Characteristic Properties of Cutting Fluid Additives Derived from the Adducts of Diamines and Acid Chlorides

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A number of N,N′-diacylalkyldiamines were prepared from the reaction of acid chlorides with 1,8-diaminooctane and 1,12-diaminododecane and screened for anti-rust properties and antimicrobial activity in spent coolants of water-based cutting fluids. Aqueous solutions of N,N′-dihexanoyl-1,8-diaminooctane and N,N′-isobutyroyl-1,12-diaminododecane showed good anti-rust properties for water-based cutting fluids. Aqueous emulsions of N,N′-dibutyroyl-, dipentanoyl-, dihexanoyl- and dioctanoyl-1,12-diaminododecane showed good lubricities and antimicrobial activity for water-based cutting fluids.

KEY WORDS: N,N′-diacylalkyldiamine, N,N′-dihexanoyl-1,8-diaminooctane, antimicrobial activity, anti-rust activity, anti-rust additives, cutting fluid additives, water-based cutting fluids.

A variety of water-soluble cutting fluids are used for machine operations. For water-soluble cutting fluids, good anti-rust, lubrication and anti-bacterial properties are essential (1). We have previously reported that para-alkoxybenzoic acids have excellent properties as anti-rust additives for water-soluble cutting fluids (2). We examined the anti-rust properties, lubricity characteristics and antimicrobial activities of various N,N′-diacylalkyldiamines. This paper describes our recent evaluation of these new additives for use in water-soluble fluids.

EXPERIMENTAL PROCEDURES

Preparation of N,N′-diisobutyroyl-1,8-diaminooctane [III, R = $(CH_3)_2CH$]. Isobutyroyl chloride (5.33 g, 0.05 mol) in tetrahydrofuran (30 mL) was added to tetrahydrofuran (30 mL) solution of 1,8-diaminooctane (1) (7.21 g, 0.05 mol) and pyridine (5.0 g) at 0°C and stirred for 6 h. The reaction mixture was quenched by adding water and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate and evaporated to give crude N,N′-diisobutyroyl-1,8-diaminooctane (**III**, R = C_3H_7). It was recrystallized from ethanol and melted at 143–145°C. The microanalysis was in satisfactory agreement with the calculated values: C ± 0.30%, H ± 0.05 %. It showed the following spectral data: Infrared (IR) (cm^{-1}): 3280 (-NH), 1630 (>C=O); nuclear magnetic resonance (NMR) (δ,ppm): 1.07 (12H, *d*, J = 4.0HZ, $CH_3 \times 4$), 1.23 (12H, *m*, $CH_2 \times 6$), 2.09 (4H, *m*, -CH_2NH × 2), 3.10 (2H, *m*, $(CH_3)_2CH \times 2$), 5.50 (2H, broad, -NH × 2); mass spectrum (MS) (*m/e*): FAB method $(M + 1)^+ = 285.2540$ ($M = C_{16}H_{32}O_2N_2$). Other diamides were prepared in a similar manner.

Lubricity characteristic tests. As the solubilities of these amides in water were low, two kinds of test solutions were prepared as follows. Test solution A: Aqueous solutions of triethanolamine (2.0 g), a diamide (0.2 g) and water (100 g) were used as the test solutions. Test solution B: Aqueous emulsions of water (97 g), a diamide (1.0 g) and polyoxyethylene nonylphenylether (EO 5 mols) (2.0 g) as an emulsifier were used. Japanese city water (Osaka and Chiba) was used for all tests. The same results were obtained in all tests as with distilled water.

Corrosion tests with cast iron chips were carried out as follows. Two grams of cast iron chips (JIS G5501, GC-20, gray iron casting; NEOS Central Research Laboratory, Shiga-ken, Japan), 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 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) (4). A desirable value for the coefficient of friction is under 0.23.

Welding loads (kgf/cm^2) were measured on a Soda-type four-ball lubricating oil testing machine at 200 rpm. The welding load should be as high as possible, the desirable value being more than 5.0 kgf/cm^2 (5). This testing machine and friction tester mentioned above have been officially authorized by the Agency of Industrial Science and Technology of Japan as JIS K2519 and 2219.

Surface tensions (dyn/cm) were measured at 25°C with a DuNoüy tensiometer. The desirable value of surface tension is under 60. These results are shown in Tables 2 and 3.

