Antimicrobial Properties of Boric Acid Esters of Alcohols

S. Watanabe*, T. Fujita and **M. Sakamoto**
Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoicho, Chiba, Japan 260

A variety of boric acid esters of various alcohols were prepared and screened for antimicrobial activity in spent coolants of water-based cutting fluids. Boric acid esters of triethylene glycol, dipropylene glycol, geranic acid monodiethylene glycol and some hydroxy amines, such as 5-aminopentanol, showed good antimicrobial activity.

Recently, many long chain fatty acid derivatives were used for additives of water-based cutting fluids (1). These water-soluble fluids are easily degraded by various microorganisms. The bacterial flora in metal cutting fluids has been investigated extensively in recent years, and a variety of organisms have been isolated (2,3). It is known that some mixed diesters of aliphatic diols have antimicrobial properties (4). However, the relationship between the antimicrobial properties of water-soluble cutting fluid additives and the chemical structures of these additives has not been reported in detail. Antimicrobial properties of a variety of boric acid esters of various alcohols were prepared, and antimicrobial activity was screened in a spent coolant of water-based cutting fluid.

EXPERIMENTAL

Preparation of boric acid esters of alcohols. The esters of boric acid were prepared by direct reactions of boric acid (1/3 equivalent per one equivalent of hydroxyl group) and an alcohol at 80–90°C under reduced pressure (30–40 mmHg) for one to two hr. When water produced by esterification was completely removed, the reaction mixture became colorless and transparent. The crude boric acid esters were used for antimicrobial tests without purification. In the case of the reaction of surface active agents and boric acid, one part of boric acid was used per 10 parts (weight ratio) of surface active agents. Thus boric acid derivatives were used for antimicrobial tests without purification.

All surface active agents used in this work were commercially available. Although we can't know their detailed chemical structures, the outlines of their chemical structures are as follows. Emulgen is an adduct of ethylene oxide to lauryl alcohol. L 202 is an adduct of ethylene oxide with a fatty amine. Ethoxy castor oil is a partly ethoxylated product of castor oil. Tween 20, ethoxy sorbitol and fatty acid diethanolamide, being on the market, were used.

Microbial activity tests (5). Preparation of sample solutions: Simplified testing of bio-resistant raw materials was performed as follows. When a sample was soluble in water, a mixture of sample (4.0 g), diethanolamine (0.5 g), YCC Broth standard medium (10 ml), cast-iron chips (FC-20, 8 g), water (110 ml) and spent coolant (1.0 g) was incubated at 35°C in an incubator. When a sample was insoluble in water, a mixture of sample (4.0 g), YCC Broth standard medium (10 ml) and water (110 ml) was emulsified by adding diethanolamine (0.5 g), emulgen 108 (1.0 g) and FA-30 (1.0 g). To these solutions, cast-iron chips (FC-20, 8 g) and spent coolant (1.0 g) were added, and the mixture was kept in an incubator at 35°C. Every three days, 1.0 g of spent coolant was added to all sample solutions. With the passage of time, the presence or absence of an offensive odor and the pH of the sample solution were observed. When a rotton odor was noted, it was judged that the sample had been spoiled. Standard medium was prepared by dissolving YCC Broth, Eiken (2.8 g), in 100 ml water and sterilized at 121°C for 15 min. YCC Broth, Eiken is a stock culture, and sold from Eiken Chemical Corp. Ltd., Tokyo, Japan. The composition of a culture (100 ml) was as follows: yeast extract (5 g), peptone M (15 g), glucose (4.5 g), K_2HPO_4 (2 g), $Na_2S_2O_3 \cdot 5H_2O$ (1.1 g), and Na_2SO_3 (0.2 g) (pH=7.2).

