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New water-soluble cutting fluid additives derived from aromatic hydroxycarboxylic acids

S. WATANABE*, T. FUJITA, M. SAKAMOTO, T. KURAMOCHI
Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoicho, Chiba 260, Japan

H. NAKAGAWA
NEOS Central Research Laboratory, Kohsei-cho, Kohga-gun, Shiga-ken 520-32, Japan

A variety of alkoxyaromatic carboxylic acids and acyloxyaromatic carboxylic acids were prepared from various hydroxyaromatic carboxylic acids, and screened for anti-rust properties, lubrication properties and antimicrobial activity in spent coolants of water-soluble cutting fluids. The triethanolamine salt of alkoxydiphenyl carboxylic acids showed good anti-rust activity and lubrication properties. The triethanolamine salts of *p*-alkoxyphenyl propionic acid showed good antimicrobial activity together with good anti-rust properties and lubrication properties.

1. Introduction

A variety of water-soluble cutting fluids is used for many machine operations. For water-soluble cutting fluids, antibacterial, anti-rust and good lubrication properties are essential [1]. The relationship between the properties of water-soluble cutting fluids and the chemical structures of various organic additives has not been researched in detail. We have previously reported that triethanolamine salts of *p*-alkoxybenzoic acids have excellent properties as anti-rust additives for water-soluble cutting fluids [2]. In the present work, we prepared many alkoxyaromatic carboxylic acids and acyloxyaromatic carboxylic acids, and examined their anti-rust properties, lubricity properties and antimicrobial activities for water-soluble cutting fluid additives.

2. Experimental procedure

2.1. Preparation of 4′-octyloxy-diphenyl-4-carboxylic acid (II)

A mixture of 4′-hydroxy-diphenyl-4-carboxylic acid (I) (2.14 g, 0.01 mol), potassium hydroxide (1.23 g, 0.022 mol) and ethylene glycol (50 ml) was refluxed for 1 h. Octylbromide (2.12 g, 0.011 mol) was added to this mixture. The mixture was refluxed for 5 h and poured into excess water. The aqueous solution was acidified by adding diluted sulphuric acid to give white crystals. These crystals were recrystallized with ethyl alcohol to give a pure 4′-octyloxy-diphenyl-4-carboxylic acid (II) (2.28 g, yield 70.0%). Compound (II) showed the following data, IR(cm^{-1}): 3100–3400 (–COOH), 1680 (=CO), 1120, 1200 (–O–), 830 (*p*-substituted); NMR (δ, p.p.m.): 0.88 (3H, t, $J = 7.0$ Hz, CH_3–), 1.33 (12H, m, –$(CH_2)_6$–), 3.93 (2H, t, $J = 6.0$ Hz, –CH_2CH_2–O–), 6.93 (4H, m, aromatic protons), 7.73 (4H, m, aromatic protons), 9.50 (1H, s, –COOH); MS (FAB method, m/e): $M^+ = 326$, $(MH)^+ = 327$, calculated for $C_{21}H_{26}O_3 = 326$. Other alkoxyaromatic carboxylic acids were prepared in the similar manner.

4-Acetyloxyphenyl acetic acid was prepared by the reaction of acetyl chloride with 4-hydroxyphenyl acetic acid. Other acyloxyaromatic carboxylic acids were prepared in the similar way.

2.2. Lubricity characteristic tests

Aqueous solutions of water (100.0 g), triethanolamine (2.0 g) and a carboxylic acid (1.0 g) listed in Table I were used. City water in Japan (Osaka and Chiba) was used for all tests. The same results were obtained in all the tests as with distilled water.

Corrosion tests with cast iron chips were carried out as follows. Cast iron chips (JIS G 5501, FC-20, grey iron casting), weighing 2 g, 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 II. This method is a standardized test in Japan and is based on the I.P. Corrosion Test 125/63 T [3].

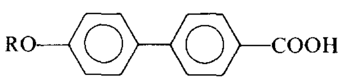
The coefficient of friction was measured at 25 °C by a pendulum-type oiliness and friction tester (Shinko Engineering Co. Ltd, Tokyo) [4].

