NOTE

Water-Soluble Metal Working Fluids Additives Derived from the Esters of Acid Anhydrides with Higher Alcohols for Aluminum Alloy Materials

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Abstract: Water-soluble metal working fluids are used for processing of aluminum alloy materials. This short article describes properties of new additives in water-soluble metal working fluids for aluminum alloy materials. Many half esters or diesters were prepared from the reactions of higher alcohols with acid anhydrides. Interestingly, diesters of PTMG (tetrahydrofuran oligomer, MW = 650 and 1000) and polybutylene oxide (MW = 650) with maleic anhydride and succinic anhydride showed both of an excellent anti-corrosion property for aluminum alloy and a good hard water tolerance. The industrial soluble type processing oils including these additives also showed anti-corrosion property and hard water tolerance.

Key words: water-soluble metal working fluids additives, aluminum alloy material, diesters of tetrahydrofuran oligomer, diesters of polybutylene oxide, hard water tolerance

1 INTRODUCTION

A variety of water-soluble metal working fluids are widely used for the processing of aluminum alloy materials similarly to the case of iron materials. It is well known that higher fatty acids such as oleic acid, ricinoleic acid and ricinoleic acid oligomers are used as one of the components of water soluble metal working fluids. Alkanolamines such as triethanolamine or diethanolamine are used to dissolve acidic ingredients into water, to increase anti-microbial activity of the fluids, and for other purposes. The long use of these fluids is apt to produce precipitates (for example, calcium salts of fatty acids) owing to calcium ion in hard water as well as heavy metals in aluminum alloy materials. Some patents on corrosion inhibitor in metal working and cutting of aluminum alloy materials are known. For example, a mixture of palm oil and oleic acid¹⁾, ionic lithium compounds²⁾, a polyalkyl[(N-aminoalkyl) iminoalkyl]-siloxane³⁾, organic phosphonic esters⁴⁾, organic phosphoric esters⁴⁾, a mixture of castor oil phosphoric esters⁵⁾, and many others are made public.

Usually, these commercial water-soluble metal working

fluids consist of many components, however the detailed compositions of these fluids have not been known. The additives which possess both an anti-corrosion property for aluminum and a good hard water tolerance have not been reported up to now. The present authors have been engaged in the syntheses of water-soluble metal working fluids additives and have published some patents⁶⁻⁸⁾ and some papers⁹⁾ on this subject. In this short article the authors describe the evaluations of some esters of higher alcohols with acid anhydrides as an aluminum corrosion inhibitor accompanying a good hard water tolerance.

2 EXPERIMENTAL

2.1 Materials

Abbreviations of raw materials used in this work and, in some cases, their sources are shown below. For polymer samples, the abbreviations are accompanied by numerals which indicate the average molecular weights of the polymer.

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Tetrahydrofuran oligomer (PTMG, trade name; Mitsubishi Kagaku Co. Ltd.)

Polybutylene oxide (PBO, Mitsubishi Kagaku Co. Ltd.)

Blockcopolymer of propylene oxide and ethylene oxide (PO-EO, Sanyo Kasei Co. Ltd.; the average molecular weights are 1100, 2000 (PE-61), 2250 (PE-62), and 3000 (PE-64))

Polypropylene oxide (PO, Dow Chemical Co. Ltd.)

Polyethylene oxide (EO)

Blockcopolymer of butylene oxide and ethylene oxide with 1:1 molar ratio (BO-EO, NOF CORPORATION)

Maleic anhydride (MA)

Hexahydrophthalic anhydride (HHPA)

Succinic anhydride (SA)

Phthalic anhydride (PA)

Branched decanoic acid, $C(R_1R_2R_3)COOH$ (NPG, trade name)

Oleyl Alcohol (Kyowa Technos Co. Ltd.; #700 and #900 mean that the samples contain 70% and 90% of oleyl alcohol, respectively)

2.2 Reaction of PTMG 650 (I) with maleic anhydride (II)

2.2.1 Monoester (III)

A mixture of PTMG 650 (I) (130 g, 0.2 mol) and maleic anhydride (II) (19.6 g, 0.2 mol) was heated with agitation at 140°C for 2 h and left overnight at room temperature (see **Scheme 1**). The degree of reaction was checked by IR spectrum.

