New Water-soluble Metal Working Fluids Additives from Phosphonic Acid Derivatives for Aluminum Alloy Materials

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Abstract: Water-soluble metal working fluids are used for processing of aluminum alloy materials. This short paper describes properties of new additives for water-soluble cutting fluids for aluminum alloy materials. Some alkylphosphonic acids were prepared with known method. Amine salts of these phosphonic acids showed anti-corrosion property for aluminum alloy materials. However, they have no hard water tolerance. Monoesters of octylphosphonic acid were prepared by the reaction of octylphosphonic acid dichloride with various alcohols in the presence of triethylamine. Amine salts of monoester of octylphosphonic acid with diethylene glycol monomethyl ether, ethylene glycol monomethyl ether and triethylene glycol monomethyl ether showed both of a good anti-corrosion property for aluminum alloy materials and hard water tolerance.

Key words: water-soluble metal working fluids additives, aluminum alloy material, diphosphonic acid, octylphosphonic acid monoester, anti-corrosion, hard water tolerance

1 INTRODUCTION

Various water-soluble metal working fluids are widely used for the mechanical processing of aluminum alloy materials similarly to the case of iron materials. Aluminum materials are apt to be blackish, owing to corrosion of aluminum surface. It is known that sodium metasilicate is effective as corrosion inhibitor for aluminum materials. When these fluids containing sodium metasilicate are diluted with hard water and used for long periods, precipitates owing to calcium ion in hard water and to heavy metals in aluminum materials are apt to form in coolant tank. Many attempts to prepare high performance additives for aluminum alloy materials have recently been made, and a lot of patents are known. For example, organic phosphonic esters and organic phosphoric esters, a mixture of castor oil of phosphoric esters, esters of acid anhydrides with higher alcohols and many others are released.

Usually commercial water soluble cutting fluids consist of many components, and the detailed compositions and performance of the commercial products have not been opened. It is recently thought that alkyl phosphonic acids are used for water-soluble metal working fluids. In this short article the authors describe preparations of some phosphonic acid derivatives and their properties as an aluminum corrosion inhibitor with a good hard water tolerance.

2 EXPERIMENTAL

2.1 Materials

Octylphosphonic acid (compound V in Scheme 4) was supplied by Rohdia Co. Ltd. Triethylphosphite was supplied from Toho Chemical Industrial Co. Ltd. All other reagents were obtained from Tokyo Kasei Co. Ltd.

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2.2 Preparation of octane-1,8-diphosphonic acid (compound II in Scheme 1)

A mixture of 1,8-dibromo-octane (28.5 g, 0.105 mol) and triethylphosphite (51.5 g, 0.310 mol) was refluxed for 8.5 h. The reaction mixture was kept at 100°C under 10 mmHg to remove completely low boiling fractions (bp 45 - 80°C / 10 mmHg). The residue was nearly pure tetrabutyl-octane-1,8-diphosphonate (I) (22.5 g). A mixture of 25.0 g of compound (I), 50 g of conc. HCl and 80 g of water was refluxed for 8 h. After leaving overnight, most of water was removed to give solidified product (Scheme 1).

This product was dissolved in diethyl ether. The ether solution was washed with saturated NaCl aq. solution two times and dried over anhydrous sodium sulfate. The ether was evaporated to give 25 g of octane-1,8-diphosphonic acid (II). It showed the following spectral data and melting point:

IR (cm\(^{-1}\)): 2932, 2852, 2304, 1466, 1275, 1151
NMR (\(d\), ppm): 1.25 (m, 8H, -CH\(_2-\)(a)), 1.42 (m, 4H, -CH\(_2-\)(b)), 1.62 (m, 4H, -CH\(_2-\)(c)), 7.25 (broad s, 4H, -OH)
mp: 164 – 165°C

Decane-1,10-diphosphonic acid (III) and dodecane-1,12-diphosphonic acid (IV) were prepared in the similar way.

