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New Additives Derived from Fatty Acids for Water-Based Cutting Fluids

S. WATANABE* and **T. FUJITA**, Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoicho, Chiba, Japan 260, and **T. YONESHIMA**, NEOS Center Research, Ohikemachi, Koseicho, Kohgagun, Shiga, Japan 520-32

ABSTRACT

A variety of derivatives from long chain fatty acids were prepared, and corrosion and lubricity tests for these products as water-based cutting fluid additives were carried out. We have found that triethanolamine salts of 11-(carboxymethylthio)-undecanoic acid (II), 10,11-dichloromethylene undecanoic acid (IV) and 12-isovaleroyloxy stearic acid (VI) showed effective rust-inhibiting and anti-wear properties for water-based cutting fluids.

INTRODUCTION

A variety of cutting fluids is used for machining operations. Recently, the use of water-based cutting fluids has been considered. The relationship between the properties of water-soluble cutting fluids and the chemical structures of various organic compounds has not been reported in detail. The authors previously have reported that some aromatic carboxylic acid (1) and α-substituted fatty acids (2) have excellent properties for water-soluble cutting fluids. We examined anti-rust properties and lubricity characteristics of various long chain fatty acid derivatives. This paper will describe our evaluation of new additives for water-soluble cutting fluids.

*To whom correspondence should be addressed.

EXPERIMENTAL

Reaction of Undecylenic Acid (I) with Mercaptoacetic Acid

11-(Carboxymethylthio)-undecanoic acid (II) (14.6 g) was obtained from 12.0 g (65 mmol) of 10-undecenoic acid (I) and 11.4 g (124 mmol) of mercaptoacetic acid as reported previously (mp 99 C) (3). Other carboxymethylthio derivatives from oleic acid, linoleic acid, linolenic acid and ricinoleic acid were prepared in a similar fashion.

10,11-Dichloromethylene Undecanoic Acid (IV)

Methyl 10,11-dichloromethylene undecanoate was prepared from the reaction of methyl undecylenate (III) and chloroform using cetyltriethylammonium chloride as a phase transfer catalyst (4,5). Saponification of this ester with sodium hydroxide gave 10,11-dichloromethylene undecanoic acid (IV). Other dichloromethylene fatty acids were prepared in a similar manner.

12-Isovaleroyloxy Stearic Acid (VI)

From the reaction of isovaleryl chloride and 12-hydroxy stearic acid (V) in pyridine, 12-isovaleroyloxy stearic acid was prepared. Esterification of hydroxy group of

TABLE I

Cutting Fluids Characteristics of Various New Additive Derivatives from Fatty Acids

Fatty acids or alcohol	Adducts of mercaptoacetic acid[a]	Welding load ($kg\ cm^{-2}$)	Coefficient of friction	Surface tension ($dyne\ cm^{-1}$)	Corrosion test	
					Method A	Method B
Undecylenic acid	11-(Carboxymethylthio)-undecanoic acid	15	0.13	48	10	8
Oleic acid	9(10)-(Carboxymethylthio)-stearic acid	16	0.14	42	10	8
Ricinoleic acid	9(10)-(Carboxymethylthio)-12-hydroxystearic acid	>20	0.23	46	10	8
Linoleic acid	9(10)- or 12(13)-(Carboxymethylthio)-octadecenoic acid	>20	0.16	35	10	8
Linolenic acid	9(10), 12(13) or 15(16) (Carboxymethylthio)-octadecadienoic acid	20	0.09	38	10	10
Oleil alcohol	9(10)-(Carboxymethylthio)-octadecanol	17.5	0.06	38	10	10

[a]Aqueous solutions (0.5 per cent) of triethanolamine salts were used.

12-hydroxy stearic acid and ricinoleic acid was performed similarly by the action of acylhalide in pyridine.

Test Method

Aqueous solutions (0.5%) of triethanolamine salts of the acids listed in Table I were used. Distilled and deionized water was used for corrosion tests.

Method A (Corrosion test with cast iron chips), Method B (Corrosion test with steel panels), Welding load (kg/cm^2), the coefficients of friction and the surface tensions (dyne/cm) were measured as reported previously (2).

