NOTE

New Adamantane Derivatives as Water-Soluble Cutting Fluids

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Abstract : A number of adducts were prepared from the reaction of adamantanecarbonyl chloride (I) with aminoalcohols or aminoacids, and screened for anti-rust properties and antimicrobial activity in spent fluids of water-based cutting fluids. Aqueous solutions of *N*-(1-admantanecarbonyl)-*O*-(1-admantanecarbonyl) mono-ethanolamine (III) showed good antirust and antimicrobial properties for water-based cutting fluids.

Key words : adamantane derivatives, water-soluble cutting fluids, antirust properties

1 Introduction

A variety of cutting fluids are used for various machining operations. These fluids may be classified into two main types, mineral oil-based and water-miscible (which includes oil-water emulsions). Mineral oil-based fluids are especially suitable for heavy duty and special service operations where good lubrication is essential. In other, less severe operations, there has been a recent trend toward water-based fluids. These offer the advantages of low toxicity and excellent cooling capacity, and also overcome the problems associated with mineral oil-based products such as unpleasant odour, oil mist formation and fumes at high temperatures. However, for water-based cutting fluids to offer a practical alternative, they must possess good rust inhibiting, antiwear and antimicrobial activity. The authors previously reported that various derivatives of fatty acids have excellent rust inhibition properties for water-soluble fluids¹⁾. In this short paper, new additives for water-soluble cutting fluids are described.

2 Results and Discussion

It is known that many adamantane derivatives have industrial applications. For example, adamantane derivatives with biological activity²⁾, ester derivatives as synthetic lubricants^{3)~5)}, bromoadamantane as an anti-wear additive for lubricating oils⁶⁾ and the use of hydroxyphenyladamantane derivatives as antioxidants⁷⁾ have all been reported. Various ethanolamines and their derivatives have been used as antimicrobial agents and corrosion inhibitors^{8)~10)}. It was therefore anticipated that adamantane derivatives could be used as additives for water-soluble cutting fluids. In this short paper, we prepared a variety of derivatives from adamantanecarbonyl chloride and various compounds containing amino group.

To monoethanolamine (II) (1 equivalent) in a mixture of pyridine and tetrahydrofuran, adamantanecarbonyl chloride (I)(2 equivalents) in tetrahydrofuran was added dropwise. The reaction mixture was treated as usual to give a 65% yield of *N*-(1-admantanecarbonyl)-*O*-(1-admantanecarbonyl)-monoethanolamine (III). The structure was deduced from the

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spectral data shown in the Experimental Section.

Interestingly, it was found that compound (III) is fairly soluble in water (about 3~5%). An aqueous solution of a mixture of compound (III) (1%) and triethanolamine (2%) showed excellent properties in a corrosion test with cast iron chips¹¹). The test was performed as described in the Experimental Section. The weld load of the aqueous solution was about 20 kg/cm² at 200 rpm with Soda-type four ball lubricating oil testing machine¹²). The weld load should have as high a value as possible, the desirable value being more than 10 kgf cm⁻². Adducts of compound (I) with some amino acids were similarly prepared. Only *N*-(1-adamantanecarbonyl)-leucine (IV) showed excellent properties in a corrosion test with cast iron chips as shown in Table 1. Reaction of adamantaneacetyl chloride with alkanolamines and amino acids were similarly prepared. Compound (V) showed good antirust properties as shown in Table 1.

Water-soluble cutting fluids are easily degraded by various microorganisms^{8),13}). In this study, the authors examined the antimicrobial properties of compound (III) in water-based cutting fluids. After incubating them at 30°C, the bacterial contents of the sample solution were observed. It was concluded that compound (III) showed a fair antimicrobial activity in a spent fluid equal to that of a commercially available antimicrobial agent (see Table). Similarly, other derivatives from the reaction of 1-adamantanecarbonyl chloride (I) with alkanolamines have excellent properties; their characteristic properties are listed in the Table. These new additives for water-based cutting fluids were not previously known.

3 Experimental

3.1 Reaction of adamantaneacetyl chloride (I) with monoethanolamine (II)

To monoethanolamine (II) (0.61 g, 0.01 mol) in a mixture of pyridine (2 mL) and tetrahydrofuran (18 mL), adamantaneacetyl chloride (I) (3.98 g, 0.02 mol) in tetrahydrofuran (10 mL) was added dropwise. The reaction mixture was agitated for 2 h, neutralised by dilute hydrochloric acid and extracted with diethylether. The ether extract was evaporated to give a 65% yield of *N*-(1-adamantanecarbonyl)-O-(1-adamantanecarbonyl)-monoethanolamine (III) (2.51 g) which, after recrystallisation from acetone, had mp 152~153°C. The structure was indicated by spectral evidence as follows; IR (cm⁻¹): 3290, 1710; NMR (δ , ppm) (CDCl₃): 1.90 (30H, m, ring protons), 3.50 and 4.15 (2H and 2H, each triplet, $-\text{CH}_2-$

Table 1 Properties of Cutting Fluids Containing Various Adducts of Adamantane Carbonyl Chloride and Adamantaneacetyl chloride with Alkanolamines and Amino Acids.

