Characteristic Properties of Cutting Fluid Additives Derived from Fatty Alcohols

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Many 3-aminopropyl alkyl ethers were prepared and their characteristics as water-based cutting fluids were examined. 3-Aminopropyl octyl-, decyl- and dodecyl ethers showed good lubricities and antimicrobial properties for a water-based cutting fluid.

KEY WORDS: 3-Aminopropyl alkyl ethers, anti-microbial activity, anti-rust activity, cutting fluid additives, water-based cutting fluids.

A variety of water-soluble cutting fluids are used for machine operations. For water-soluble cutting fluids, anti-rust, good lubrication property and anti-bacterial property are essential (1). The relationship between the properties of water-soluble cutting fluids and the functional groups of various organic additives has not been reported in detail. The authors have previously shown that epoxides of unsaturated fatty acids have excellent properties as anti-rust additives for water-soluble cutting fluids (2). In this work, we examined the anti-rust properties, lubricity characteristics and antimicrobial properties of various derivatives from fatty alcohols and acrylonitrile. This short paper will describe our recent evaluation of these new additives for use in water-soluble cutting fluids.

EXPERIMENTAL PROCEDURES

*Preparation of 2-cyanoethyl dodecyl ether (***III***, $R=C_{12}H_{25}$).* A mixture n-dodecyl alcohol (**I**, $R=C_{12}H_{25}$) (16.3 g, 0.1 mol), acrylonitrile (**II**) (10.6 g, 0.2 mol) and potassium hydroxide (1.0 g) in dry tetrahydrofuran (120 mL) was refluxed for 8 hr and left overnight. The reaction mixture was diluted with water (200 mL) and extracted with diisopropyl ether. The ether extracts were washed with a solution of salt and dried over sodium sulfate. On removal of the solvent, distillation gave 2-cyanoethyl dodecyl ether (**III**, R= $C_{12}H_{25}$) in 68% yield: b.p. 126°C/25 mmHg, IR(cm^{-1}): 2220(CN), 1150(-O-). Other ethers were prepared in the similar manner.

*Preparation of 3-aminopropyl dodecyl ether (***IV***, $R=C_{12}H_{25}$).* Compound (**III**, $R=C_{12}H_{25}$) (10.55 g, 0.05 mol) in dry diethyl ether (25 mL) was added dropwise to the suspension of $LiAlH_4$ (1.90 g, 0.05 mol) in dry diethyl ether (50 mL) at 0°C. After agitation for 5 hr, the reaction mixture was quenched by adding diluted hydrochloric acid dropwise. Unreacted materials were removed by extraction with diisopropyl ether. The water solution was alkalined with 5% sodium hydroxide solution. Compound (**IV**, $R=C_{12}H_{25}$) was extracted with diisopropyl ether. The ether solution was washed with water and dried over anhydrous sodium sulfate. On removal of the solvent, distillation gave 3-aminopropyl dodecyl ether (**IV**, $R=C_{12}H_{25}$) (6.34 g) in 59% yield: bp 150°C/25 mmHg; IR(cm^{-1}): 3300(NH_2), 1150(-O-); NMR(δ, ppm): 0.85(3H, t, J=5.0 Hz, CH_3-), 1.2~1.5(22H, m, -CH_2-×10 and NH_2), 1.71(2H, t, J=6.0Hz, -CH_2-), 2.13(2H, t, J=6.0Hz, -$\underline{CH_2}$-NH_2), 3.45 (4H, m, -$\underline{CH_2}$-O-$\underline{CH_2}$). Other amino ethers were prepared in a similar way.

Test methods. Aqueous emulsions of water (198.0 g), an amino ether (1.0 g) and polyoxyethylene alkylether (EO 5 mols) as an emulsifier were used. City water in Japan (Chiba and Osaka) was used for all tests. The same results were obtained in all the tests as with distilled water.

Corrosion tests with cast iron chips were carried out as follows. Two grams of cast iron chips (JIS G 5501, FC-20, gray iron casting) which had been washed with benzene were immersed in a sample solution (5 mL) in a watch glass. The container was covered. After 10 min, the solution was removed by tilting the watch glass. The rust-preventive effect was determined as shown in Table 1. This method is a standardized test in Japan and is based on the I.P. Corrosion Test 125/63 T (3).

