Adducts of Cyclic Acid Anhydrides and Fatty Amines as Anti-Rust Additives in Water-Based Cutting Fluids

S. Watanabe[*,a], **H. Kawahara**[b] and **T. Kuramochi**[a]

[a]Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoicho, Chiba, Japan 260 and [b]NEOS Central Research Laboratory, Kohsei-cho, Kohga-gun, Shiga-ken, Japan 520-32

A variety of *N*-alkyl carboxylic acid amides was prepared from the reaction of cyclic dicarboxylic acid anhydrides and various amines, and screened for anti-rust properties and antimicrobial activity in spent coolants of water-based cutting fluids. The triethanol amine salts of the adducts of maleic anhydride with octylamine, decylamine, dodecylamine and oleylamine, and the one of phthalic anhydride with octylamine showed both good anti-rust and antimicrobial activity.

KEY WORDS: *N*-alkyl carboxylic acid amide, *N*-alkyl maleamidic acid, anti-microbial activity, anti-rust activity, anti-rust additives, water-based cutting fluid.

Recently, a variety of fatty acid derivatives was used for additives of water-based cutting fluids (1). For water-soluble cutting fluids, anti-rust, good lubrication, and anti-bacterial properties are essential. Water-soluble cutting fluids prepared from fatty acids are easily spoiled by various microorganisms. We reported that various boric acid esters of amino alcohols show good anti-microbial activity in spent coolants of water-based cutting fluids (2). However, the additives which possess both anti-rust and anti-microbial properties have not been known. In this paper, we prepared new additives from the reactions of cyclic acid anhydrides and various amines, and tested these for anti-rust activity and anti-microbial activity.

EXPERIMENTAL

Reaction of maleic anhydride (**I**) *with octyl amine* (**II**) *(Scheme 1).* To a mixture of maleic anhydride (**I**) (9.8 g, 0.1 mol) and carbon tetrachloride (100 mL), carbon tetrachloride (20 mL) solution of octyl amine (**II**) (12.9 g, 0.1 mol) was added drop by drop at 70°C. The mixture was agitated for 4 hr and left overnight. The precipitated product was separated by filtration from the reaction mixture. It was washed with carbon tetrachloride three times and dried under reduced pressure to give crude N-(n-octyl)-maleamidic acid (**III**) (20.4 g, 90%) (Scheme 1). Infrared (IR) (cm^{-1}): 3250, 1700, 850, 614; mass spectra (MS) (m/e): M^+=227.1520 ($C_{12}H_{21}NO_3$). Other amido carboxylic acids were prepared in a similar manner. Aqueous solutions of triethanolamine salts of these amido carboxylic acids were used in the cutting fluids characterization.

Test methods of anticorrosion and lubricity. Aqueous solutions of triethanolamine salts of the products listed in Table 1 were used. City water in Japan was used for corrosion tests (1) and antimicrobial activity tests (2,3). The same solutions were used for all tests. The same results were obtained in the tests using either distilled water or city water in Chiba, Japan.

Method a—corrosion test with cast iron chips. Two grams of cast iron chips (JIS G 5501, FC-20) which had been washed with benzene were immersed in a sample solution (5 mL) of cutting fluids in a watch glass. The container was covered. After 10 min, the solution was removed by tilting the watch glass. The rust-preventive effect (the amount of rust on the cast-iron chips) was observed after 24 hr. A score of ten points shows no appearance of rust; eight points show a little appearance of rust (1).

Method b—corrosion test with iron chips using filter paper. A filter paper (Toyo filter paper 7 cm 5B) was placed on the bottom of a watch glass. Ten grams of cast iron chips on the filter paper were immersed in a sample solution. After 10 min, the aqueous solution was removed. After 24 hr, the amount of rust transferred onto the filter paper was observed. The evaluation of the anti-rust property is as follows: A) no rust; B) spots of rust are 1∼10; C) spots of rust are over 10; D) area of rust is less than 50% of the filter paper; E) area of rust is more than 50% of the filter paper (1).

The coefficients of friction were measured at 25°C by a pendulum-type oiliness and friction tester according to the method of reference 1.

The surface tensions (dyne/cm) were measured at 25°C by a Du Nouy Tensiometer.

