acetone to remove remaining lubricant, and analyzed by X-ray photoelectron spectrometry (XPS) using an ESCA Lab. 200X manufactured by VG Scientific.

2.5. Measurement of total acid number (TAN)

TAN was measured in substantially the same manner as ISO 6618, except that 0.01 mol/l solution of potassium hydroxide was used in place of 0.1 mol/l solution.

3. Results and discussion

3.1. Lubricating properties of basic fluorinated alkyl aryl ether compound

Lubricating properties of BisA-TFE and conventional high performance lubricants (naphthene mineral oil, ester oil and turbine oil) are shown in Table 1. BisA-TFE had the lowest coefficient of friction, at 0.13, and the highest four-ball test fail load, at 9 kg/cm^2.

Falex fail load and wear tests were carried out to further investigate BisA-TFE performance in comparison with

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[2] ASTM Designation D2670-88.
[3] ASTM Designation D783-88 (Reproved 1993).

naphthene mineral oil. Naphthene mineral oil is widely used as base oil for refrigeration lubricants in refrigerating machines using conventional chlorofluorocarbon (CFC) refrigerant. Though the lubricity of naphthene mineral oil alone is not sufficient, it improves substantially when metal chlorides form on metal surfaces with chlorine atoms from CFC refrigerants [2,3]. To compensate for this effect in the Falex wear test, 1,1-dichloro-1,1-difluoromethane (CFC-12) was blown into the sample oil during testing.

In order to measure the performance of BisA-TFE without the metal chloride effect, its Falex wear test was conducted without CFC refrigerants. However, in order to attain test results comparable with those of naphthene mineral oil, 1,1,1,2-tetrafluoroethane (HFC-134a) was blown into the BisA-TFE during testing to reproduce any reduction in viscosity which may result from dissolution of refrigerant gas in the sample oil, as well as any detrimental effect on lubricity which may result from the presence of refrigerant bubbles on the metal wear surfaces.

Falex test results are also shown in Table 1. The fail load for naphthene mineral oil was 180 kgf, but no fail load for BisA-TFE was observed up to the test limit 680 kgf. The wear for BisA-TFE was 14.2 mg, while that for naphthene mineral oil was 40 mg. Considering that the lubricity of the naphthene mineral oil was improved by the effect of metal chloride formation, the lubricity of BisA-TFE was clearly superior.

It is believed that the excellent lubricity of BisA-TFE can be explained by examining its molecular structure, as illustrated in Fig. 1. The low coefficient of friction is attributed to weak intermolecular forces between the fluorine atoms of the Rf groups. The outstanding extreme-pressure properties are attributed to the strong coordination of the ether oxygen atoms to fresh metal surfaces. It has been reported that under boundary lubrication conditions, metal oxides and adsorbed impurities are removed from asperity contacts on the wear surfaces [4]. The fresh metal surfaces thus exposed are believed to enable strong ether oxygen coordination, resulting in very high strength lubricant film. These characteristics of the BisA-TFE molecule are expected to be common to all derivative species, barring the effects of substituent groups.

3.2. Relationship between lubricity and the molecular structure

Table 2 shows Falex test results for various fluorinated alkyl aryl ethers. Tests were conducted with HFC-134a blown in sample oils. Fail load and wear results varied somewhat, but lubricity of all fluorinated alkyl aryl ethers were clearly superior to that of naphthene mineral oil.

The fail load for PTOP-TFE was the lowest among the fluorinated alkyl aryl ethers, at 360 kgf. It has been shown that dihydric alcohols have better lubricating properties than monohydric alcohols, because of the stronger coordination to metal surfaces which results from the greater number of coordination sites [2,5]. The authors believe that similarly, BisA-TFE, with two ether groups, coordinates more strongly to metal surfaces than PTOP-TFE, which has only one ether group. With only one coordination site per molecule, PTOP-TFE forms a weaker film than BisA-TFE which has two sites per molecule. The relative weakness of the film then explains the lower fail load result.

Bis-MIBK-TFE and BisP-OT-TFE are compounds with an iso-butyl group and an *n*-hexyl group, respectively, substituted on the central carbon of BisA-TFE. As with BisA-TFE, the fail loads of both exceeded the 680 kgf limit of the test apparatus, indicating that alkyl group substitution on the central carbon had no observable effect on extreme-pressure properties.

BisP-IOTD-TFE, on the other hand, gave a fail load result of 460 kgf. As reported previously [1], BisP-IOTD-TFE has relatively poor thermal and oxidative stability. Decomposition by heat generated from friction is believed to explain the low extreme-pressure property of BisP-IOTD-TFE.

BisC-TFE and BisOSBP-A-TFE are compounds with methyl groups and *sec*-butyl groups, respectively, substituted at *ortho*-positions with the ether linkage groups of BisA-TFE. Their fail loads were significantly lower than that of BisA-TFE, at 480 and 440 kgf, respectively. It is believed that these compounds have inferior extreme-pressure performance because *ortho*-position substituents prevent the coordination of ether oxygen atoms to the metal surface, in contrast to substituents on the central carbon which do not prevent such coordination, as illustrated in Fig. 2.

