✤Epoxides of Unsaturated Fatty Acids as Anti-rust Additives in Water-Based Cutting Fluids

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Epoxides from a variety of unsaturated fatty acids were prepared, and corrosion tests for these products as water-based cutting fluid additives were performed. The triethanolamine salt of an epoxide of undecylenic acid showed very effective rust-inhibiting properties in a water-based cutting fluid.

A variety of cutting fluids are used for various machining operations. Recently, the use of water-based cutting fluids has been considered because of the following desirable properties: sufficient lubricating and cooling power, low cost, low toxicity and good results. For water-soluble cutting fluids, rust inhibition is essential. The relationship of rust inhibition and chemical structures of various organic compounds has not been reported in detail. The authors previously reported that various derivatives of fatty acids have excellent rust inhibition properties for water-soluble cutting fluids (1). This short paper describes our evaluation of some epoxides derived from unsaturated fatty acids for corrosion inhibitors additives in water-soluble cutting fluids.

EXPERIMENTAL

Preparation of 10,11-epoxyundecanoic acid (III). Methyl 10,11-epoxyundecanoate (II) was prepared from the reaction of methyl undecylenate (I) and m-chloroperbenzoic acid in dichloroethane as known in a general method. A mixture of compound (II) (2.5 g), lipase MY (*Candida cylindracea*, Meito Sangyo Co. Ltd.) (10 g) and water (100 ml) was agitated for six hr at 38 C. The mixture was extracted with diisopropyl ether. The ether extract was washed with water several times, dried over anhydrous sodium sulfate, filtered and evaporated to remove the solvent. The residue was distilled to give 10,11-epoxyundecanoic acid (III) (1.5 g) (yield, 64.2%). Other epoxides of unsaturated fatty acids were prepared in a similar manner.

Test methods. Aqueous solutions of triethanolamine salts of the epoxides listed in Table I were used. Distilled and deionized water was used for corrosion tests. The same results were obtained in the corrosion tests using either distilled water or city water in Japan (Tokyo and Chiba).

Method a: Corrosion test with cast iron chips. Two g of cast iron chips (JIS G 5501, FC-20) (in Japanese JIS) 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 filtration. The rust-preventive effect (the amount of rust on the cast-iron chips) was observed after 24 hr. Ten points show no appearance of rust. Eight points show a little appearance of rust (1, 2).

Method b: Corrosion test with steel panels. Two panels (JIS G 3141, SPCC-B) (in Japanese JIS) were polished with emery paper (no. 610), followed by a benzene rinse, and immersed in a sample solution of cutting fluids. After 10 min, the panels were removed from the solution and allowed to remain in the air at room temperature. After 74 hr, the amount of rust on the steel panels was observed. Ten points show no rust. Eight points show a small amount of rust. These methods are based on the I.P. Corrosion Test 125/63T (aqueous cutting fluids corrosion of cast-iron chips and steel panels, JIS G 3310) (1, 2).

Method c: Corrosion test with cast iron chips using filter paper. The following modified method was used. A filter paper (Toyo filter paper 7cm 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 (4.0%, 2.0%, 1.0% and 0.5% aqueous solution). After 10 min, the aqueous solution was removed. After 24 hr, the amount of rust transferred on the filter paper was observed. The evaluation of anti-rust property is as follows: A, no rust; B, spots of rust are 1–10; C, spots of rust are over 11; D, area of rust is less than 50% of the filter paper; E, area of rust is more than 50% of the filter paper. The rust on the filter paper can be preserved in the same state for many hours. We can contrast one test with another at any time. This is an advantage of the Method c Corrosion test.

The coefficients of friction were measured at 25 C by a pendulum type oiliness and friction tester (Shinko Engineering Co., Ltd., Tokyo. 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 point contact. Formation of boundary oil film is easily made. (ii) Free from friction heat because of pendulum type. (iii) Measuring is simple but accurate and easily reproducible. Main particulars are as follows: test ball, 3/16″ (4.75 mm) JIS B 1501 high class; test roller pin, diameter × length 2.0ϕ (+0 to -0.012) × 30 mm: material SK3 (JIS G 4401): hardness HRC 60 ∿ 66; cycle of pendulum swing, ca. four sec; max. pendulum swing, 0.7 radian; test load (max Herz/stress), 15,000 kg/cm^2; temperature of test oil, room temp to 300 C (2,3).

