

Characteristic Properties of Cutting Fluid Additives Derived from the Derivatives of Ricinoleic Acid Polymers

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A number of esters were prepared from the reaction of acid chlorides with ricinoleic acid polymers and screened for anti-rust properties and antimicrobial activity in spent coolants of water-based cutting fluids. Aqueous solutions of triethanolamine salts with decanoic acid, undecanoic acid and oleic acid esters of ricinoleic acid dimer, trimer, tetramer and hexamer showed good anti-rust properties for water-based cutting fluids. Dehydrates of ricinoleic acid polymers also showed good anti-rust properties for water-based cutting fluids.

KEY WORDS: Anti-rust activity, anti-rust additives, cutting fluid additives, dehydrates of ricinoleic acid polymers, esters of ricinoleic acid dimer, esters of ricinoleic acid polymer, water-based cutting fluids.

A variety of cutting fluids is used for various machining operations. These fluids may be classified into two main types, mineral oil-based and water-miscible (which include oil-water emulsions). Mineral oil-based fluids are especially suitable for heavy-duty and special-service operations where good lubrication is essential. In other, less severe operations, there has been a recent trend toward water-based fluids. These offer the advantages of low toxicity and excellent cooling capacity and also overcome problems associated with mineral oil-based products, such as unpleasant odor, oil mist formation and fumes at high temperature. However, for water-based cutting fluids to offer a practical alternative, they must possess good rust-inhibiting, anti-wear and antimicrobial activity (1). We have previously reported that the adducts of diamines and acid chlorides 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 derivatives of ricinoleic acid polymers. This paper describes our recent evaluation of these new additives for use in water-soluble cutting fluids.

EXPERIMENTAL PROCEDURES

Ricinoleic acid polymers. Ricinoleic acid dimer, trimer, tetramer and hexamer were available from commercial sources (Ogura Gosei Co. Ltd., Kitakyushu-shi, Japan; and Toyokuni Seiyu Co. Ltd., Hachio-shi, Japan). Their properties are shown in Table 1.

Preparation of acetate (II) of ricinoleic acid dimer (I). Acetyl chloride (1.57 g, 0.02 mol) in anhydrous tetrahydrofuran (5.0 mL) was added to a tetrahydrofuran (30 mL) solution of the dimer (I) (11.56 g, 0.02 mol) and pyridine (1.58 g, 0.02 mol) at 0°C and stirred for 10 h. The reaction mixture was quenched by adding 3N HCl aqueous solution (20 mL) and extracted with ether. The ether extract was washed with water and brine, dried over anhydrous sodium sulfate, and evaporated to give 9.5 g of crude acetate (II, R = CH₃). It was purified by short-path liquid chromatography on silica gel with a mixture of *n*-hexane and dichloromethane as the solvent. The purified product (7.0 g) showed the following spectral data: infrared

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TABLE 1

Physical Properties of Ricinoleic Acid Polymers

Properties	Dimer	Trimer	Tetramer	Hexamer
Color ^a	6	6	6-7	7
Acid value	95	60	47	34
Saponification value	195	196	198	200
Iodine value	91	92	93	93
Hydroxyl value	76	41	28	10
Viscosity ^b	R	V	W	X-Y
Specific gravity d_4^{25}	0.934	0.933	0.932	0.930
Refractive index n_D^{25}	1.471	1.473	1.474	1.476
Average molecular weight	600	900	1200	1800

^aGardner Color Meter (Shimadzu Seisakusho Co., Ltd., Kyoto, Japan).

^bGardner-Holdt Viscometer (Shimadzu).

(IR) (cm⁻¹): 3500 (OH and COOH), 1730 (ester), 1695 (COOH); nuclear magnetic resonance (NMR) (δ , ppm): 0.86 (6H, *t*, $J = 6.0$ Hz, CH₃ × 2), 1.27 (40H, broad *s*, CH₂ × 20), 1.98 (3H, *s*, COCH₃), 2.22 (14H, *m*, other protons), 5.26 (4H, *m*, olefinic protons), 11.3 (1H, *s*, COOH); hydroxy value, 0; saponification value, 270. Other esters were prepared in a similar way.