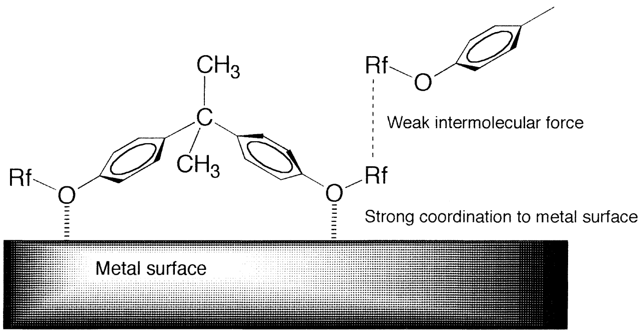

Fig. 1. Suggested mechanism of lubricity of BisA-TFE.

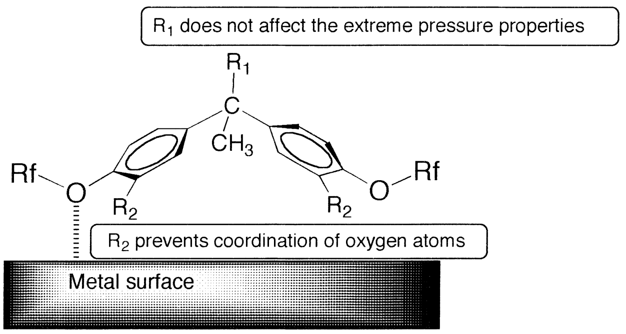

Fig. 2. Effects of substituent group position on extreme pressure lubricity.

These results support the suggested mechanism described above, that the strong coordination of the ether oxygen atoms to metal surfaces results in the formation of lubricant film which is very durable under extreme-pressure.

Wear results in the range of 10.0–17.7 mg were observed for all fluorinated alkyl aryl ethers, much less than that for naphthene mineral oil. The relationship between wear results and steric effects of substituents was not clear. As wear test load was 230 kgf, much lower than the fail loads, and wear test period was 2 h, much longer than the fail load tests, other properties of lubricants, for example, viscosities and thermal stabilities, are presumed to have influenced wear results. Further investigations by authors will be concerned with the relationship between wear properties and molecular structures of fluorinated alkyl aryl ethers.

3.3. Lubricity comparison with perfluoropolyethers

Table 3 shows lubricity of fluorinated alkyl aryl ethers and perfluoropolyethers, which also contain fluorinated alkyl groups and ether linkage groups, as evaluated by extreme-pressure four-ball tests.

Three types of perfluoropolyether were evaluated. Their last non-seizure loads were 20 and 32 kgf. Last non-seizure loads for BisOSBP-A-TFE and BisP-OT-TFE were higher than those of the perfluoropolyethers, at 50 kgf, indicating that the load range where seizure does not occur is clearly broader with the fluorinated alkyl aryl ethers than perfluoropolyethers. Due to weak basicity of their ether oxygen atoms, perfluoropolyethers are not expected to form strong lubrication film. Therefore, local seizure will be caused at the asperity contacts under boundary lubrication conditions. In contrast, the strong lubrication film of the fluorinated alkyl aryl ethers prevents local seizure, resulting high last non-seizure loads.

Table 3
Lubricity of fluorinated alkyl aryl ethers and perfluoropolyethers

Compound	Viscosity[a] (cSt at 40°C)	Last non-seizure load[b] (kgf)
BisOSBP-A-TFE	112	50
BisP-OT-TFE	91	50
Perfluoropolyether		
Fluid K[c]	85	20
Fluid F[d]	94	32
Fluid D[e]	65	32

[a] Measured with E-type rotational viscometer manufactured by Tokyo Keiki K.K.

[b] Measured with four-ball extreme-pressure tester manufactured by Falex.

[c] Krytox 143AB, manufactured by E.I. DuPont De Nemours and Company.

[d] Fomblin Y25A, manufactured by Nippon Montedison K.K.

[e] Demnum S-65, manufactured by Daikin Industries.

Table 4
XPS analysis of journal surface[a]

Specimen	Lubricant	Refrigerant gas blown into lubricant	Wear (mg)
Sample A	BisOSBP-A-TFE	HFC-134a	1.7
Sample B	BisOSBP-A-TFE	None	0.9

[a] Test conditions — Tester: Falex pin and vee-block test machine, manufactured by Shinko Engineering; Starting temperature: 80°C; Load: 68 kgf; Test duration: 120 mm.

3.4. XPS analysis of wear surface

The formation of ferric fluoride (FeF_3) through the interaction of perfluoropolyethers with steel surfaces under boundary conditions has been well researched [6–9] and it is known that iron fluoride act as wear reducer [10].