When the absorptions of carbonyl group of (II) at 1779 and 1848 cm^{-1} disappeared and the strong absorption of an ester at 1729 cm^{-1} was recognized, the reaction was stopped. The product was nearly pure monoester (III) (150

g, quantitative yield). The crude product was used for the test of metal working fluids additives without refining. This material (1.0 g) was chromatographed by short path column packed with silica gel using benzene as a solvent to give 0.7 g of compound (III). It showed the following spectral data: IR (cm^{-1}): 3446, 1729, 1641, 1111, 820; NMR (δ , ppm): 1.62 [s, 36H, $-CH_2(a)-$], 3.41 [s, 32H, $-OCH_2(b)-$], 4.20 [t, 2H, $-CH_2(c)OH$, $J=6.6$ Hz], 4.29 [t, 2H, $-CH_2(d)OCO$, $J=6.36$ Hz], 6.31 [d, 1H, $-COCH(e)=CHCOOH$, $J=11.0$ Hz], 6.40 [d, 1H, $-CH=CH(f)-COOH$, $J=11.0$ Hz].

2.2.2 Diester (IV; see **Scheme 3**)

A mixture of PTMG 650 (I) (65 g, 0.1 mol) and maleic anhydride (II) (19.6 g, 0.2 mol) was heated with agitation at 150°C for 3 hrs and left overnight at room temperature. With the progression of the reaction, the absorption in IR spectrum of the mixture due to carbonyl group of maleic anhydride (1779 and 1848 cm^{-1}) diminished and finally disappeared, while the new absorption of an ester at 1724 cm^{-1} appeared. It is suggested that the product is nearly pure diester (IV) (yield 83 g, quantitative yield). The crude product was used for the test of metal working fluids additives without refining. This product (1.0 g) was chromatographed by short path column packed with silica gel using toluene as a solvent to give 0.65 g of compound (IV). This substance was identified to be the diester (IV) from the following spectral data: IR (cm^{-1}): 3446, 1724, 1287, 1111, 743; NMR (δ , ppm): 1.62 [s, 32H, $-CH_2(a)-$], 3.42 [s, 32H, $-CH_2(b)-$], 4.20 [m, 4H, $-CH_2(c)CH_2OCO$], 4.29 [t, 4H, $J=6.32$ Hz, $-CH_2(d)OCO$], 6.32 [d, 2H, $J=11.0$ Hz, $-COCH(e)=CH-COOH$], 6.40 [d, 2H, $J=11.0$ Hz, $-CH=CH(f)-COOH$].

Other monoesters and diesters were prepared by the reactions of each dibasic acid anhydride with each higher alcohol in a similar way, and they were also identified by IR, NMR and other indices. The products with maleic anhydride are listed in **Table 1**, and those with succinic anhydride, phthalic anhydride and hexahydrophthalic anhydride are shown in **Table 2**.

2.3 Anti-corrosion test of aluminum alloy materials

2.3.1 Preparation of sample solution

A sample solution (100 g) was prepared by dissolving 0.50 g of test materials (**Tables 1** and **2**) and 5.0 g of tri-

Scheme 1 Reaction of PTMG 650 (I) with Maleic Anhydride (II).

Scheme 2 Monoester (III).

Scheme 3 Diester (IV).

Table 1 Reaction Products of Various Alcohols with Maleic Anhydride and Their Anti-corrosion Tests for Aluminum and Hard Water Tolerance.