The surface tensions (dyne/cm) were measured at 25 C by Dü Nouy tensiometer (2,3).

RESULTS AND DISCUSSION

The authors previously have reported that fatty acids containing a thioether group (4) and fatty acids containing a dichlorocyclopropane ring (4) have excellent properties for rust inhibition additives. It is well known that epoxides of unsaturated fatty acids are now used for various industrial applications (5,6). However, the rust-inhibiting property of these epoxides has not been investigated. We prepared various epoxides of unsaturated fatty acids and examined the anti-rust prop-

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TABLE 1

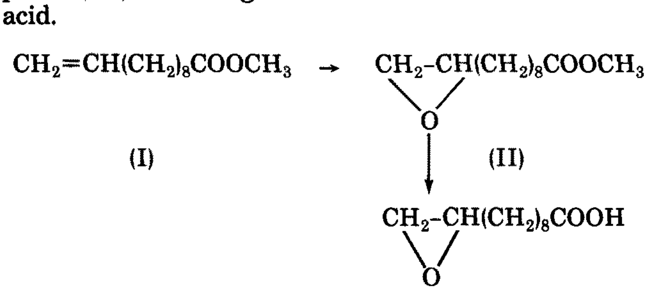
Cutting Fluid Characterization of Fatty Acids Epoxides

Fatty acid	Concentration[a] (%)	Rust inhibition tests[b]			Friction coefficient	Surface tension (dyne/cm)
		a	b	c		
Undecylenic acid	4.0	10	10	A		
	2.0	10	10	A		
	1.0	10	10	A	0.108	45
	0.7	10	10	A		
	0.5	8	10	C		
Oleic acid	2.0	10	10	A		
	1.0	10	10	C	0.110	43
Ricinoleic acid	4.0	10	10	A		
	2.0	10	10	A		
	1.0	10	10	A	0.130	41
	0.5	9	10	B		
Linoleic acid (mono epoxide)	2.0	10	10	A		
	1.0	10	10	C	0.122	43
Linoleic acid (di epoxide)	2.0	10	10	A		
	1.0	10	10	C	0.125	43
Erucic acid	1.0	10	10	C	0.130	45
Commercial sample	4.0	10	10	A		
	2.0	10	10	B		
	1.0	8	9	C		
Citronellic acid	4.0	10	10	A		
	2.0	10	10	C		
	1.0	9	10	C		
	0.5	8	9	D		

[a]Aqueous solutions (4.0, 2.0, 1.0, 0.5%) of triethanolamine salts were used.
[b]Method a is a corrosion test with cast iron chips. Method b is a corrosion test with steel panels. Values of 10 show no rust, and values of 8 show a small amount of rust. Method c is a modified test with cast iron chips using a filter paper. Symbols of evaluation (A, B, C, D and E) are described in the Experimental Section.

erties of water-soluble cutting fluids prepared from them.

Methyl 10,11-epoxyundecanoate (II) was prepared from methyl undecenoate (I) and m-chloroperbenzoic acid in the usual manner. 10,11-Epoxyundecanoic acid (III) was easily prepared by hydrolysis of compound (II) with lipase MY. Other epoxy fatty acids were prepared in a similar way. Hydrolysis of (II) with alkali cleaves the epoxy ring. A direct epoxidation of undecylenic acid with m-chloroperbenzoic acid gives compound (III) containing a small amount of m-chlorobenzoic acid.



(I) (II)

(III)

We have found that some triethanolamine salts of these epoxy fatty acids have rust inhibition properties. In particular, an aqueous solution (1.0%) of the triethanolamine salt of 10,11-epoxyundecanoic acid (III) showed excellent properties in corrosion tests with cast iron chips (method a), steel panels (method b) and a modified cast iron chips test (method c). Other results are shown in Table 1.

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