Practical tests were performed as follows. Grinding conditions: machine, surface grinder; peripheral wheel speed, 1800m/min; raw steel, S-45C; grinding tool, WA-46JV; depth setting, 0.02 mm. Sample A is a mixture of compound (II) (10 weight %), triethanolamine (20%) and distilled water (70%). Sample B is a mixture of compound (IV) (10 weight %), triethanolamine (20%) and water (70%). Sample C is a mixture of sodium nitrite (10%), triethanolamine (20%) and water (70%). These samples were diluted fifty fold with water for testing.

Cutting conditions: machine, band saw disk; cutting sample, connecting rod S 40C (hardening); cutting velocity, 200m/min. Sample D is a mixture of oleic acid (5 weight %), compound (II) (10%), triethanolamine (20%), sodium petroleum sulphonate (10%), amine type antiseptics (3%) and water (52%). Sample E is a mixture of oleic acid (5%), compound (IV) (10%), triethanolamine (20%), sodium petroleum sulphonate (10%), amine type antiseptics (3%) and water (52%). Sample F is a mixture of oleic acid (5%), triethanolamine (20%), sodium petroleum sulphonate (10%), amine type antiseptics (3%) and water (62%). These samples were diluted twenty fold with water for testing.

In the case of using city water in Japan, practically the same results were obtained in the corrosion, lubricity and practical tests as with distilled water.

RESULTS AND DISCUSSION

The authors previously have reported that some aromatic carboxylic acid derivatives (1) and hydroxy acids (2) have excellent properties for water-soluble cutting fluids. This paper describes new additives prepared from higher fatty acids for water-soluble cutting fluids.

It is known that thioether can be prepared from the reaction of long-chain mono-unsaturated fatty acids and mercaptoacetic acids (3). However, the industrial applications of these easily accessible carboxylic acids containing thioether groups has been a subject of some interest. We prepared

$$\underset{(I)}{CH_2{=}CH(CH_2)_8COOH} \xrightarrow{H_2SCH_2COOH} \underset{(II)}{HOOCCH_2SCH_2(CH_2)_9COOH}$$

various carboxylic acids containing a thioether group from the reaction of fatty acids with mercaptoacetic acid and examined the properties of water-soluble cutting fluids of these fatty acid derivatives. By chance, we have found that triethanolamine salts of higher fatty acids containing a thioether group have excellent anti-rust and anti-wear properties. Thus, 11-(carboxymethylthio)-undecanoic acid (II) was prepared from undecylenic acid (I) and mercaptoacetic acid. Aqueous solutions (0.5%) of triethanolamine disalts with (II) showed excellent properties in corrosion tests with cast iron chips (method A) and steel panels (method B). The anti-wear load of this aqueous solution was about 15 kg/cm^2 at 200 rpm with a 4-ball type lubricating oil testing machine. Anti-wear loads should have as high a value as possible, the desirable value being more than 10 kg/cm^2. Similarly, other thioacetic acid derivatives have excellent properties in anti-wear and anti-rust tests, and their characteristics are shown in Table I.

The selective dichlorocarbene reaction with phase transfer catalyst is well known (4). We prepared various carboxylic acids containing dichlorocyclopropane ring system from fatty acids and dichlorocarbene using phase-transfer catalyst.

$$\underset{(III)}{CH_2{=}CH(CH_2)_8COOMe} \xrightarrow[2\ NaOH]{1{:}CCl_2} \underset{(IV)}{\overset{\displaystyle CH_2 - CH(CH_2)_8COOH}{\underset{\displaystyle Cl\quad Cl}{\diagdown\ C\ \diagup}}}$$

By chance, we have found that triethanolamine salts of those higher fatty acids containing the dichlorocyclopropane system have excellent anti-rust and anti-wear properties (6). Thus, 10,11-dichloromethylene undecanoic acid (IV) was prepared from methyl undecylenate (III) and dichlorocarbene as reported previously (4). Aqueous solutions (0.5%) of triethanolamine salt with compound (IV) showed excellent properties in corrosion tests with cast iron chips and steel panels. The anti-wear load of this aqueous solution was about 20 kg/cm^2 at 200 rpm with a 4-ball type lubricating oil testing machine. Similarly, other dichlorocyclo-