Entry No.	Alcohols	Acid anhydride	Molar ratio	Anti-corrosion test of aluminum After 24 hr	Hard water tolerance After 24 hr
1	PTMG 650	MA	1 : 1	△	×
2	PTMG 650	MA	1 : 2	◎	◎
3	PTMG 1000	MA	1 : 1	△	×
4	PTMG 1000	MA	1 : 2	◎	◎
5	PTMG 2000	MA	1 : 1	△	×
6	PTMG 2000	MA	1 : 2	△	×
7	PBO 650	MA	1 : 1	×	○
8	PBO 650	MA	1 : 2	◎	◎
9	PBO 1000	MA	1 : 2	◎	○
10	PBO 2000	MA	1 : 2	△	—
11	PE-61	MA	1 : 1	×	◎
12	PE-61	MA	1 : 2	×	◎
13	PE-62	MA	1 : 1	×	◎
14	PE-64	MA	1 : 1	×	◎
15	PO 1000	MA	1 : 2	×	◎
16	PO 420	MA	1 : 2	×	△
17	PO (9) - EO (1)	MA	1 : 2	×	◎
18	Oleyl alcohol #700	MA	1 : 1	○	×
19	Ricinoleic acid	MA	1 : 1	◎	×
20	Ricinoleic acid dimer	MA	1 : 1	◎	△
21	Ricinoleic acid tetramer	MA	1 : 1	◎	×
22	12-Hydroxystearic acid	MA	1 : 1	◎	×
	Ricinoleic acid			◎	×
	NPG			×	◎
	Tall oil fatty acids			◎	×
	Undecylenic acid			△	×
	Dodecanoic acid			△	×

Detail of the procedure for anti-corrosion tests and hard water tolerance tests are shown in Experimental Section 2.3 and 2.4.

Entry No. 17: Weight ratio of PO/EO is 9/1.

The same results were obtained in all tests regardless of the quality of water, deionized water (hardness of 0) or city water (hardness of about 30).

ethanolamine into deionized water (94.5 g). This solution corresponds to the 0.50% solution of the test materials. The pH of these test solutions was adjusted at 9.0 ± 0.2 by adding boric acid or sodium hydroxide solution. Similarly, sample solutions were prepared with city water (Shiga, Japan; hardness 30).

2.3.2 Anti-corrosion test of aluminum pieces

Size of test piece of aluminum alloy (ADC-12)¹⁰⁾ is 6 cm × 3 cm × 0.5 cm. The test piece was washed with acetone, polished with emery paper (# 240), and washed with acetone again, and then, was immersed 3 cm depth in each sample solution (50 cm³). After keeping for 24 h at 30°C, the change of color on an aluminum piece surface was checked by visual observation. The corrosion-inhibiting effect was

Table 2 Reaction Products of Various Alcohols with Some Acid Anhydrides, and Their Anti-corrosion Tests and Hard Water Tolerance.

Entry No.	Alcohols	Acid anhydride	Molar ratio	Anti-corrosion test of aluminum After 24 hr	Hard water tolerance After 24 hr
23	PTMG 650	SA	1 : 2	◎	◎
24	PBO 650	SA	1 : 2	○	◎
25	Oleyl alcohol # 700	SA	1 : 1	○	△
26	Oleyl alcohol # 900	SA	1 : 1	○	△
27	Ricinoleic acid	SA	1 : 1	◎	△
28	Ricinoleic acid dimer	SA	1 : 1	◎	△
29	Ricinoleic acid tetramer	SA	1 : 1	○	△
30	Ricinoleic acid hexamer	SA	1 : 1	△	△
31	PBO 650	PA	1 : 2	△	○
32	PBO 1000	PA	1 : 2	×	—
33	PTMG 650	PA	1 : 2	△	○
34	PTMG 1000	PA	1 : 1	××	×
35	PTMG 2000	PA	1 : 2	△	×
36	Oleyl alcohol #700	PA	1 : 1	△	×
37	Ricinoleic acid	PA	1 : 1	◎	×
38	Ricinoleic acid dimer	PA	1 : 1	○	△
39	PBO 650	HHPA	1 : 2	◎	—
40	PBO 1000	HHPA	1 : 1	×	—
41	EO 1000	HHPA	1 : 2	×	◎
42	EO 1500	HHPA	1 : 2	×	◎
43	PO-EO (1100)	HHPA	1 : 1	××	◎
44	PO (470)	HHPA	1 : 1	×	◎
45	PE-61	HHPA	1 : 1	××	◎
46	PO (1000)	HHPA	1 : 1	×	◎
47	BO-EO (1000)	HHPA	1 : 2	×	○
48	BO-EO (2000)	HHPA	1 : 2	×	◎
49	Oleyl alcohol #900	HHPA	1 : 1	○	×
50	Behenic alcohol	HHPA	1 : 1	○	×

Details of the procedure for anti-corrosion tests and hard water tolerance tests are shown in Experimental Section 2.3 and 2.4.