Welding load (anti-wear load) (kgf/cm^2): the anti-wear tests of the desired solution were run on a Soda-type four-ball lubricating-oil testing machine at 200 rpm. Anti-wear load should have as high a value as possible, the desirable value being more than 10 kgf/cm^2.

Antimicrobial activity tests for spent coolants of water-based cutting fluids (2,3,6). A mixture of a sample (1.0 g), triethanolamine (2.0 g) and water (97.0 g) was prepared. To this solution (100.0 g), cast-iron chips (FC-20, 1.0 g) and a spent coolant (1.0 g) were added, and the mixture was kept at 35°C for 28 days. After 7, 14 and 21 days, the bacteria contents were measured. Spent coolant was supplied by NEOS Central Research Laboratory (Shiga-ken, Japan). It is known that spoilage may be caused by several different organisms working together (4,5). The spent coolant contains microorganisms, such as *Staphylococcus aureus, Desulfovibrio desulfuricans, Pseudomonas aeruginosa, Pseudomonas oleovorans, Klebsiella pneumoniae, Escherichia coli, Proteus mirabilis* and *Fusarium up.* The bacteria content of the spent coolant was over 10^7 mL. The bacteria contents of the sample solutions were measured according to the following procedure (6). A standard agar medium was placed in a sharle and solidified. A standard amount of the sample solution was dropped on the center of the agar and spread uniformly with a sterile, bent glass rod. The agar was kept at 35°C for 48 hr. After 48 hr, the numbers of the colonies appearing on the agar were counted with the naked eye using a microscope. When the bacteria content was under 10^3/mL, it was judged that the sample had not been spoiled. In the case of 10^3∼10^6/mL, it was

*To whom correspondence should be addressed.

TABLE 1

Anti-Rust Activity and Lubricity Property of the Products from the Reactions of Cyclic Acid Anhydrides with Various Amines

Acid anhydride	Amines	pH of sample solution	Rust inhibition test[a]		Friction coefficient	Surface tension dyne/cm	Welding load kgf/cm^2
			Test a	Test b			
Maleic anhydride	octylamine	8.4	10		0.15	36.5	13.0
Methylmaleic anhydride	octylamine	8.6	9		0.33	33	16.0
Bromomaleic anhydride	octylamine	8.8	9		0.16	33	19.0
Succinic anhydride	octylamine	8.6	9		0.16	31	7.0
Glutalic anhydride	octylamine	9.1	9		0.50	34	10.0
Phthalic anhydride	octylamine	8.9	10		0.16	33	10.0
Hexahydrophthalic anhydride	octylamine	8.9	9		0.18	35	15.0
1,2,3,6-Tetrahydrophthalic anhydride	octylamine	9.0	9		0.24	34	16.5
4-Methyl-1,2,3,6-tetrahydrophthalic anhydride	octylamine	9.0	10		0.15	34	15.0
Itaconic anhydride	octylamine	8.5	9		0.16	30	11.0
Maleic anhydride	*t*-Butylamine	8.1	7	E	0.25	—	—
Maleic anhydride	hexylamine	8.3	8	E	0.26	—	—
Maleic anhydride	heptylamine	8.3	9	D	0.23	—	—
Maleic anhydride	octylamine	8.4	10	A	0.15	36.5	13.0
Maleic anhydride	decylamine	8.5	10	B	0.18	38.0	10.0
Maleic anhydride	dodecylamine	8.9	10	B	0.12	40.1	7.5
Maleic anhydride	oleyl	9.1	10	B	0.11	43.0	9.0
Maleic anhydride	toluidine	8.2	7	E	0.23	—	—
Phthalic anhydride	hexylamine	8.5	7	E	0.20	45	7.0
Phthalic anhydride	octylamine	8.9	10	A	0.16	33	10.0
Phthalic anhydride	decylamne	8.7	9	B	0.15	31	9.0
Phthalic anhydride	dodecylamline	8.9	9	B	0.14	35	11.0
Blank	triethanolamine	10.2	8	E	0.33	60	3.0
Blank	maleic anhydride and triethanolamine	7.8	5	E	0.40	—	—

[a]Aqueous solutions of adduct (1.0 g), triethanolamine (2.0 g) and water (100.0 g) were used as the test solutions. The method of anti-rust test is a corrosion test with cast iron chips (method a and method b).