The coefficient of friction was measured at 25°C by a pendulum-type oiliness and friction tester (Shinko Engineering Co., Ltd., Tokyo, Japan). The special features are as follows: i) Use of four balls and a pin made of high-quality steel assures the accuracy of test pieces and prevents fitting errors. High testing load is applicable because of the point contact. Formation of boundary oil film is easily made. ii) The apparatus is free from friction heat because of the pendulum type. iii) Measuring is simple but accurate and easily reproducible. The main particulars were as follows: test ball, diameter 5 mm (SUJ-2, bearing ball); test roller pin, diameter 2 mm (SJU-2 bearing ball); cycle of pendulum swing, ca. 4 seconds; maximum pendulum swing, 0.7 rad; test load (max. hertz/stress), 15000 kg/cm^2; temperature of test oil, room temperature to 300°C (4).

TABLE 1

Valuation of Anti-Rust Effect

Time (hr)	The amount of rust	Valuation point
72	No appearance of rust	10
48~72	1~2 Points of rust	9
24~48	1~2 Points of rust	8
24	1~2 Points of rust	7
24	Some points of rust	6
12~24	Some points of rust	5
8	Some points of rust	4
6	Some points of rust	3
3	Some points of rust	2
1	Some points of rust	1

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Welding loads ($kgf \cdot cm^{-2}$) were measured on a Soda-type four-ball lubricating oil testing machine at 200 rpm. This testing machine and friction tester mentioned above have been officially authorized by the Agency of Industrial Science and Technology of Japan as JIS K 2519 and 2219. The main particulars were as follows: test ball diameter, 19.05 mm (SUJ-2 bearing ball); revolution of spindle, 150–1500 rpm; temperature of test oil, room temperature to 200°C; hydraulic cylinder diameter, 80 mm; maximum load on the test ball, 1000 kg; pressure of the hydraulic pump, 0–20 kg/cm^2; overall dimensions, 1700 mm (diameter) × 650 mm (width) × 1600 mm (height); weight, 450 kg. The machine was obtained from Shinko Engineering Co., Ltd. (5). Surface tentions (dyne/cm) were measured at 25°C with a Du Nouy tensiometer.

Antimicrobial activity tests were carried out as follows: A mixture of a sample (1.0 g), polyoxyethylene alkylether (EO 5 mols) (1.0 g), water (198 g), cast iron chips (FC-20) (1.0 g) and spent coolant (1.0 g) was kept in an incubator at 38°C. With the passage of time, the pH of the sample solution and the bacterial content was observed. The bacterial content of the spent coolant was about 10^7/mL. The bacterial content of sample solution was measured by Easicult-TTC plate (Medical Technology Corp., Somerset, NJ). The plate was dipped into a test solution and kept in an incubator at a temperature of 35°C. After 48 hr incubation, the bacterial content of sample solutions was determined by comparing the density of the colonies appearing on the slide with the densities shown on the model chart.

RESULTS AND DISCUSSION

The authors previously reported that 11-phenoxyundecanoic acid (6) and 10,11-epoxyundecanoic acid (7) have

TABLE 2

Cutting Fluid Characterization of Various ω-Amino Alkyl Ethers

R for amino ether ($ROC_3H_6NH_2$)	pH	Rust-inhibition test after 72 hr	Friction coefficient	Surface tension dyne/cm	Welding load $kgf \cdot cm^{-2}$
n-Butyl	10.8	10	0.23	38	7.0
n-Hexyl	10.9	10	0.28	39	9.0
n-Octyl	9.9	10	0.32	39	9.0
2-Ethylhexyl	9.9	10	0.29	38	8.0
sec-Octyl	10.3	10	0.23	38	8.0
n-Decyl	10.2	10	0.31	36	9.5
n-Dodecyl	9.8	10	0.28	36	10.5
Oleyl	9.9	10	0.21	36	12.5
Benzyl	10.2	10	0.29	39	7.0
Water only		1	0.48	72	3
Milky emulsion[a]	8.3	4	0.13	38	12
Chemical grinding fluid[b]	9.6	6	0.25	58	5

[a, b]These are commercial samples. The chemical compositions of milky emulsion are as follows: mineral oil (79 wt%), sodium sulfonate (10 wt%), alkanol amide (10 wt%), and antimicrobial agent (1 wt%). The compositions of chemical grinding fluids are as follows: boric acid (5 wt%), triethanolamine (30 wt%), antimicrobial agent (1%), and water (64%).