Falex journal specimens for XPS analysis of iron fluoride formation with BisOSBP-A-TFE were prepared as shown in Table 4. Fig. 3 shows a wide scan XPS spectrum of the surface of sample A. Narrow scan XPS spectrum of sample A (Fig. 4) indicates that the signal for fluorine was at 684.2 eV. This is very near to the 685 eV signal indicating FeF_3 which has been observed on the wear surface using perfluoropolyether as lubricant [7]. The 684.2 eV signal is therefore believed to indicate the formation of iron fluorides on the wear surface in the present test.

As sample A was a journal from a Falex test conducted with HFC-134a, the fluorine atoms of the iron fluoride may have originated from either the BisOSBP-A-TFE or the HFC-134a. However, in the narrow scan XPS spectrum of sample B, a journal from a Falex test conducted without HFC-134a, an iron fluoride signal was observed at same position (Fig. 4), indicating that fluorine from the fluorinated alkyl aryl ether does form iron fluorides on the wear surface.

It is believed that the formation of iron fluorides with fluorinated alkyl aryl ethers may be explained by the coordination of ether oxygen atoms to the metal surface, which would place the fluorinated alkyl groups very close to the metal surface. A reaction involving the fluorinated alkyl

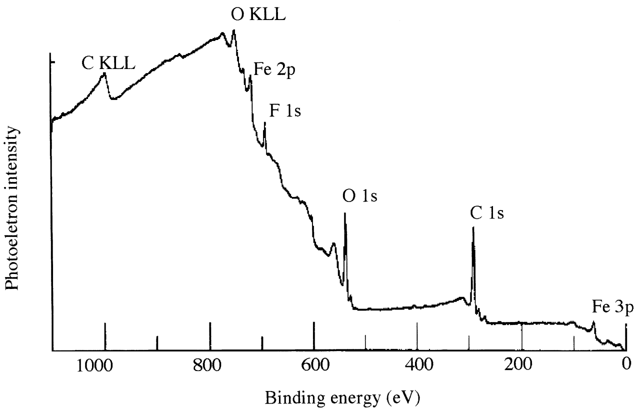

Fig. 3. Wide scan XPS spectrum of sample A.

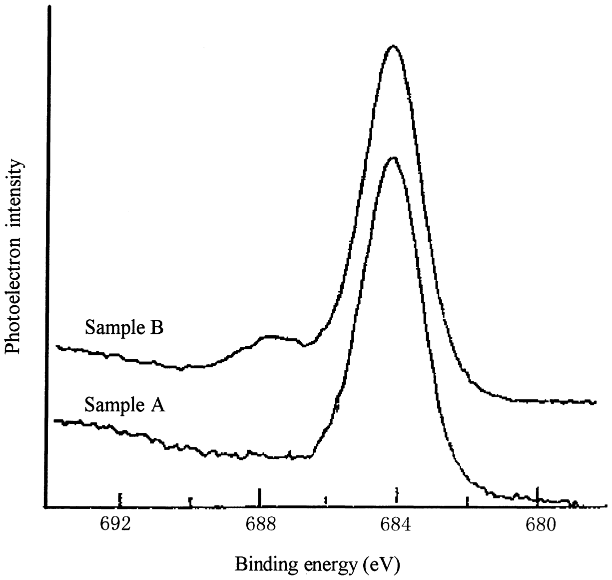

Fig. 4. Narrow scan XPS spectra of samples A and B.

groups and metal atoms at the surface would then occur by heat of friction, resulting in iron fluoride formation, which improves wear properties.

Iron fluoride also catalyzes the scission of carbon–oxygen bonds in perfluoropolyethers, resulting in degradation products and polymeric fluorocarbon compounds [6–9]. However, degradation products were not detected by infrared spectral analysis or gas chromatography for BisOSBP-A-TFE. Furthermore, total acid number (TAN) of post-test sample of BisOSBP-A-TFE showed no change, clearly indicating that the scission observed with perfluoropolyethers did not occur. The authors believe that electrons from the benzene rings strengthened the adjacent carbon–oxygen bonds, suppressing the scission reaction catalyzed by iron fluoride.

4. Conclusions

These results suggest the following conclusions: (1) the basic molecular structure of the fluorinated alkyl aryl ether series studied results in excellent lubricating properties, (2) compounds obtained by substitutions on the basic molecular structure also have excellent lubricity, but *ortho*-position substituents diminish extreme-pressure properties, (3) excellent extreme-pressure properties are believed to be due to the high lubricant film strength which results from strong coordination of ether oxygen atoms to metal surfaces, and (4) fluorine atoms from the fluorinated alkyl groups form iron fluorides on the metal wear surfaces, which improve wear properties.

These conclusions will serve as a useful guide to designing novel high-performance lubricants. In subsequent studies, the authors will evaluate practical lubricating properties of this series of fluorinated alkyl aryl ethers and lubricants derived from them.

Acknowledgements

The authors are grateful to Dr. Jun Kikuma , Mr. Masashi Watanabe and Mr. Atsushi Seo of Asahi Chemical for their helpful discussion.

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