Dehydration of ricinoleic acid dimer (I). A xylene solution (120 mL) of ricinoleic acid dimer (I) (30.0 g, 0.0519 mol) and *p*-toluene sulfonic acid (0.5 g) was refluxed with an ester tube. After water (0.93 mL, about 0.052 mol) was distilled off with xylene, the reaction solution was concentrated to give 28.0 g of crude dehydrated product. The product was purified with short-path chromatography on silica gel column with benzene as the solvent to give 25.0 g of purified product. NMR, δ ppm: 0.90 (6H, *t*, $J = 6.0$ Hz, CH₃ × 2), 3.30 (38H, broad *s*, -CH₂ × 19), 2.0-2.5 (13H, *m*, other protons), 5.45 (6H, *m*, olefinic protons), 10.0 (1H, *s*, -COOH); hydroxy value, 0. Other ricinoleic acid polymers were dehydrated in a similar manner.

Lubricity tests. Aqueous solutions of triethanolamine (2.0 g), an ester (1.0 g) and water (97.0 g) were used as the test solutions. City water from Japan (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 G 5501, FC-20, gray iron casting; Japanese Standards Association, Tokyo, 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 2.

TABLE 2

Evaluation of Anti-Rust Effect

Time (h)	Amount of rust	Evaluation score
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

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/cm²) 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/cm² (5). This testing ma-

chine and the friction tester mentioned above have been officially authorized by the Agency of Industrial Science and Technology of Japan (Minatoku, Tokyo, Japan) as JIS K 2519 and 2219 (Japanese Standards Association). The machine was obtained from Shinko Engineering Co. Ltd.

Surface tensions (dyn/cm) were measured at 25°C with a Du Noüy tensiometer. The desirable value of surface tension is under 60.

These results are shown in Tables 3 and 4.

TABLE 3

Cutting Fluid Characterization of Aqueous Solutions of the Salts of Various Esters with Triethanolamine^a

R for esters of polymer (X) (X-OCOR)	pH	Rust-inhibition test for time (h)			Friction coefficient	Surface tension (dyn/cm)	Welding load (kgf/cm ²)	Antimicrobial properties for time (d)		
		24	48	72				1	2	3
Dimer-O-COR										
CH ₃	9.4	8	8	7	0.10	39	19.5	+++	+++	+++
C ₂ H ₅	9.3	9	8	8	0.10	38	20.0	++	++	++
C ₃ H ₇	9.3	9	9	8	0.09	37	18.0	++	++	+++
C ₅ H ₁₁	9.1	10	10	9	0.09	37	15.0	++	++	+++
C ₇ H ₁₅	9.0	10	10	10	0.09	37	16.0	++	+++	+++
C ₉ H ₁₉	9.0	10	10	10	0.09	41	19.5	+++	+++	+++
C ₁₁ H ₂₃	9.1	10	10	10	0.08	41	18.0	+++	+++	+++
C ₁₃ H ₂₇	9.2	10	10	9	0.08	44	13.5	+++	+++	+++
C ₁₅ H ₃₁	9.4	10	10	9	0.08	44	16.0	+++	+++	+++
C ₁₇ H _{33^b}	9.4	10	10	10	0.08	33	20.0	++	++	++
C ₁₇ H _{33^c}	9.3	10	10	10	0.09	47	20.0	++	++	+++
p-CH ₃ Ph	8.9	10	10	9	0.08	41	14.5	++	++	+++
Trimer-O-COR										
CH _{3^d}	—	—	—	—	—	—	—	—	—	—
C ₅ H _{11^d}	—	—	—	—	—	—	—	—	—	—
C ₇ H _{15^d}	—	—	—	—	—	—	—	—	—	—
C ₉ H ₁₉	9.0	10	10	10	0.09	41	20.0	++	++	+++
C ₁₁ H ₂₃	8.9	10	10	10	0.08	42	20.0	++	++	++
C ₁₇ H _{33^b}	9.3	10	10	10	0.08	39	18.0	++	++	++
C ₆ H _{5^d}	—	—	—	—	—	—	—	—	—	—
C ₆ H _{5^d}	—	—	—	—	—	—	—	—	—	—
Tetramer-O-COR										
CH ₃	—	—	—	—	—	—	—	—	—	—
C ₅ H _{11^d}	—	—	—	—	—	—	—	—	—	—
C ₇ H _{15^d}	—	—	—	—	—	—	—	—	—	—
C ₉ H ₁₉	9.0	10	10	10	0.09	43	20.0	++	++	+++
C ₁₁ H ₂₃	9.1	10	10	10	0.08	44	20.0	++	++	++
C ₁₇ H _{33^b}	9.6	10	10	10	0.08	41	20.0	++	++	++
Hexamer-O-COR										
CH ₃	9.5	8	8	7	0.08	43	20.0	+++	+++	+++
C ₅ H ₁₁	9.6	8	8	7	0.08	40	18.0	+++	+++	+++
C ₇ H ₁₅	9.4	10	10	10	0.09	44	20.0	++	++	++
C ₉ H ₁₉	9.4	10	10	9	0.09	44	20.0	+++	+++	+++
C ₁₁ H ₂₃	9.3	10	10	10	0.09	45	20.0	++	++	++
C ₁₇ H _{33^b}	9.3	10	10	10	0.08	37	20.0	++	++	+++
C ₆ H ₅	9.5	8	7	7	0.09	45	20.0	++	++	+++
Triethanol amine										
(2% aqueous solution)	10.3	7	6	5	0.21	70	8.5	+	+++	+++
Ricinoleic acid	8.8	10	9	8	0.12	43	18.5	+++	+++	+++
Ricinoleic acid										
Dimer	9.1	10	9	8	0.10	41	19.0	+++	+++	+++
Trimer	9.7	9	9	7	0.09	37	17.0	++	+++	+++
Tetramer	9.8	9	8	7	0.09	36	18.5	+++	+++	+++
Hexamer	10.0	9	8	7	0.09	43	—	++	+++	+++
Triazine-type antiseptic										
(% aqueous solution)										
0.5								—	—	+
0.1								—	++	++
0.05								—	+++	+++
Blanc (H ₂ O)								+++	+++	+++