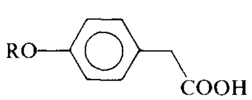
Welding loads (kgf cm^{-2}) were measured on a Soda-type four-ball lubricating oil testing machine at 200 r.p.m. This testing machine and friction tester mentioned above have been officially authorized by the

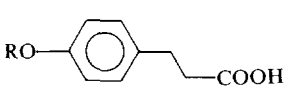
*Author to whom all correspondence should be addressed.

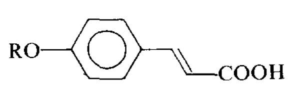
TABLE I Cutting fluid characterization of various alkoxyaromatic carboxylic acids

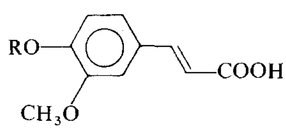
R for ether	pH	Rust-inhibition test for time (h)			Friction coefficient	Surface tension (dyn cm^{-1})	Welding load (kgf cm^{-2})	Antimicrobial properties for time (day)[c]		
		24	48	72				1	2	3
4′-Alkoxybiphenyl-4-carboxylic acid (A)[a]										
H	8.5	10	10	10	0.21	50	–	+	+ +	+ +
CH_3	8.9	10	10	10	0.16	55	–	+	+ +	+ +
C_2H_5	11.2	10	9	9	0.12	57	–	+	+ +	+ +
C_3H_7	8.5	10	10	10	0.11	36	–	+	+	+
Crotyl	9.3	10	10	10	0.15	56	–	+ +	+ +	+ +
C_4H_9	9.4	10	10	10	0.16	55	–	+	+	+ +
C_5H_{11}	9.8	10	10	10	0.14	44	–	–	+	+ + +
C_6H_{13}	9.9	10	10	10	0.14	48	–	–	+	+ + +
C_7H_{15}	11.4	10	10	9	0.20	64	–	+	+	+
C_8H_{17}	10.0	10	10	10	0.17	52	–	+ +	+ +	+ +
$C_{10}H_{21}$	10.0	10	10	8	0.12	53	–	+ +	+ +	+ +
$C_{12}H_{25}$	10.4	10	10	8	–	67	–	+ +	+ +	+ + +
Oleyl[b]	–	–	–	–	–	–	–			
4′-Alkoxyphenyl-acetic acid (B)[a]										
C_4H_9	8.4	10	10	10	0.13	42	–	+ + +	+ + +	+ + +
Crotyl	8.6	8	8	6	0.13	40	–	+ + +	+ + +	+ + +
C_5H_{11}	8.5	10	10	10	0.13	36	11.0	+ + +	+ + +	+ + +
C_6H_{13}	8.5	10	8	6	0.12	37	8.5	+ +	+ +	+ +
C_9H_{19}	8.9	10	8	6	0.11	32	–	+	+	+
$C_{12}H_{25}$	9.9	10	10	10	0.16	27	17.0	+ +	+ +	+ +
Oleyl	10.1	10	10	10	0.19	29	12.0	+ +	+ +	+ +
PhCH=CH	8.9	10	8	7	0.16	45	20.0	+ + +	+ + +	+ + +
$HO(CH_2)_6$	8.6	10	10	10	0.12	51	18.0	+	+ +	+ +
4′-Alkoxyphenyl-propionic acid (C)[a]										
C_6H_{13}	8.0	10	10	10	0.11	31	14.5	–	–	+
C_8H_{17}	9.1	10	10	10	0.11	34	10.0	–	+	+
$C_{10}H_{21}$	9.3	10	10	10	0.09	31	15.0	+	+	+
$C_{12}H_{25}$	9.5	10	10	10	0.09	28	13.5	–	+	+ +
Oleyl	9.7	10	10	10	0.10	36	20.0	+ +	+ +	+ +
$HO(CH)_6$	8.4	10	10	10	0.10	46	17.5	+ +	+ +	+ +
4′-Alkoxycinnamic acid (D)[a]										
C_8H_{17}	10.4	10	10	8	0.14	41	17.5	+ +	+ +	+ +
$C_{10}H_{21}$	11.0	10	10	8	–	59	–	+	+	+
$C_{12}H_{25}$	11.1	8	8	7	–	60	–	+	+	+
$C_{14}H_{29}$	10.2	8	8	7	–	61	–	+	+	+ +
$HO(CH_2)_6$	8.4	10	10	10	0.13	48	16.5	+	+	+
3′-Methoxy-4′-alkoxy-cinnamic acid (E)[a]										
C_8H_{17}	9.1	10	10	10	0.11	35	12.5	+ +	+ +	+ +
$C_{14}H_{29}$	10.0	10	10	8	0.10	58	–	+	+	+
Triethanol amine (2% aq. solution)		7	6	5				+ + +	+ + +	+ + +
Triazine type antiseptic										
1% aq. solution								–	–	–
0.5% aq. solution								–	–	+
0.1% aq. solution								+ + +	+ + +	+ + +
Blanc test								+ + +	+ + +	+ + +