Products	pH	Rust inhibition test duration (h)			Friction coefficient	Surface tension dyn·cm ⁻¹	Weld load kgf·cm ⁻²	Antimicrobial properties		
		24	48	72				1	2	3
		(d)								
Products with adamantanecarbonyl chloride (I)										
H ₂ NCH ₂ CH ₂ OH	9.1	10	10	10	0.21	43	20	—	—	+
H ₂ N(CH ₂) ₃ OH	8.5	10	10	10	0.21	39	18.0	—	+	++
HN(CH ₂ CH ₂ OH) ₂	9.1	10	10	10	0.21	45	18.5	—	++	+++
Aspartic acid	8.1	8	8	7	0.12	59	17.5	++	++	++
Glutamic acid	8.2	8	8	7	0.13	61	19.5	+++	+++	+++
Lysine	8.9	8	7	7	0.17	47	20.0	+++	+++	+++
Leucine	8.4	10	10	10	0.12	52	14.5	++	++	++
Products with adamantaneacetyl chloride										
H ₂ NCH ₂ CH ₂ OH	8.7	8	7	6	0.13	50	16.5	+++	+++	+++
HN(CH ₂ CH ₂ OH) ₂	8.5	8	7	7	0.16	46	20.0	+++	+++	+++
Glutamic acid	8.0	10	10	10	0.15	45	15.0	+++	+++	+++
Leucine	8.0	10	10	10	0.15	42	16.0	+++	+++	+++
Triethanolamine (2% aq. soln.)	10.3	7	6	5	0.21	70	8.5	++	+++	+++
Triazine type antimicrobial agent (1% aq. soln.)								—	—	—
(0.5% aq. soln.)								—	—	+
(0.1% aq. soln.)								+++	+++	+++

Aqueous solutions of adduct (1 g), triethanolamine (2 g) and water (100 g) were used as the test solutions. The same results were obtained in the tests using either distilled water (hardness is 0) or city water (hardness about 80) in Chiba, Japan.

and -CH₂-), 5.88 (1H, broad s, -NHCO); MS (*m/e*) FAB method, (MH)⁺ 386.2693, theoretical value 386.2695 (C₂₄H₃₅NO₃).

The product of 1-hydroxy-3-propylamine with (I) was prepared and the structure determined as *N*-(1-adamantanecarbonyl)-*O*-(1-adamantanecarbonyl)-*n*-propanolamine. It showed the following spectral properties; IR (cm⁻¹), 3285, 1710; NMR (δ , ppm) (CDCl₃): 1.90 (30H, m, ring protons), 2.70 (2H, m, -CH₂-), 3.45 and 4.00 (2H and 2H, each triplet, -CH₂- and -CH₂-), 5.80 (1H, broad s, -NHCO); MS (*m/e*): M⁺ 399, theoretical 399 (C₂₅H₃₇NO₃).

The product of (I) with diethanolamine was similarly prepared and it is thought that the structure is that of the diadamantanoyl diester. It showed the following spectral data, IR (cm⁻¹); 3295, 1710; NMR (δ , ppm) (CDCl₃): 1.90 (30H, m, ring protons), 2.90 (4H, t, -CH₂-NH), 4.20 (4H, t, -CH₂O-), 6.30 (1H, broad s, NH).

Other products were prepared in the similar manner.

3.2 Testing methods

3.2.1 Test method for corrosion resistance

Various test methods are known, and the authors have used the corrosion test with cast-iron chips as shown in reference No. 11. An aqueous solution of a mixture of compound (III) (1%) and triethanolamine (2%) was used for the following test. Cast-iron chips (JIS G 5501, FC-20) (2 g), which had been washed with benzene, were immersed in an aqueous solution (5 mL) of cutting fluids in a watch glass. 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

observed after 24 h, 48 h and 72 h. Ten points shows no appearance of rust. Seven points show a slight appearance of rust. This method is based on the I.P. Corrosion Test 125/63 T¹¹⁾.

3.2.2 Friction coefficient

The friction coefficient was measured at 25°C by a pendulum-type oiliness and friction tester (Shinko Engineering, Tokyo)¹⁴⁾.