Entry No. 47: Weight ratio of BO/EO is 1/1.

evaluated according to the following indexing.

- ◎ No appearance of discoloration of aluminum surface
- A little discoloration of aluminum surface
- △ Gray
- × Dark gray
- ×× Black

This test is a convenient method for the practical applica-

tion in a factory.

2.4 Hard water tolerance test

2.4.1 Preparation of sample solution

A sample solution (100 g) was prepared by dissolving 0.50 g of test materials (Tables 1 and 2) and 5.0 g of tri-ethanolamine into CaCl₂ deionized water solution contain-

ing 100ppm Ca^{2+} ion (94.5 g). This solution corresponds to the 0.50% solution of the test materials. The pH of these test solutions was adjusted at 9.0 ± 0.2 by adding boric acid or sodium hydroxide solution.

2.4.2 Hard water tolerance test

The test solutions were maintained at 30°C. After 24 h, the presence of precipitates was observed with eyes. The effect of the additives on the hard water tolerance was evaluated according to the following indexing.

- ◎ No precipitates were observed.
- A little precipitates were observed.
- △ Semitransparent
- × Many sediments were observed.

This test is a convenient method for the practical use in a factory, and would be sufficient to check the hard water tolerance of the test solution, although more quantitative analysis of precipitate formation such as turbidimetry may be available.

3 RESULTS AND DISCUSSION

Aluminum materials are apt to become blackish due to the corrosion of their surfaces. It is well known that sodium metasilicate is effective as corrosion inhibitor of aluminum materials¹¹⁾. However, the long-term safe keeping of the fluids containing sodium metasilicate is difficult because of the precipitate formation of inorganic compounds. Various higher fatty acids are commonly used as a component of water-soluble cutting fluids. Higher fatty acids have also anti-corrosion property for aluminum, but they have the following fault, just like the case of metasilicate. When these fluids containing higher fatty acids are diluted with hard-water and used for long hours, precipitates such as calcium salts of fatty acids are apt to form in coolant tank. This kind of precipitate formation becomes a serious problem in the storage and usage of metal cutting fluids, even though their quality is improved by the use of appropriate additives. Thus, in the present work, we concerned with the preparation of new additives in cutting fluids for aluminum alloy materials, which have both an anti-corrosion property and a hard water tolerance, i.e., no precipitate formation.

The present authors have reported that the water-soluble metal working fluids containing half esters of dodecanedioic acid have excellent anti-corrosion properties for aluminum and iron⁸⁾. It may safely be said that calcium salts of lower carboxylic acids are soluble in water. The present research was performed based on the idea that the replacement of one or two hydroxyl group in higher alcohols with lower carboxylic acid such as maleic anhydride may improve both the anti-corrosion performance for aluminum alloy and the hard water tolerance. Thus, a variety of half esters and diesters were prepared by the reactions

of various hydroxyl compounds with some acid anhydrides. In addition, the evaluations of these esters as the additives for water-soluble metal working fluids of aluminum were performed.

The esters prepared in this work are listed in **Tables 1** and **2**. Anticorrosion performance for an aluminum alloy material was measured for each sample fluid containing various additives (0.5% w/w) as mentioned in Experimental Part. Sample fluids containing adducts, MA esters (Entry Nos. 2, 4, 8, 9, 19, 20, 21 and 22 in **Table 1**), SA esters (Nos. 23, 27 and 28 in **Table 2**), and other esters (Nos. 37 and 39 in **Table 2**) showed a good anti-corrosion property. In these cases, changes of color on aluminum test pieces were not recognized (**Tables 1** and **2**).