^aTest solution: Aqueous solutions of adduct (1.0 g), triethanolamine (2.0 g) and water (97.0 g) were used as the test solutions. Antimicrobial properties: —, increase of bacteria was not observed; +, very little increase of bacteria was observed; ++, a little increase of bacteria was observed; +++, much increase of bacteria was observed.

^bOleic acid ester.

^cLinoleic acid ester.

^dSalts of triethanolamine with these acids were not dissolved in water.

CUTTING FLUID ADDITIVES FROM RICINOLEIC ACID POLYMERS

TABLE 4

Cutting Fluid Characterization of Aqueous Solutions of the Salts of Various Dehydrates of Ricinoleic Acid Polymers with Triethanolamine^a

Dehydrates	pH	Rust-inhibition test for time (h)			Friction coefficient	Surface tension (dyn/cm)	Welding load (kgf/cm ²)	Antimicrobial properties for time (d)		
		24	48	72				1	2	3
Dehydrate of dimer	9.3	10	10	10	0.09	44	—	++	+++	
Dehydrate of trimer	9.2	10	10	10	0.09	38	++	++	++	
Dehydrate of tetramer	9.3	10	10	10	0.10	41	++	++	++	

^aTest solution: Aqueous solutions of adduct (1.0 g), triethanolamine (2.0 g) and water (97.0 g) were used as the test solutions. Antimicrobial properties: —, increase of bacteria was not observed; +, very little increase of bacteria was observed; ++, a little increase of bacteria was observed; +++, much increase of bacteria was observed.

TABLE 5

Compositions of Cutting Fluids and Machining Test Data

Sample number	1	2	3	4	5
Ricinoleic acid dimer octanoic acid ester	20				
Ricinoleic acid dimer linoleic acid ester		20	20		
Ricinoleic acid				20	
Ricinoleic acid tetramer					20
Triethanolamine	15	15	15	15	15
Machine oil # 10	50	50	0	50	0
Sodium petroleum sulphonate	5	5	5	5	5
Chlorinated paraffin	5	5	0	5	0
Ethyleneoxide and propylene oxide co-polymer (surface-active agent)	0	0	5	0	5
Triazine-type antiseptic	1	1	1	1	1
Water	4	4	54	4	54
Total	100	100	100	100	100
Dilution ratio	30	30	30	30	30
Tool life of tap (maximum number of threads per one tap)	180	270	150	120	100

Antimicrobial activity tests for spent coolants of water-based cutting fluids (6,7). Agar (20 mL) was placed in a dish 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 10⁷/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 fluid was dropped, and the agar was kept at 30°C. After 1, 2 and 3 d, the degree of increase of bacteria was observed. Scoring was performed as follows: —, no bacterial growth; + very little bacterial increase; ++, little bacterial increase; +++, much bacterial increase. This method is a modification based on existing methods (6,7).