2.3 Preparation of octylphosphonic acid dichloride (compound VI in Scheme 4)

Thionyl chloride (71.4 g, 0.6 mol) was added to octylphosphonic acid (compound V in Scheme 4) (38.8 g, 0.2 mol) at 50°C, and the mixture was refluxed for 13 h and left overnight. Excess thionyl chloride was completely removed under reduced pressure. The residue (47.0 g) was nearly pure octylphosphonic acid dichloride (VI) as indicated by the following spectral data:

IR (cm\(^{-1}\)): 1174, 1016, 929
NMR (\(\delta\)): 0.88 (3H, t, CH\(_3-\)(a)), 1.28 (8H, m, -CH\(_2-\)(b)), 1.45 (2H, m, -CH\(_2-\)(c)), 1.82 (2H, m, -CH\(_2-\)(d)), 2.56 (2H, m, -CH\(_2-\)(e))

2.4 Reaction of octylphosphonic acid dichloride (VI) with diethyleneglycol monomethyl ether

A tetrahydrofuran (THF) solution (30 cc) of octylphosphonic acid dichloride (VI) (11.55 g, 0.05 mol) was added to a mixture of diethyleneglycol monomethyl ether (6.01 g, 0.05 mol), triethylamine (6.06 g, 0.06 mol) and THF (10 cc) at 50°C. After 3 h agitation, the mixture was hydrolyzed with 1N HCl aqueous solution and extracted with diethyl ether. The ether extract was washed with saturated NaCl aq. solution three times and dried over anhydrous sodium sulfate. The ether was evaporated to give a waxy monoester (VII) (10.36 g, yield 70.0%) (Scheme 4). This material was used as a sample for water-soluble cutting fluid additive without refining.

The waxy material (0.5 g) was chromatographed by short path column packed with silica gel using ethylacetate as a solvent to give 0.3 g of the purified material. This substance was assumed to be the compound VII from the following data:

IR (cm\(^{-1}\)): 3,000 (broad), 2,285, 1,100, 986
NMR (\(\delta\)): 0.99 (3H, t, CH\(_3-\)(a)), 1.25 (10H, m, -CH\(_2-\)(b)), 1.65 (2H, m, -CH\(_2-\)(c)), 1.75 (2H, m, -CH\(_2-\)(d)), 3.4 (3H, s, -OCH\(_3\))(g), 3.7 (6H, m, -CH\(_2-\)(e)), 4.2 (2H, m, -CH\(_2-\)(f))

Compounds (VIII), (IX), (X), (XI) and (XII) were obtained from the reaction of octylphosphonic acid dichloride (VI) with ethyleneglycol monomethyl ether, triethylene glycol monomethyl ether, polyethylene glycol monomethyl ether (n = 4-6), glycerin and octyl alcohol, respectively. Compounds (VIII), (IX), (X) and (XII) were also characterized by NMR, IR and other indices. However, the structure of compound (XI) could not be confirmed.

2.5 Anti-corrosion test of aluminum alloy materials

Preparation of sample solution: A solution (100 g) was prepared by dissolving 0.50 g of test material and 0.5 g of diethanolamine in deionized water (99.0 g). This solution corresponds to 0.50% solution. The pHs of these test solu-
Phosphonic acid derivatives for cutting fluids additives

Preparation of sample solution: A sample solution (100 g) was prepared by dissolving 0.50 g of test materials and 0.50 g of diethanolamine in aqueous CaCl₂ solution containing 100 ppm Ca²⁺ ion (99.0 g). This solution corresponds to 0.50% solution of the test materials. The pHs of these test solutions were adjusted at 9.0 ± 0.2 by adding acetic acid or NaOH solutions.

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

- No precipitates were observed
- A little precipitates were observed
- Precipitates were observed

This test method is a convenient method for the practical use in factory, and is the modified way of the Ca²⁺ stability test⁶ and other tests⁷-⁸.

2.7 Evaluations of practical water-soluble metal working fluids

Practical undiluted water-soluble metal working fluids were prepared by blending various additives as shown in Table 2. These fluids were diluted twenty folds with aqueous CaCl₂ solution containing 100 ppm Ca²⁺ ion, and the diluted solutions were used for anti-corrosion tests and hard water tolerance tests.