As for the hard water tolerance test in the presence of Ca^{2+} ion, sample fluids containing adducts, MA esters (Entry Nos. 2, 4, 8, 11, 12, 13, 14, 15 and 17 in **Table 1**) and other esters (Nos. 23, 24, 41, 42, 43, 44, 45, 46 and 48 in **Table 2**) showed good hard water tolerance. In these cases, no precipitates were recognized in their diluted solutions (**Tables 1** and **2**). Judging from the above results, it may be concluded that maleic acid diesters (IV) of PTMG 650 and PTMG 1000 (Nos. 2 and 4), MA diesters of PBO 650 (No. 8) and succinic acid diester of PTMG 650 (No. 23) enhance both of the anti-corrosion property for aluminum alloy materials and the hard water tolerance.

Industrial water-soluble metal working fluids were prepared by blending various additives as shown in **Tables 3**. The fluids containing 0.20 wt% diester (Entry No. 8 and 9 in **Table 3**) and 0.25 wt% diester (No. 2, 4 and 23 in **Table 4**) showed a good anti-corrosion property as well as a hard water tolerance.

4 CONCLUSION

The diesters of PTMG (650 and 1000) and PBO (650) with maleic anhydride and diester of PTMG (650) with succinic anhydride showed both anti-corrosion property for aluminum alloy materials and hard water tolerance.

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Table 3 The Anti-corrosion Tests of Aluminum and Hard Water Tolerance of Industrial Water-soluble Metal Working Fluids Containing PBO Diesters.

Constituents	Compositions of the samples 1 ~ 4, wt %			
	1	2	3	4
Monoisopropanolamine	0.3	0.3	0.3	0.3
Triethanolamine	2	2	2	2
Dodecanedioic acid	0.3	0.3	0.3	0.3
1, 2, 3 - Benzotriazole	0.01	0.01	0.01	0.01
PO - EO blockpolymer	2	2	2	2
Isononanoic acid	0.3	0.3	0.3	0.3
Nonanoic acid	0.2	0.2	0.2	0.2
PBO (650) + MA(1:2) Diester (Entry No.8)	0.1	0.2	0.5	
PBO (1000) + MA(1:2) Diester (Entry No.9)				0.2
Water	94.79	94.69	94.39	94.69
Anti-corrosion test for aluminum after 24 hr	◎	◎	◎	◎
Hard water tolerance after 24 hr	◎	◎	◎	○

The same results were obtained in all tests regardless of the quality of water, deionized water, city water, and deionized water containing 100 ppm Ca^{++} ion.

Table 4 The Anti-corrosion Tests of Aluminum and Hard Water Tolerance of Industrial Water-soluble Metal Working Fluids Containing PTMG Diesters.

Constituents	Compositions of the samples 1 ~ 3, wt %		
	1	2	3
N-Cyclohexyl-N,N-diethanolamine	0.5	0.5	0.5
Triisopropanolamine	0.5	0.5	0.5
<i>t</i> -Butylbenzoic acid	0.25	0.25	0.25
1,2,3-Benzotriazole	0.01	0.01	0.01
1,3-Bis(aminomethyl)cyclohexene	0.1	0.1	0.1
NPG	0.5	0.5	0.5
BO - EO copolymer	1.0	1.0	1.0
PO polymer	1.5	1.5	1.5
PTMG 650 + MA (1:2) Diester (Entry No. 2)	0.25		
PTMG 1000 + MA (1:2) Diester (Entry No. 4)		0.25	
PTMG 1000 + SA (1:2) Diester (Entry No. 23)			0.25
Water	95.39	95.39	95.39
Anti-corrosion test of aluminum after 24 hr	◎	◎	◎
Hard water tolerance after 24 hr	◎	◎	◎

The same results were obtained in all tests regardless of the quality of water, deionized water, city water, and deionized water containing 100 ppm Ca^{++} ion.

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