Spent coolant was supplied by Johnson Co. Ltd. It is known that spoilage may be caused by several different organisms working together (2,3). The spent coolant contains microorganisms, such as *Staphylococcus aureus*, *Desulfovibrio desulfuricans*, *Pseudomonas aeruginosa*, *Pseudomonas oleovorans*, *Klebsiella pneumoniae*, *Escherichia coli*, *Proteus mirabilis* and *Fusarium sp.* The bacterial content of the spent coolant was about 10^7/ml. The bacterial content of sample solutions was measured by Easicult-TTC plate. Easicult-TTC plate is on the market from Medical Technology Corp., Somerset, New Jersey. The plate was dipped into a test solution and kept in an incubator at a temperature of 35°C. After 48 hr incubation, the bacterial content of sample solutions was determined by comparing the density of the colonies appearing on the slide with the densities shown on the model chart.

RESULTS AND DISCUSSION

The relationship between the chemical structures of compounds and the antimicrobial property is not well known. This paper describes the antimicrobial properties of various compounds in water-based cutting fluids. As materials of water-based cutting fluids, various derivatives of fat- and oil-related compounds are used widely. We prepared a variety of boric acid esters and screened for antimicrobial activity against the bacteria of a spent coolant.

It is known that boric acid has a fair antimicrobial property. We suggested that boric acid derivatives probably have antimicrobial properties. After incubating them at 35°C, appearance of an offensive odor and lowering of pH of the sample solution were observed. We concluded that the absence of these effects shows good activity against bacteria. As shown in Tables 1 and 2, boric acid esters of triethylene glycol, dipropylene glycol and amino alcohols such as 5-aminopentanol showed excellent antimicrobial activity in a spent coolant. After incubating 20 days at 35°C, these samples did not have a rotton odor.

*To whom correspondence should be addressed.

TABLE 1

Antimicrobial Activity of Some Boric Esters of Alcohols for a Spent Coolant

			Time (days)							
Sample	Substrate		initial	3	7	10	13	17	20	22
1	Ethylene glycol	pH	9.15	9.00	9.05	8.94				
		odor		w	w	s				
2	Diethylene glycol	pH	9.50	9.28	9.25	9.15				
		odor		s	s	s				
3	Glycerine	pH	9.18	9.05	9.00	8.90				
		odor		s	s	s				
4	Propylene glycol	pH	9.08	9.12	9.00	8.90	8.90	8.80		
		odor		w	w	w	w	s		
5	1,6-Hexanediol	pH	9.45	9.41	9.27	9.27	9.20			
		odor			w	w	s			
6	Carbitol	pH	9.15	9.15	9.04	9.01	8.95			
		odor					none			
7	Triethylene glycol	pH	8.85	8.92	8.74	8.76	8.80	8.78	8.71	8.73
		odor								none
8	Dipropylene glycol	pH	8.52	8.55	8.42	8.43	8.45	8.47	8.44	8.13
		odor								none
9	Diethylene glycol	pH	8.65	8.28	8.25					
		odor		w	s					
10	Monoolein	pH	8.41	8.38						
		odor		s						
11	Monoacetin	pH	8.43	7.35	7.30					
		odor		w	s					
12	Diacetin	pH	8.85	7.20	6.20	6.00	6.00			
		odor		w	w	w	s			
13	Geranic acid mono	pH	8.80	8.70	8.60	8.60	8.60	8.60	8.60	8.70
	DEG ester	odor								none
14	L-Tartaric acid	pH	8.31	7.69	7.49					
	Diester	odor		w	s					
15	$C_6H_{11}COOC_2H_4OH$	pH	8.95	8.70	8.30	8.20	8.10	8.02		
		odor			w	w	w	s		
16	$C_2H_5CH(Br)Coo-$	pH	8.85	6.00	5.98					
	C_2H_4OH	odor		w	s					
17	α-Thioglycerine	pH	10.0	6.0						
		odor		s						
18	3-Nitro-2-butanol	pH	9.00	8.88	8.80	8.40	8.10	8.00		
		odor		w	w	w	w	s		
19	Ethylene	pH	9.00	8.90	8.80	8.60	8.25	8.20		
	cyanhydrine	odor			w	w	w	s		

None, bad odor does not appear; w, weak bad odor appears; s, strong bad odor appears.