TABLE II

Cutting Fluids Characterization of Carboxylic Acids Containing Dichlorocyclopropane Ring System

Sample[a]	Welding load ($kg\ cm^{-2}$)	Coefficient of friction	Surface tension ($dyne\ cm^{-1}$)	Corrosion test	
				Method A	Method B
3,4-Dichloromethylene octanoic acid	9.5	0.15	43.0	9	10
10,11-Dichloromethylene undecanoic acid	>20	0.09	42.0	10	10
10,11-Dibromomethylene undecanoic acid	>20	0.09	40.8	9	10
3,7-Dimethyl-6,7-dichloromethylene octanoic acid	17	0.14	40.8	7	9
9,10-Dichloromethylene octadecanoic acid	>20	0.09	29.4	10	10
9,10-Dibromomethylene octadecanoic acid	>20	0.11	29.4	9	10
9,10;12,13-Bidichloromethylene octadecanoic acid	>20	0.09	37.9	10	10
Sodium nitrite	3.0	0.48	72.1	6	10
m-Bromobenzoic acid	10	0.22	50.4	5	10
m-Iodobenzoic acid	12	0.22	50.7	10	10
Oleic acid	9	0.15	40.1	6	6
10-Undecylenic acid	8	0.14	41.1	7	8

[a]Aqueous solutions (0.5 per cent) of triethanolamine salts were used.

TABLE III

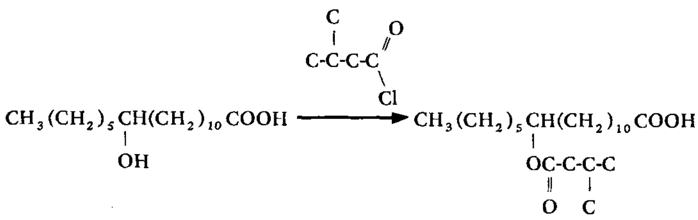
Cutting Fluids Characterization of Derivatives from 12-Hydroxy Stearic Acid and Ricinoleic Acid

Sample[a]	Welding load (kg/cm^2)	Coefficient of friction	Surface tension (dyn/cm)	Corrosion test Method A
12-Isovaleroyloxy stearic acid	>20	0.086	28	10
12-Caproyloxy stearic acid	15	0.093	30	10
12-Acetoxy stearic acid	16	0.079	33	10
12-Acetoxy 9-octadecenoic acid	15.5	0.106	33	10
12-Butyroxy 9-octadecenoic acid	20.0	0.108	33	10
12-Isobutyroxy 9-octadecenoic acid	16.0	0.109	32	10
12-Carpoxy 9-octadecenoic acid	10.5	0.112	33	10

[a]Aqueous solutions (0.5 per cent) of triethanolamine salts were used.

propane and dibromocyclopropane derivatives from higher fatty acids have excellent properties in anti-wear load and anti-rust tests, and their characteristics are shown in Table II.

Esterification of hydroxy group of 12-hydroxy stearic acid (V) and ricinoleic acid was carried out by the action of acyl halides on these hydroxy compounds. Some fatty acids containing ester group have anti-rust and anti-wear properties. For example, aqueous solution of triethanolamine salt of 12-isovaleroyloxy stearic acid (VI) has excellent anti-wear property as shown in Table III.



(V) (VI)

Some practical tests on these water-based cutting fluids provided the following results. Using our new grinding fluid coolant [sample A, compound (II)], loading did not occur after 25 min. Using sample B containing compound (IV), loading did not occur after 20 min. However, using a sodium nitrite solution system (sample C), loading occurred after 14 min. The effect of compound (II) as an anti-wear additive for oleic acid system cutting fluids was studied. Using a cutting fluid containing compound (II) (sample D), the number of abrasive cut-off pieces was about 21,000. Using a cutting fluid containing compounds (IV), (sample E), the number of abrasive cut-off pieces was about 20,000. However, using a cutting fluid (sample F), which had not contained compound (IV), the number of abrasive cut-off pieces was about 10,000.

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