New Water-soluble Cutting Fluids Additives Derived from the Thermal Reaction Products of Unsaturated Fatty Acids with Acrylic Acid and Maleic Anhydride

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(Received October 20, 2003 ; Accepted December 1, 2003)

Abstract : Water-soluble cutting fluids are used for processing of aluminium materials. This short article describes properties of new additives of water-soluble cutting fluids for aluminium materials. Various Diels-Alder adducts of unsaturated fatty acids with acrylic acid of maleic anhydride were prepared by thermal reactions. Triethanolamine salts of Diels-Alder adducts of dehydrated castor oil fatty acids with acrylic acid or maleic anhydride showed excellent anti-corrosion property of aluminium materals. These thermal adducts showed anti-rust property for cast-iron chips, too.

keywords : water-soluble cutting fluid, additives, aluminium materal, dehydrated castor oil fatty acid, acrylic acid.

1. Introduction

It is well known that the thermal reactions of conjugated unsaturated fatty acids with acrylic acid[1] of maleic anhydride[2] give their corresponding cyclic compounds that are called as Diels-Alder adducts. These adducts are widely used as raw materials for synthetic drying oil, water-soluble paints, metal-working oil and others[3]. However, it is not known to use those adducts for water-soluble cutting fluids against aluminium and iron materials. The present author reported that some half esters of dodecanedioc acid have anti-corrosion property for aluminium materials[4]. In this short article the author describes the evaluations of some Diels-Alder adducts of conjugated fatty acids for the additives of water-soluble cutting fluids as an aluminium corrosion inhibitor.

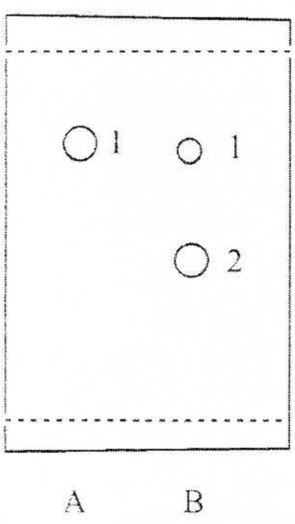
2. Experimental

2.1. Materials

Dehydrated castor oil fatty acid was supplied from Harima Kasei Co. Ltd. (Japan). Linoleic acid was supplied from Nihon Yushi Co. Ltd. (Japan). Other reagents were supplied from Tokyo Kasei Co. Ltd. (Japan).

2.2. Reaction of Dehydrated Cator Oil Fatty Acid (I) with Acrylic Acid (II)

A mixture of 28.0g (0.1 mol) of (I), 7.2 g (0.1 mol) of acrylic acid (II) and 5 mg of anhydrous aluminium chloride as a catalyst was stirred for 6 hr at a temperature of 140 ℃ to give 33.0 g of oily material. Unreacted (II) was removed by vacuum distillation to give a crude product (31.5 g). This product was used as it was in the water soluble cutting fluids tests. The thin layer chromatogram of this product is shown as Fig. 1. Part (1 g) of the product was chromatographed with a short-column packed with silica gel using a mixture of *n*-hexane and ethyl acetate (80:20 v/v) as a solvent to obtain a pale yellow oil (0.1 g) corresponding to spot 1 on Fig. 1 and a pale yellow viscous oil (0.4 g) corresponding to spot 2 on Fig. 1. Spot 1 was a mixture of various fatty acids. Spot 2 was determined to be the Diels-Alder adducts (III) from the following characterization. IR(cm^{-1}): 3100 (-COOH), 1706 (>C=O), 725 (cis-double bond). NMR (δ, ppm) : 0.90 (CH_3, s, 3H), 1.25 ($-CH_2-$, 22H), 1.6 (ring $-CH_2-$, 2H), 2.0 (-CH-C=C-, 2H), 2.4 (CH_2CO-, -CH-CO-, 3H), 5.7 and 5.3 (-CH=CH-, 2H), 11.0 (-COOH, 2H, broad s). ^{13}C NMR (δ, ppm): 18 (CH_3-), 34, 38 nad 44 (-CH-, 3C), 129 and 132 (-C=C-), 180 and 185 (-COOH).