Antimicrobial activity tests for spent coolants of water-based cutting fluids (6,7). Agar (20 mL) was placed in a sharle with a diameter of 90 mm and solidified. One mL of bacterial culture was dropped on the center of the agar and spread uniformly with a sterile, bent glass rod, and dried for 10 min at room temperature. The above-mentioned bacterial culture was prepared as follows: a spent coolant (live fungi above 10^7/mL) was collected from an industrial factory, and the bacteria were cultured on a liquid broth for 48 h at 30°C. On the center of the agar inoculated with this culture, one mL of the sample solution of the new cutting fluids was dropped, and the agar was kept at 30°C. After 1, 2 and 3 d, the degree of increase

TABLE 1

Valuation of Anti-Rust Effect

Time (h)	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	1

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TABLE 2

Cutting Fluid Characterization of Aqueous Solutions (Test solution A) for Various N,N′-diacylalkyldiamines[a]

R	pH	Rust-inhibition test for time (h)			Friction coefficient	Surface tension (dyn/cm)	Welding load (kgf/cm^2)	Antimicrobial properties for time (d)[b]		
		24	48	72				1	2	3
$RCONH(CH_2)_8NHCOR$										
CH_3	10.2	10	8	8	0.16	49	8.5	+	++	++
$CH(CH_3)_2$	10.1	10	10	8	0.20	65	10.0	+	++	++
C_4H_9	10.1	10	10	9	0.21	55	15.0	−	+	++
C_5H_{11}	10.0	10	10	10	0.23	46	20.0	−	+	+++
C_6H_{13}	9.9	10	10	10	0.20	49	18.0	−	+	+++
C_7H_{15}	9.8	10	10	9	0.18	51	17.0	−	++	+++
$C_{17}H_{33}$	9.7	8	8	7	0.12	53	16.5	+	++	+++
C_6H_5	9.9	8	7	7	0.17	65	18.5	+	++	+++
$RCONH(CH_2)_{12}NHCOR$										
CH_3	9.9	10	9	8	0.17	53				
C_2H_5	10.0	10	9	8	0.17	51	10.0			
C_3H_7 (3_b)	10.5	10	9	8	0.18	48	12.0	+	++	+++
$CH(CH_3)_2$	10.7	10	10	10	0.18	45	14.0	+	++	+++
C_4H_9	10.3	10	9	8	0.19	50	14.5	+	+++	+++
C_5H_{11}	10.1	10	9	8	0.20	55	15.5	++	+++	+++
C_6H_{13}	9.9	10	8	7	0.18	60	16.0	++	+++	+++
C_9H_{19}	9.7	9	8	7	0.16	65	17.0	+	+	+
$C_{11}H_{23}$	9.9	8	8	7	0.11	62	18.0	++	+++	+++
$C_{13}H_{27}$	9.8	8	8	7	0.18	63	18.5	++	++	++
$C_{17}H_{33}$	9.6	8	8	7	0.15	37	20.0	++	++	++
C_6H_5	9.0	8	8	7	0.11	63	11.5	+	++	+++
Triethanolamine (2% aq. sol.)	10.3	7	6	5	0.21	70	8.5	++	+++	+++
Triazine type antiseptic										
1% aq. sol.								−	−	−
0.5% aq. sol.								−	−	+
0.1% aq. sol.								+++	+++	+++
Blanc								+++	+++	+++

[a]Test solution A: Aqueous solutions (aq. sol.) of adduct (0.20 g), triethanolamine (2.0 g) and water (100.0 g) were used as the test solutions.
[b]Antimicrobial properties: −, increase of bacteria was not observed; +, a very little increase of bacteria was observed; ++, a little increase of bacteria was observed; +++, large increase of bacteria was observed.

of bacteria was observed. Scoring was performed as follows: − is no bacterial growth, + is very little bacterial increase, ++ is little bacterial increase, +++ is a large bacterial increase. This method is a modification based on the reference's methods (6,7).

It is known that spoilage may be caused by several different organisms working together (8–12). The spent coolant contains microorganisms, such as *Staphylococcus aureus, Desulfovibrio desulfuricans, Pseudomonas aeruginosa, P. oleovorans, Klebsiella pneumoniae, Escherichia coli, Proteus mirabilis* and *Fusarium* sp. The bacteria content of the spent coolant was over 10^7/mL.