It is known that spoilage may be caused by several different organisms working together (8–12). The spent coolant contained the microorganisms *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 10⁷/mL.

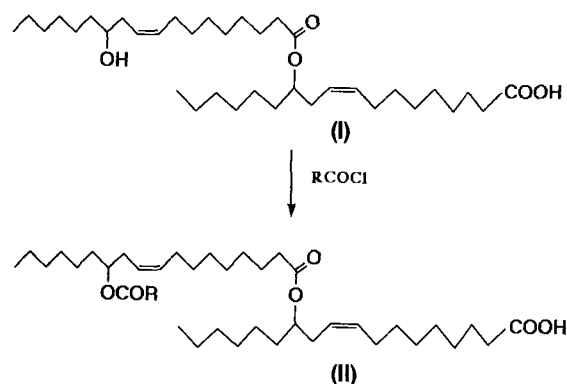
Practical tests. Practical tests (cutting test) were performed as follows: Machine tool, vertical NC milling machine (Enshu Seiki Mfg. Co., Hamamatsu-shi, Japan); tool, hand tap M 12 × 1.25 (high-speed steel; Yamawa Mfg. Co.,

Chuoku, Tokyo, Japan); machining condition, cutting speed 6 m/min, feed 200 mm/min, depth 20 mm dead end, hole size before threading 10.7 mm; workpiece material, S 45C (carbon steel of 0.45% C); evaluation, machined internal threads were inspected by a thread gage (GPII-M 12 × 1.25; Kuroda Seiki Co. Ltd., Kawasaki-shi, Japan), and machining was continued until abnormal thread was detected. Then, the maximum number of threads that were machined normally was considered as the tool life. Compositions of cutting fluids and machining test data of cutting test are shown in Table 5.

RESULTS AND DISCUSSION

It is well known that thermal reaction of ricinoleic acid gives a mixture of undecylenic acid and enanthol together with ricinoleic acid polymers. Recently, the dimer, trimer and other oligomers of ricinoleic acid have been selectively prepared under various appropriate reaction conditions, and they are on the market. For this paper, we prepared various esters from the reaction of ricinoleic acid polymers with acid chlorides and examined the characteristic properties of water-soluble cutting fluids prepared from them. Acetate (II, R = CH₃) was prepared from the reaction of ricinoleic acid dimer (I) and acetyl chloride in the presence of pyridine (Scheme 1). Various esters from trimer, tetramer and hexamer were prepared in a similar way.

Aqueous solutions of the salts of these esters (II) with triethanolamine were evaluated as cutting fluids additives, and the results are listed in Table 3. Aqueous solutions of decyl, undecyl and oleyl esters of dimer (I), trimer, tetramer and hexamer have excellent anti-rust and anti-wear properties. Thus, compound (II, R = C₉H₁₉) demonstrated excellent corrosion resistance in a test with



SCHEME 1

cast-iron chips. The load capacity of this solution was about 19 kgf/cm² at 200 rpm.

Ricinoleic acid dimer (I), trimer and tetramer were dehydrated catalyzed by *p*-toluene sulfonic acid in xylene. Aqueous solutions of the salts of these dehydrates with triethanolamine were evaluated as cutting fluid additives, and the results are shown in Table 4. These compounds showed excellent corrosion resistance and anti-wear properties.

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 (10–12). We examined the antimicrobial properties of these esters in water-based cutting fluids. After incubating them at 38°C, the bacterial contents of the sample solutions were observed. As shown in Tables 3 and 4, these esters and dehydrated products did not show antimicrobial properties in spent coolants.

Some practical cutting tests were performed with these water-soluble fluids as shown in the Experimental Procedures section. Cutting ability was estimated as the tool life of tap (Table 5). For a cutting fluid containing ricinoleic acid dimer ester, the number of threads was 150–270 (samples No. 1, 2 and 3), whereas with a cutting fluid containing no ricinoleic acid dimer ester, the number of threads was 100–120 (samples No. 4 and 5).

The additives described above for water-based cutting fluids were previously unknown.

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