A : Conjugated fatty acid (I)
B : Raw products
Solvent: *n*-hexane ethyl actate 80:20 v/v

Fig. 1. Thin layer chromatogram of the Diels-Alder adduct (III).

The reaction of linoleic acid with acrylic acid was performed in the similar fashion.

2.3. Reaction of Dehydrated Castor Oil Fatty Acid (I) with Maleic Anhydride

A mixture of 28.0 g (0.1 mol) of (I), 9.8 g (0.1 mol) of maleic anhydride and 5 mg of anhydrous aluminium chloride was heated at 190℃ with agitation. It was treated as the case of the reaction of (I) with (II) to give 36.5 g of the thermal reaction product. This product was used as a sample for water-soluable cutting fluid without refining. One gram of this sample was purified with a short path chromatography column on silica gel using *n*-hexane-diethylether (80:20 v/v) as an elution solvent. The main eluate (0.6 g) showed the following TLC spots as shown in Fig. 2. Spot 3 on Fig. 2 was unreacted maleic anhydride. Spot 1 was a mixture of various unsaturated fatty acids. Spot 2 was suspected to be the Diels-Alder adduct from the IR spectrum. IR (cm^{-1}): 3,100 (-COOH), 1857 and 1779 (>CO in ring), 1710 (>CO of carboxylic acid).

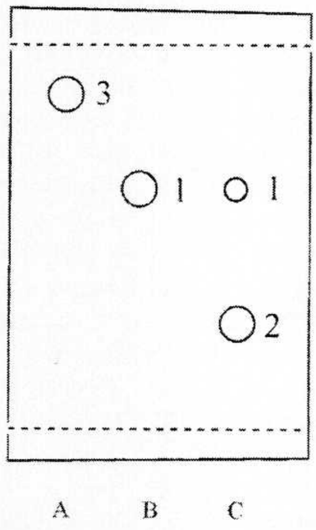
2.4. Preparation of Sample Solution

A test solution (100 g) was prepared by dissolving 1 g of specimen material and 3 g of triethanolamine into water (96 g). The followiong experiments were undertaken with the test solution. City water (Shigaken, Japan) was used for all tests.

2.5. Method for Corrosion Test with Aluminium Pieces

To the each sample solution, half of the test piece of aluminium alloy (ADC-12)[5], which had been washed with acetone, polished with emery paper (# 240) and washed with acetone again, was immersed. After 24hr, change of color on an aluminium piece surface was observed with the naked eye, The corrosion-inhibition effect was evaluated according to the following 6-grade indexing.

- ◎: No appearance of discoloration of aluminium surface
- ○○: A little discoloration of boundary line between solution and air
- ○: A little discoloration of aluminium surface
- △: Gray
- ×: Dark gray
- ××: Black



A : Maleic anhydride
B : Conjugated fatty acid (I)
C : Raw products
Solvent : n-hexane diethylether 80:20 v/v

Fig. 2. Thin layer chromatogram of the Diels-Alder adduct of (I) with maleic anhydride.

2.6. Corrosion Test with Cast-Iron Chips[6]

Cast-iron chips (5 g) (FC-200; NEOS Central Research Laboratory, Shiga-ken, Japan)[7] that had been washed with benzene were immersed in the sample solution of 10 ml of cutting fluid in a watch glass. The container was covered. After 10 min, the solution was removed by titling the watch glass. The rust preventive effect was evaluated after 72 hr according to the following 2-grade indexing.

- ○: No appearance of rust
- ×: Appearance of rust

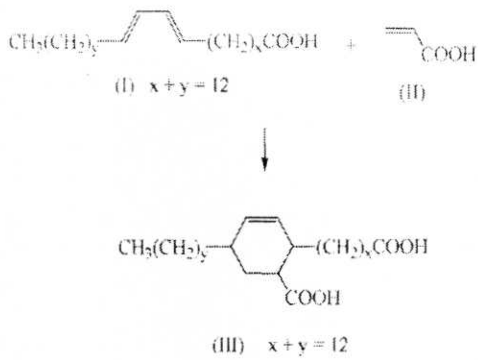
3. Results and Discussion

Water-soluble cutting fluids are applied for processing of aluminium materials. The surfaces of aluminium materials are apt to be blackish, owing to corrosion of aluminium surface. It is well known that sodium metasilicate is effective as a corrosion inhibitor for aluminium material[3]. However, its solubility to water is very poor. Many attempts to prepare high performance additives for aluminium materials are reported[4].