3 RESULTS AND DISCUSSION

In this short paper the authors describe the evaluations of some alkylphosphonic acid derivatives as the additives for an aluminum alloy materials corrosion inhibitor. Alkyldiphosphonic acids were prepared as follows.

Fig. 1 Photographs of Aluminum Pieces.

The indexing is ⊠, ○, △ and × from left to right.

× Dark gray

The photographs corresponding to the indexing are shown in Figure 1. This test is a convenient method for the practical application in a factory.

2.6 Hard water tolerance test

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3 RESULTS AND DISCUSSION

In this short paper the authors describe the evaluations of some alkylphosphonic acid derivatives as the additives for an aluminum alloy materials corrosion inhibitor. Alkyldiphosphonic acids were prepared as follows.
Tetraethyl octane-1,8-diphosphonate (I) was obtained by the thermal reaction of octyl dibromide with triethylphosphite. The hydrolysis of (I) with hydrochloric acid gave octane-1,8-diphosphonic acid (II) as shown in Scheme 1. Decane-1,10-diphosphonic acid (III) and dodecane-1,12-diphosphonic acid (IV) were prepared in the usual way9).

Table 1  Characteristics of Alkylphosphonic Acids and Their Esters for Aluminum Alloy Materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration %</th>
<th>Anti-corrosion tests for aluminum pH 9.0</th>
<th>Hard water tolerance pH 9.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank (diethanolamine solution)</td>
<td>—</td>
<td>×</td>
<td>○</td>
</tr>
<tr>
<td>Hexylphosphonic acid</td>
<td>0.50</td>
<td>×</td>
<td>○</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>×</td>
<td>○</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>×</td>
<td>○</td>
</tr>
<tr>
<td>Octylphosphonic acid (V)</td>
<td>0.50</td>
<td>☉</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td>Octane-1,8-diphosphonic acid (II)</td>
<td>0.50</td>
<td>☉</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td>Decane-1,10-diphosphonic acid (III)</td>
<td>0.50</td>
<td>☉</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td>Dodecane-1,12-diphosphonic acid (IV)</td>
<td>0.50</td>
<td>☉</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td>Ester of octylphosphonic acid (V) with ethyleneglycol monomethyl ether (VIII)</td>
<td>0.50</td>
<td>☉</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td>Ester of (V) with diethyleneglycol monomethyl ether (VII)</td>
<td>0.50</td>
<td>☉</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td>Ester of (V) with triethyleneglycol monomethyl ether (IX)</td>
<td>0.50</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td>Ester of (V) with polyethyleneglycol monomethyl ether (X)</td>
<td>0.50</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>☉</td>
<td>◇</td>
</tr>
<tr>
<td>Ester of (V) with glycerin (XI)</td>
<td>0.50</td>
<td>☉</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>☉</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>☉</td>
<td>×</td>
</tr>
<tr>
<td>Ester of (V) with octanol (XII)</td>
<td>0.50</td>
<td>☉</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>☉</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>☉</td>
<td>×</td>
</tr>
</tbody>
</table>

The same results were obtained in all anti-corrosion tests regardless of the quality of water, deionized water, city water (hardness of 30) or aqueous solution containing 100 ppm Ca$^{2+}$ ion.
Phosphonic acid derivatives for cutting fluids additives

Anti-corrosion performance for aluminum alloy materials was measured for each sample fluid containing various additives (0.50, 0.15, 0.05% w/w) as mentioned in Experimental Part. Diethanolamine salts of the above mentioned diphosphonic acids (II, III and IV) showed good anti-corrosion property for aluminum alloy material. The results are shown in Table 1. However, when these additives were diluted with hard water containing Ca\(^{2+}\) (100 ppm), much precipitates were recognized. That is, they have no hard water tolerance.