[a] (A) 

(B) 

(C) 

(D) 

(E) 

[b] Unsoluble in water

[c] – Increase of bacteria was not observed.
[+] A very little increase of bacteria was observed.
[++] A little increase of bacteria was observed.
[+++] Much increase of bacteria was observed.

TABLE II Valuation of anti-rust effect

Time (h)	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	2
1	Some points of rust	1

Agency of Industrial Science and Technology of Japan as JIS K 2519 and 2219. The machine was obtained from Shinko Engineering Co. Ltd (Tokyo) [5].

Surface tension (dyn cm^{-1}) was measured at 25 °C using a Dü Noüy tensiometer.

2.3. Antimicrobial activity tests for spent coolants of water-based cutting fluids [6.7]

Agar (20 ml) was placed in a sharle having a diameter of 90 mm, and solidified. A 1 µl drop of bacterial culture was dropped on to the centre 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^{-1}) was collected from an industrial factory and the bacteria were cultured on a liquid broth for 48 h at 30 °C. On the centre of the agar inoculated with this culture, 1 ml sample solution of the new cutting fluids was dropped, and the agar was kept at 30 °C. After 1, 2 and 3 days, the degree of increase of bacteria was observed. The judgement was performed as follows, " – " indicates no bacterial growth, " + " is a very little bacterial increase, " + + " is a little bacterial increase, " + + + " is a large bacterial increase. This method is a modified method based on literature methods [6, 7].

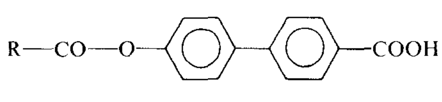
It is known that spoilage may be caused by several different organisms working together [8–12]. The spend coolant contains micro-organisms, such as *Staphylococcus aureus*, *Desulphovibrio desulphuricans*, *Pseudomonas aeruginosa*, *Pseudomonas oleovorans*, *Klebsiella pneumoniae*, *Escherichia coli*, *Proteus mirabilis*, and *Fusarium* sp. The bacterial content of the spent coolant was over 10^7 ml^{-1}.

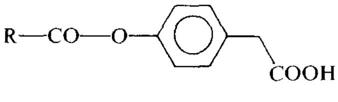
3. Results and discussion

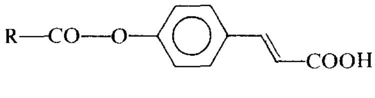
Water-soluble cutting fluids prepared from fatty acids are easily spoiled by various micro-organisms. Recently we reported that various *p*-alkoxybenzoic acids show good antimicrobial activity in spent coolants of water-soluble cutting fluid [2]. The development of the additives which possess both anti-rust and antimicrobial properties is an urgent subject of study. We prepared a variety of alkoxyaromatic carboxylic acids and acyloxyaromatic carboxylic acids, and then screened them for anti-rust activity as water-soluble cutting fluids and anti-microbial activity against the bacteria of a spent coolant. Alkoxycarboxylic acids

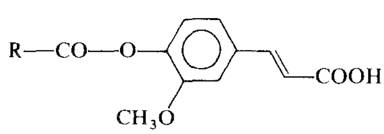
TABLE III Cutting fluid characterization of various acyloxyaromatic carboxylic acids