TABLE 2

Antimicrobial Activity Tests of Some Boric Esters of Amino Alcohols in a Spent Coolant

			Time (days)										
Sample	Substrate		initial	3	6	9	12	15	18	21	24	27	30
1	2-Amino butanol	pH	10.0	10.0	9.90	9.80	9.80	9.85	9.82	9.80	9.78	9.75	9.70
		odor											n
2	Triisopropanol-amine	pH	9.20	8.83	8.43	8.71	8.66	8.76	8.89	8.90	8.70	8.68	
		odor										w	
3	5-Aminopentanol	pH	10.83	10.80	10.56	10.55	10.55	10.63	10.54	10.52	10.61	10.60	10.59
		odor											n
4	2-(2-Aminoethoxy) ethanol	pH	10.01	10.00	10.01	9.90	9.90	9.88	9.86	9.83	9.84	9.81	9.80
		odor											n
5	1-Amino-2-pentanol	pH	9.90	9.90	9.90	9.88	9.84	9.86	9.80	9.78	9.75	9.73	9.70
		odor											n
6	2-(2-Aminoethyl-amino) ethanol	pH	9.95	9.90	9.88	9.83	9.85	9.85	9.82	9.79	9.78	9.75	9.75
		odor											n
7	3-Amino-2,2-dimethyl-1-propanol	pH	10.0	9.90	9.90	9.85	9.80	9.80	9.76	9.73	9.70	9.72	9.70
		odor											n
8[a]	Triethanol-amine (only)	pH	11.0	10.7	9.70								
		odor		w	s								

n, A bad odor does not appear; w, a weak odor appears; s, a strong bad odor appears.

[a]In this case, only triethanolamine was used. We suggest that pH has no effect on the antimicrobial property of triethanolamine under our test conditions.

TABLE 3

Antimicrobial Activity of Some Boric Esters from Surface Active Agents

			Time (days)							
Sample	Substrate		initial	3	7	10	13	17	20	22
1	Emulgen	pH	9.90	9.50	9.60	9.00	9.50	9.50	9.50	9.40
		odor								none
2	L 202	pH	9.15	9.10	8.90	9.00	9.10	9.08		
		odor				w	w	s		
3	L 202[a]	pH	9.00	8.85	8.75	8.70	8.80	8.65	8.60	8.60
		odor								w
4	Ethoxy castor oil	pH	9.20	8.50	9.20	9.18				
		odor				s				
5	Tween 20	pH	8.41	8.40						
		odor		s						
6	Ethoxy sorbitol	pH	8.90	8.65	8.12	7.80	7.77			
		odor			w	w	s			
7	Fatty acid diethanol-amide	pH	8.85	8.75	8.60	8.60	8.50	8.43		
		odor				w	w	s		

[a]Weight ratio of L 202/H_3BO_3 was 10:1.5.

None, a bad odor does not appear; w, a weak bad odor appears; s, a strong bad odor appears.

TABLE 4

Numbers of Bacterium in the Sample Solution After 30 Days of Incubation

Sample	Bacterium (cbu/ml)
Boric ester of diethylene glycol monogeranate	10^5
Boric ester of triethylene glycol	10^4
Boric ester of dipropylene glycol	10^6
Boric ester of triisopropanol amine	10^7
Boric ester of Emulgen	10^6
Boric ester of L-202	10^6
Boric ester of 2-aminobutanol	0
Boric ester of 2-(2-aminoethyoxy) ethanol	0
Boric ester of 3-amino-2,2-dimethyl-1-propanol	0
Boric ester of 5-aminopentanol	0

Some surface active agents are applied for water-soluble cutting fluids as an additive. Aqueous solutions of boric acid esters of surface active agents were also screened for antimicrobial properties in a spent coolant. As shown in Table 3, the boric acid ester of Emulgen showed good antimicrobial properties.

The bacterial contents of these good sample solutions were estimated by Easicult-TTC plate, and the results are shown in Table 4. We found that the boric acid ester of an amino alcohol such as 5-aminopentanol had excellent antimicrobial acivity.

These new additives for water-based cutting fluids were not known previously. The effective inhibition of the organisms by several of these compounds indicates the desirability of a more thorough investigation and suggests that some of these compounds may have a potential as biostatic additives in commercial use of water-based cutting fluids. Practical tests of these new additives as antimicrobial agents are now in progress at our laboratory.

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