RESULTS AND DISCUSSION

We previously reported that *p*-alkoxy-benzoic acids have excellent properties for rust inhibition (2). In that research (2), aqueous solutions of triethanolamine salts of these fatty acid derivatives were evaluated as cutting fluid additives. In this paper, we describe a new type of cutting fluid additives. We prepared various N,N′-diacylalkyldiamines from the reaction of 1,8-octyldiamine (I) or 1,12-dodecyldiamine with acid chlorides and examined characteristic properties of water-soluble cutting fluids prepared from them. N,N′-diisobutyroyl-1,8-octyldiamine (**III**, R = *i*-C_3H_7) was prepared from the reaction of 1,8-diaminooctane (**I**):

$NH_2(CH_2)_8NH_2$ + RCOCl

(I) (II)

↓

$RCONH(CH_2)_8NHCOR$

(III)

SCHEME 1

and isobutyroyl chloride (**II**, R = *i*-C_7H_7) in the presence of pyridine (Scheme 1).

As the solubilities of these diamides to water were low, two types of sample solutions were employed as test solutions as shown in the Experimental Procedures section. Aqueous solutions (0.5%) of these samples (Test solution A) were evaluated as cutting additives, and the results are

TABLE 3

Cutting Fluid Characterization of Aqueous Emulsions (Test solution B) for Various N,N′-diacylalkyldiamines[a]

R	pH	Rust-inhibition test for time (h)			Friction coefficient	Surface tension (dyn/cm)	Welding load (kgf/cm^2)	Antimicrobial properties for time (d)[b]		
		24	48	72				1	2	3
$RCONH(CH_2)_8NHCOR$										
C_3H_7	8.7	10	10	8	0.18	42	9	−	−	−
C_4H_9	8.6	10	10	8	0.18	41	10	−	−	−
C_6H_{13}	8.6	10	10	8	0.17	41	11	−	−	+
C_7H_{15}	8.4	10	10	8	0.17	40	13	−	−	+
$RCONH(CH_2)_{12}NHCOR$										
C_2H_5	8.4	10	10	8	0.17	38	12	−	−	+
C_3H_7	8.6	10	10	10	0.18	35	13	−	−	+
C_4H_9	8.5	10	10	10	0.15	39	15	−	−	+
C_5H_{11}	8.3	10	10	10	0.14	39	15	−	−	+
C_7H_{15}	8.3	10	10	10	0.12	39	16	−	−	+
Polyoxyethylenenonylphenylether	7.2	8	7	6	0.28	31	2	−	+	++
Triethanolamine (2% aq. sol.)	10.3	7	6	5	0.21	70	8.5	++	+++	+++
Triazine type antiseptic										
1% aq. sol.								−	−	−
0.5% aq. sol.								−	−	+
0.1% aq. sol.								+++	+++	+++
Blanc								+++	+++	+++

[a]Test solution B: Aqueous solutions (aq. sol.) of adduct (1.0 g), polyoxyethylene nonylphenylether (2.0 g) and water (98.0 g) were used as the test solutions.
[b]Antimicrobial properties: −, increase of bacteria was not observed; +, a very little increase of bacteria was observed; ++, a little increase of bacteria was observed; +++, large increase of bacteria was observed.

listed in Table 2. Aqueous solutions of these compounds (**III**) containing amide groups have excellent anti-rust and anti-wear properties. Thus, aqueous solutions of N,N′-diisobutyroyl, N,N′-dipentanoyl, N,N,′-dihexanoyl or N,N,′-diheptanoyl-1,8-diaminooctane and N,N′-diisobutyroyl-1,12-diaminododecane demonstrated excellent corrosion resistance in a test with cast-iron chips. The load capacity of this solution was about 14–20 kgf/cm^2 at 200 rpm. Aqueous emulsions of compound (**III**) with polyoxyethylene nonylphenylether were evaluated as cutting fluid additives, and the results are listed in Table 3. N,N′-dibutyroyl-, dihexanoyl- and dioctanoyl-1,12-diaminododecane showed excellent corrosion resistance and load capacity.

Water-soluble cutting fluids are easily degraded by various microorganism. Many materials, such as alkanolamines, were studied for their antimicrobial properties against a mixed flora of fungi and bacteria in cutting fluids (10–12). We examined the antimicrobial properties of these amides in water-based cutting fluids. After incubating them at 38°C, the bacterial contents of the sample solutions were observed. As shown in Tables 2 and 3, aqueous emulsions of N,N,′-diacyl-1,12-diaminododecanes showed a fair antimicrobial property in spent coolants, together with anti-rust properties. Though aqueous emulsions of N,N′-diacyl-1,8- diaminooctanes showed fair antimicrobial properties, their corrosion resistances are somewhat inferior to those of N,N′-diacyl-1,12-diaminododecanes. The new additives described above for water-based cutting fluids were not previously evaluated.

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