3.2.3 Welding loads

The welding loads (kgf cm⁻²) were measured on a Soda-type four ball lubricating oil testing machine at 200 rpm. The machine was obtained from Shinko Engineering, Tokyo¹²⁾.

3.2.4 Surface tension

The surface tension (dyn·cm⁻¹) was measured at 25°C using a Dū Noüy tensiometer.

3.2.5 Microbial activity tests

Agar (20 mL) was placed in a sharle having a diameter of 90 mm, and solidified. A one μ L drop bacterial culture was dropped on to the center of the agar and spread uniformly with a sterile, bent glass rod, and dried for 10 min at room temperature. On the center of the agar inoculated with this culture, 1 mL of the sample solution of the new cutting fluids was dropped, and the agar was kept at 30°C. After 1, 2 and 3 d, the degree of increase of bacteria was observed. The assessment was as follows, “-” indicates no bacterial growth, “+” very little bacterial increase, “++” is little bacterial increase, “+++” large bacterial increase. This method is modified from literature methods^{15), 16)}. The above mentioned bacterial culture was prepared as follows; a spent fluid (live fungi about 10⁷ mL⁻¹) was collected from an industrial factory and the bacteria were cultured on a liquid broth for 48 h at 30°C. The spent fluid contains microorganisms, such as *Staphylococcus aureus*, *Desulfovibrio desulfuricans*, *Pseudomonas aeruginosa*, *Pseudomonas oleovorans*, *Klebsiella pneumoniae*, *Escherichia coli*, *Proteus mirabilis*, and *Fusarium* sp. The bacteria content of the spent fluid was over 10⁷ cm⁻³.

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[報文] 両端にフルオロアルキル基を有する新規
アクリレートオリゴマー
によるポリエステル SR加工

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過酸化フルオロアルカノイルとポリオキシエチレンメタクリレートから得られる、両端にフルオロアルキル基を有する新規アクリレートオリゴマーのSR加工剤としての有効性について、ポリエステルの表面改質から検討した。

空気中のような疎水性環境下では、表面は撥油性に改質され、その表面自由エネルギー値は 25mJ/m^2 以下であり、分散力および極性力成分はそれぞれ $16\sim 18$ 、 $2\sim 6\text{mJ/m}^2$ であった。ESCA分析の結果、フルオロアルキル基は空気に向かって配列し表面を撥油性にしている事が示された。さらに、表面自由エネルギーの分散力および極性力成分とESCA分析によるエーテル結合炭素の C_{1s} および F_{1s} ピークの含有率との間に高い相関があった。この関係を基に、布の表面自由エネルギーを見積もった。

一方、時間とともに水の接触角は減少し未改質の時よりも低くなった。これは、水中のような親水性環境下ではポリオキシエチレン基が表面へしみ出して来てオリジナル表面よりも親水性へと変化する(HLIP-FLOP機構)ことによると説明できる。モデル洗浄実験の結果も、これら新規オリゴマーがFLIP-FLOP型のSR加工剤として機能することを支持した。

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[ノート] 新しい水溶性切削油添加剤としての
アダマンタン誘導体

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アダマンタンカルボニルクロリド(I)とアミノアルコール、アミノ酸の反応で多数の付加物を合成し、水溶性切削油剤としての性能を検討した。N-(1-アダマンタンカルボニル)-O-(1-アダマンタンカルボニル)モノエタノールアミン(III)の水溶液は水溶性切削油剤として優れた防錆性と抗菌性を示した。

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[ノート] 海産ケイソウ *Phaeodactylum Tricornerutum* の
産生する遊離イコサペンタエン酸

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海産珪藻 *Phaeodactylum Tricornerutum* に存在する遊離脂肪酸(FFA)の組成を求めた。FFAは、バッチ培養した定常期の試料の脂質中に18%含まれており、トリアシルグリセリン(TG)、炭化水素、ステロールおよび極性脂質(PL)とともに、*P. tricornerutum* の主要な脂質成分であった。FFA、TG及びPLの主要構成脂肪酸は14:0、16:0、16:1(n-7)、16:2(n-4)、16:3(n-4)、18:1(n-9)、および20:5(n-3)であった。FFA中38%が20:5(n-3)であり、FFAに多量の20:5(n-3)が含まれる特徴を認めた。一方、20:5(n-3)含量はPLでは全脂肪酸中17%、TGでは9%にすぎなかった。TGに対するパーゼ活性はほとんど認められず、PLに対してホスホリパーゼA(PLaseA)活性が認められた。以上の結果から、本珪藻の遊離20:5(n-3)は、主にPLaseAの作用によりPLから生成すると考えられる。PLaseA1活性がPLaseA2活性よりも高いことを考察した。

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