It is known that oleic acid, ricinoleic acid and dehydrated castor oil fatty acids (I) have a considerable anti-corrosion property for aluminium material. This research was made based on the idea that the substitution of bulky group by long chain unsaturated fatty acid may improve the cutting and anti-corrosion performace for aluminium material. In this short article the author describes the evaluations of some thermal product of unsaturated fatty acids with acrylic acid and maleic anhydride for the additives as an aluminium corrosion inhibitor.

A mixture of (I) with acrylic acid (II) in the presence of anhydrous aluminium chloride was heated at 140℃ to give a Diels-Alder adduct (III) with various by-products (Scheme 1). The crude product was refined with column chromatography to give compound (III). The product was suspected to be the corresponding Diels-Alder adduct. Similarly, other Diels-Alder products were prepared from the reaction of (I) with some dienophiles. From the thermal reactions of linoleic acid with acrylic acid, a mixture of (III)-like product and various isomers of linoleic acid was obtained. It was proposed that linoleic acid isomerized to conjugated linoleic acid, followed by thermal adduct had been produced.

Triethnolamine salt of compound (III) showed good anti-corrsion properties for aluminium as shown in Table 1. The thermal adduct of (I) with maleic anhydride and that of linoleic acid with acrylic acid or maleic anhydride exhibited superior anti-corrosion



Scheme 1. Reaction of dehydrated castor oil fatty acid (I) with acrylic acid (II).

Table 1. Anti-Corrosion Test of Thermal Reaction Products for Aluminium and Iron

Thermal Reaction: Unsaturated fatty acid	Thermal Reaction: Dienophiles	Anti-corrosion test for iron chips[*1] after 72 hr[*2]				Anti-corrosion test for aluminium materials[*3] after 24hr
		×1	×2	×3	×4	×1
Dehydrated castor oil fatty acid	Maleic anhydride	○	○	×	×	◎
Dehydrated castor oil fatty acid	Acrylic acid	○	×	×	×	◎
Dehydrated castor oil fatty acid	Methyl acrylate	○	○	×	×	○○
Dehydrated castor	Methacrylic acid	○	×	×	×	○
Linoleic acid	Maleic anhydride	○	×	×	×	◎
Linoleic acid	Acrylic acid	○	×	×	×	◎
Linoleic acid	Methyl acrylate	○	○	×	×	○○
Linoleic acid	Methacrylic acid	○	×	×	×	○
Dehydrated castor oil fatty acid	-	○	×	×	×	○
Linoleic acid	-	○	×	×	×	○
Dodecanedioic acid	-	○	○	○	○	×

*1 Aqueous solution of an adduct (1 g), triethanolamine (3 g) and water (96 g) was used as the test solution. This solution is shown as symbol ×1. two folds diluted solution, three folds dilutes solution and four folds diluted solution of the solution ×1 are shown as symbol ×2, ×3 and ×4, respectively.

*2 Evaluation of rust inhibition test: ○ No appearance of rust, ×Appearance of rust

*3 Evaluation of anti-corrosion test: ◎ No discoloration, ○○ A little discoloration of boundary line between solution and air, ○ A little discoloration of aluminium surface, △ Gray, × Dark gray, ×× Blacky behavior for aluminium, respectively. Interestingly, the anti-corrosion properties of these thermal adducts were better than those of (I) and linoleic acid. These thermal adducts showed anti-rust property for iron chips, too as shown in Table 1. These results appear to indicate that the presence of the bulky alkyl group in higher unsaturated fatty acid molecule enhances their anti-corrosion property for aluminium material.

4. Conclusion

The thermal adducts of dehydrated castor oil fatty acid with acrylic acid or maleic anhydride showed excellent anti-corrosion property for aluminium. It may be suspected that the presence of the bulky alkyl group in higher unsaturated fatty acid molecule enhances their anti-corrosion property for aluminium material.

Acknowledgement

This research was performed in the laboratory of NEOS Center Research (Kosei-cho, Shiga-ken, Japan). The author is thankful to Dr. Yoneshima and Dr. Tomoda of NEOS Co. Ltd. for their helpful supports.

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