TABLE 2

Antimicrobial Properties of the Products from the Reaction of Acid Anhydride with Various Amines

Adducts Acid anhydride	Amines	Bacterium (cbu/mL) After 7 days	After 14 days	After 21 days
Maleic anhydride	*t*-butylamine	6×10^4	5×10^5	
Maleic anhydride	hexylamine	7×10^3	8×10^4	
Maleic anhydride	heptylamine	under 10^3	under 10^3	
Maleic anhydride	octylamine	under 10^3	under 10^3	10^5
Maleic anhydride	decylamine	under 10^3	2×10^5	
Maleic anhydride	dodecylamine	under 10^3	under 10^3	10^5
Maleic anhydride	oleyl	under 10^3	under 10^3	
Maleic anhydride	toluidine	3×10^3	10^5	
Phthalic anhydride	hexylamine	under 10^3	10^5	$>10^6$
Phthalic anhydride	octylamine	under 10^3	under 10^3	under 10^3
Phthalic anhydride	decylamine	under 10^3	under 10^3	$>10^6$
Phthalic anhydride	laurylamine	under 10^3	under 10^3	10^5
Succinic anhydride	octylamine	under 10^3	10^5	$>10^6$
Glutaric anhydride	octylamine	under 10^3	10^4	$>10^6$
1,2,3,6-Tetrahydrophtharic anhydride	octylamine	under 10^3	10^4	$>10^6$
Bromomaleic anhydride	octylamine	under 10^3	under 10^3	under 10^3
—	triethanolamine	under 10^3	10^5	$>10^6$
A mixture of maleic anhydride (50%) and triethanolamine (50)		2×10^4	3×10^4	

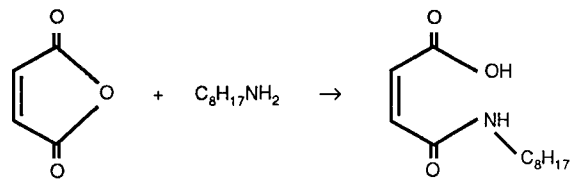
judged that the sample was going to be spoiled. When the content was over 10^5, it was judged that the sample had been spoiled.

RESULTS AND DISCUSSION

The relationship between the various properties of water-soluble cutting fluids additives and the chemical structures of these additives is not known in detail. Especially, the additives which possess both anti-rust and antimicrobial properties have not been reported. We prepared a variety of *N*-alkyl carboxylic acid amides and screened them for anti-rust activity as water-soluble fluids and antimicrobial activity against the bacteria of a spent coolant.

It is known that *N*-alkyl maleimide has a fair antimicrobial property (7,8). We suggested that alkyl amidocarboxylic acid of an intermediate of *N*-alkyl maleimide probably has an antimicrobial activity. Then we prepared a variety of alkyl carboxylic acid amides from the reaction of cyclic dicarboxylic acids anhydrides and octyl amine. As shown in Table 1, triethanolamine salts of the adduct of maleic anhydride and phthalic anhydride with octyl amine showed good anti-rust properties. Various amidocarboxylic acids were prepared from the reaction of maleic anhydride or phthalic anhydride with various amines. As shown in Table 1, triethanolamine salt of compound (**III**) prepared from (**I**) and (**II**) showed anti-rust property for water-soluble cutting fluids additives (Scheme 1). These adducts from heptyl, octyl, dodecyl and oleyl amines showed good anti-rust property. Interestingly the adducts from the reaction of phthalic anhydride with octyl, decyl and dodecyl amine also showed fairly good anti-rust property.

As shown in Table 2, after incubating 14 days at 35°C, the products from heptyl, octyl dodecyl and oleyl amines with maleic anhydride showed good anti-microbial activities. The adducts from octyl, dodecyl and lauryl amines with phthalic anhydride showed fairly good anti-



I II III

SCHEME 1

microbial activities, too. The bacteria contents of these good sample solutions were under 10^3 as shown in Table 2. Thus, we have found that the adducts of (**I**) and phthalic anhydride with heptylamine, octylamine, decylamine, dodecylamine and oleylamine showed anti-rust and anti-microbial properties at the same time. These new additives for water-based cutting fluids were not known previously. Practical tests of these new additives are now in progress at our laboratory.

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