R for acyl	pH	Rust-inhibition test for time (h)			Friction coefficient	Surface tension (dyn cm^{-1})	Welding load (kgf cm^{-2})	Antimicrobial properties for time (day)[b]		
		24	48	72				1	2	3
4′-Acyloxybiphenyl-4-carboxylic acid (A′)[a]										
CH_3CO	8.1	8	7	6	0.30	55	–	+	+ + +	+ + +
$C_5H_{11}CO$	10.0	10	10	10	0.15	47	–	+ +	+ +	+ +
$C_7H_{15}CO$	9.3	10	10	10	0.14	45	–	+ + +	+ + +	+ + +
4′-Acyloxyphenyl-acetic acid (B′)[a]										
CH_3CO	9.6	9	8	7	0.34	62	20.0	+ +	+ +	+ +
C_2H_5CO	8.6	9	8	7	0.15	60	–	+	+	+
$C_5H_{11}CO$	9.2	8	7	7		60	–	+ + +	+ + +	+ + +
$C_7H_{15}CO$	9.0	8	7	6		56	–	+ + +	+ + +	+ + +
4′-Acyloxycinnamic acid (D′)[a]										
CH_3CO	7.9	8	7	6	0.25	58	–	+ +	+ +	+ + +
4′-Acyloxy-3-methoxy-cinnamic acid (E′)[a]										
CH_3CO	8.1	8	8	6	0.20	60	–	+ +	+ +	+ +

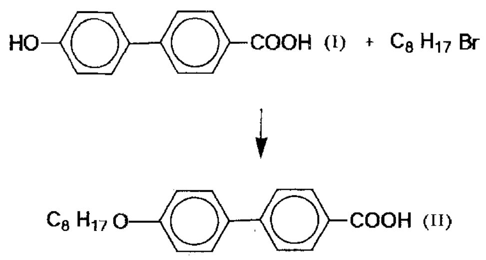
[a] (A′) 

(B′) 

(D′) 

(E′) 

[b] – Increase of bacteria was not observed.
[+] A very little increase of bacteria was observed.
[++] A little increase of bacteria was observed.
[+++] Much increase of bacteria was observed.



Scheme 1

used in this paper were prepared as shown in Scheme 1. For example, 4′-octyloxy-biphenyl-4-carboxylic acid (II) was prepared by the reaction of 4′-hydroxy-biphenyl-4-carboxylic acid (I) with octylbromide in the presence of potassium hydroxide. *p*-Alkoxyphenylacetic acids, *p*-alkoxyphenylpropionic acids and others were prepared in the similar way. Acyloxycarboxylic acids were prepared from the reaction of hydroxyaromatic carboxylic acids and acylhalides in the usual way.

Cutting fluid characterization of aqueous solutions of triethanolamine salts of various alkoxyaromatic carboxylic acids are shown in Table I. Aqueous solutions of triethanolamine salts with almost all 4′-alkoxybiphenyl-4-carboxylic acid, 4′-alkoxyphenylpropionic acid and 3′-methoxy-4′-alkoxycinnamic acid have excellent properties for water-soluble cutting fluids. For example, aqueous solutions of triethanolamine salt with 4′-propyloxybiphenyl-4-carboxylic acid (II, R = *n*–Pr) showed excellent corrosion resistance in a test with cast-iron chips. The surface tensions of these solutions were about 40 dyn cm^{-1}. Friction coefficients were under 0.2. Aqueous solutions of triethanolamine salts with some 4′-alkoxyphenylacetic acid (R = C_4H_9, C_5H_{11}, $C_{12}H_{25}$, oleyl, $HO(CH_2)_6$) and 4′-alkoxycinnamic acid (R=$HO(CH_2)_6$) show good properties for anti-rust tests. However, these compounds did not show good antimicrobial activities. Aqueous solutions of triethanolamine salts of alkoxyphenylpropionic acids have excellent anti-rust properties and lubricity for water-soluble cutting fluids. Interestingly, these compounds showed good antimicrobial activity. Antimicrobial activities of hexyloxy- and octyloxyphenyl propionic acids are nearly equal to that of a commercial triazine-type antiseptic. Characteristics of aqueous solutions of triethanolamine salts of various acyloxyaromatic carboxylic acids are shown in Table III. Only, 4′-hexanoyloxy- and 4′-octanoyloxy-biphenyl-4-carboxylic acid show good anti-rust properties, but all other carboxylic acids did not show good anti-rust properties. All these compounds did not show antimicrobial activity.

From the above-mentioned results, 4′-alkoxy-phenylpropionic acids are good additives having both anti-rust and antimicrobial properties. These new additives described above for water-soluble cutting fluids were not previously known. Practical tests of these new additives are now in progress at our laboratory.

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