It is thought that introduction of hydrophilic group into phosphonic acid molecule increase the solubility in water. This research was performed based on the idea that the replacement of one acid group in phosphonic acid with lower alcohols may improve hard water tolerance. Some mono esters of octylphosphonic acid (V) were prepared from the reactions of some lower alcohols with octylphosphonic acid dichloride (VI) (Scheme 4). Octylphosphonic

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Compositions of the samples (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>7.5</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>15</td>
</tr>
<tr>
<td>Dicyclohexylamine</td>
<td>4</td>
</tr>
<tr>
<td>Nonanoic acid</td>
<td>13</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>0.5</td>
</tr>
<tr>
<td>EO-PO Block Copolymer</td>
<td>20</td>
</tr>
<tr>
<td>Cationic Polymeric Coagulator</td>
<td>1</td>
</tr>
<tr>
<td>Compound (VIII)</td>
<td>1.5</td>
</tr>
<tr>
<td>Compound (VII)</td>
<td>—</td>
</tr>
<tr>
<td>Compound (IX)</td>
<td>—</td>
</tr>
<tr>
<td>Compound (X)</td>
<td>—</td>
</tr>
<tr>
<td>Compound (XI)</td>
<td>—</td>
</tr>
<tr>
<td>Compound (XII)</td>
<td>—</td>
</tr>
<tr>
<td>Octylphosphonic acid (V)</td>
<td>—</td>
</tr>
<tr>
<td>Water</td>
<td>37.5</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 3 Properties of Samples 1 — 7 Shown in Table 2.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphonic acid derivatives</td>
<td>VIII</td>
<td>VII</td>
<td>IX</td>
<td>X</td>
<td>XI</td>
<td>XII</td>
<td>V</td>
</tr>
<tr>
<td>pH of 20 folds diluted solutions</td>
<td>9.4</td>
<td>9.4</td>
<td>9.5</td>
<td>9.5</td>
<td>9.4</td>
<td>9.5</td>
<td>9.2</td>
</tr>
<tr>
<td>Anti-corrosion property for aluminum</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
</tr>
<tr>
<td>Hard water tolerance</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
</tr>
</tbody>
</table>

The same results were obtained in all anti-corrosion tests regardless of the quality of water, deionized water, city water (hardness of 30) or aqueous solution containing 100 ppm Ca\(^{2+}\) ion.

acid dichloride (VI) was obtained from the reaction of octylphosphonic acid (V) with thionyl chloride\(^\text{10}\). The desired monoester (VII) was prepared by the popular reaction of dichloride (VI) with diethylene glycol monomethyl ether in the presence of triethylamine\(^\text{11}\). Using this procedure, some monoesters (VIII - XII) could be obtained from ethylene glycol monomethyl ether, triethylene glycol monomethyl ether, polyethylene glycol monomethyl ether, glycerin and octyl alcohol in the similar way (Scheme 4). Aqueous solution of diethanolamine salts with (VII) showed superior anti-corrosion property for aluminum even at such low concentrations as 0.15 - 0.50\%. Diethanolamine salts of compounds (IX), (X), (XI) and (XII) showed good anti-corrosion property for aluminum at 0.50\% concentration. Hard water tolerance against aqueous solution containing Ca\(^{2+}\) ion was performed as shown in Experimental Part. Sample fluid containing ester (VII) showed good hard water tolerance. When diethanolamine salt of compound (VII) was diluted with water containing 100 ppm Ca\(^{2+}\) ion and left for 24 h, no precipitates were observed (Table 1). Compounds (IX) and (X) showed good hard water tolerance for aluminum.

Some practical undiluted cutting fluids were prepared as shown in Table 2. These fluids were diluted twenty folds with water containing 100 ppm Ca\(^{2+}\) ion. Anti-corrosion ability for aluminum and hard water tolerance were estimated, and the results are shown in Table 3. Cutting fluids containing compound (VII) showed both good anti-corrosion property and good hard water tolerance. The fluids containing compounds (VIII) and (IX) showed fairly good properties.

4 CONCLUSION

These results appear to indicate that octylphosphonic acid diethylene glycol monomethyl ether monoester (VII) has both anti-corrosion property for aluminum alloy material and hard water tolerance.

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References