TABLE 3

Antimicrobial Activity of Some ω-Aminopropyl Alkyl Ethers

	Time (days)							
	Initial		7		14		21	
R for amino ether ($ROC_3H_6NH_2$)	pH	Bacterium (cbu/mL)	pH	Bacterium (cbu/mL)	pH	Bacterium (cbu/mL)	pH	Bacterium (cbu/mL)
n-Butyl	10.8	10^4	10.4	10^5	9.8	10^6	8.9	10^6
n-Hexyl	10.9	10^4	10.2	10^5	9.6	10^5	8.9	10^6
n-Octyl	9.8	10^4	9.3	10^6	8.9	10^6	8.7	10^6
sec-Octyl	10.3	10^4	10.0	10^5	9.7	10^5	9.4	10^6
Decyl	10.2	10^4	10.0	10^5	9.6	10^6	9.3	10^6
Lauryl	10.1	10^4	9.8	10^5	9.5	10^6	9.2	10^6
Oleyl	9.8	10^4	9.0	10^6	8.0	10^6	7.9	10^6
Benzyl	9.9	10^4	9.2	10^6	8.8	10^6	8.6	10^6
Milky emulsion[a]	9.6	10^4	9.0	10^7	8.4	10^7	8.0	$>10^7$
Chemical grinding fluid[b]	9.4	10^3	9.0	10^6	8.6	10^6	8.0	$>10^7$

[a, b]These are commercial samples. The compositions of these samples are indicated in Table 2.

excellent properties for rust inhibition. In this research aqueous solutions of triethanolamine salts of these fatty acid derivatives were evaluated as cutting fluid additives. In this short paper, we describe a new type of cutting fluid additive without using triethanolamine. We prepared various amino ethers from fatty alcohols, and examined characteristic properties of water-soluble cutting fluids prepared from them.

2-Cyanoethyl alkyl ether (**III**) was prepared from the reaction of fatty alcohol (**I**) and acrylonitrile (**II**) in the presence of potassium hydroxide. Reduction of (**III**) with lithium aluminium hydride gave 3-aminopropyl alkyl ether (**IV**) by the synthetic route, as shown in Scheme 1.

$$\mathrm{ROH\ (I)} + \mathrm{CH_2{=}CHCN\ (II)}$$
$$\downarrow$$
$$\mathrm{RO(CH_2)_2CN\ (III)}$$
$$\downarrow$$
$$\mathrm{RO(CH_2)_3NH_2\ (IV)}$$

SCHEME 1

Aqueous emulsions of compound (**IV**) with polyoxyethylene alkylether were evaluated as cutting fluids additives, and the results are listed in Table 2. We have found that the emulsions of these compounds (**IV**) containing an amino group and an alkyl group have excellent anti-rust and anti-wear properties. Thus, aqueous emulsions of 3-aminopropyl dodecyl ether (**IV**, $R=C_{12}H_{25}$) demonstrated excellent corrosion resistance in a test with cast-iron chips. The load capacity of this emulsion was about 10.5 $kgf{\cdot}cm^{-2}$ at 200 rpm. The anti-wear load should have as high a value as possible, the desirable value being more than 10 $kgf{\cdot}cm^{-2}$. Water soluble cutting fluids are easily degraded by various microorganisms. Many materials, such as alkanolamines, were studied for their antimicrobial properties against a mixed flora of fungi and bacteria in cutting fluids (8–10). In this paper, we examined the antimicrobial properties of 3-aminopropyl alkyl ethers in water-based cutting fluids. After incubating them at 38°C, a decrease in the pH and the bacterial contents of the sample solution were observed. As shown in Table 3, we concluded that ω-aminopropyl hexyl-, octyl- and decyl-ethers showed a fair antimicrobial property in a spent coolant. These new additives described above for water-based cutting fluid were previously unknown.

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