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REPLACED SHEETS

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Description

Alkenylsuccinic acid derivatives as metalworking auxiliaries

- 5 The use of metalworking auxiliaries extends to numerous working processes for pre- and after-treatment of metals. The field of work comprises cutting and non-cutting shaping of metal components. Drilling and cutting oils are employed for cutting shaping, and milling and drawing oils are employed for non-cutting shaping.
- 10 Anticorrosion agents and emulsifiers in emulsifiable metalworking fluids should meet the following requirements:
1. pronounced corrosion protection properties with respect to ferrous metals
 - 15 2. emulsifying power with respect to mineral oils, possibly also in combination with selected nonionic compounds
 3. low tendency to foam or rapid collapse of foam
 4. prevention of the growth of microorganisms
- 20 These requirements are only partly met by the compounds which are already known.
- Salts of C₆-C₁₂-alkenylsuccinic acid half-amides and their use as anticorrosion agents are known from EP-A-127 132. However, these compounds do not exhibit an adequate
- 25 emulsifying power, which leads to inadequate service lives of the emulsion to be used. Furthermore, emulsions comprising these compounds tend to foam, which is a disadvantage in particular during working processes such as grinding, when the emulsions are exposed to high
- 30 mechanical influences.

Alkanolamine salts of C₆-C₁₈-alkenylsuccinic acid half-amides, where a primary amine having a C₁-C₁₀-alkyl chain is employed for half-amide formation, are described in DE-A-33 00 874.



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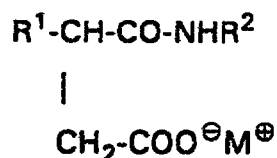
DE-A-33 41 013 describes C₆-C₁₈-alkenylsuccinic acid half-amides, where secondary amines having 1 to 10 carbon atoms are employed for the half-amide formation.

5 The abovementioned requirements also cannot be met in full by the use of these compounds.

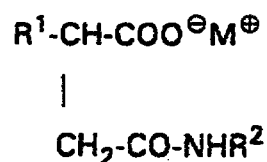
The object of the invention is to provide derivatives of alkenylsuccinic acids which combine the properties described above.

10 Surprisingly, it has now been found that this object can be achieved by salts of alkenylsuccinic acid half-amides which contain alkoxyalkylamines as the amine component, if appropriate as a mixture with salts of alkenylsuccinic acid half-amides which contain an alcoholamine as the ester group, and alkenylsuccinic acid imides.

15 The invention relates to salts of alkenylsuccinic acid alkoxyalkyl-half-amides of the formula Ia and/or Ib



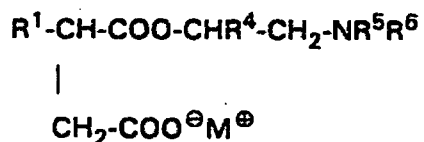
Ia



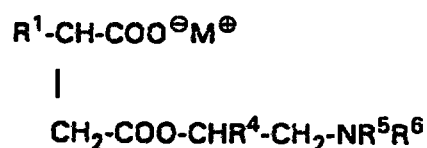
Ib

if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formula IIa and/or IIb

IIa

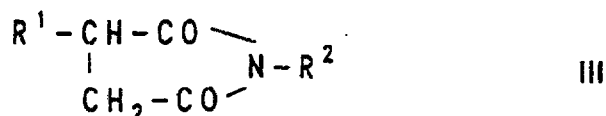


IIb





and/or alkenylsuccinic acid imides of the formula III



in which

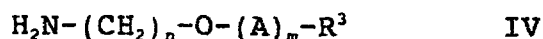
- R^1 is C_6 - C_{30} -alkenyl or C_6 - C_{30} -alkyl, preferably C_9 - C_{18} -alkenyl or C_9 - C_{18} -alkyl, in which R^1 can be straight-chain or branched;
 R^2 is $-(\text{CH}_2)_n-\text{O}-(\text{A})_m-\text{R}^3$, where
 A is $-\text{CH}_2-\text{CH}_2-\text{O}-$ or $-\text{CH}(\text{R}^4)-\text{CH}_2-\text{O}-$, in which
 R^3 is C_1 - C_{18} -alkyl, and in which R^3 can be straight-chain or branched,
 R^4 is hydrogen or methyl,
 n is a number from 1 to 6,
 m is a number from 0 to 8 and
 M^+ is an alkali metal or alkaline earth metal cation or an ammonium ion of the formula $\text{HNR}^5\text{R}^6\text{R}^7$, in which R^5 , R^6 and R^7 are identical or different and are hydrogen, C_1 - C_6 -alkyl or hydroxy- (C_1-C_6) -alkyl, in particular 2-hydroxyethyl and 2-hydroxypropyl.

The alkenylsuccinic acid half-ester amine salts of the formula IIa and IIb and the alkenylsuccinic acid imides of the formula III can occur as by-products during preparation of the alkenylsuccinic acid alkoxyalkyl-half-amide salts of the formula Ia and Ib and are usually present in concentrations of 0 to 40 % by weight, preferably 0 to 20 % by weight, as a mixture with the alkenylsuccinic acid alkoxyalkyl-half-amide salts of the formula Ia and Ib.

The invention likewise relates to a process for the preparation of salts of alkenylsuccinic acid alkoxyalkyl-half-amides of the formula Ia and/or Ib, if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formulae IIa and/or IIb and/or alkenylsuccinic acid imides of the formula III, which



comprises reacting alkenylsuccinic acid anhydrides with alkoxyalkylamines of the formula IV



in which

- 5 R^3 is C_1 - C_{18} -alkyl, in which R^3 can be straight-chain or branched,
 n is a number from 1 to 6 and
 m is a number from 0 to 8,
 in a molar ratio of 1 : 0.7 to 2.5, preferably 1 : 0.8
10 to 1.2, at temperatures of 20 to 120°C, preferably 60 to 100°C, and carrying out this reaction in the presence of an amount of base which is equimolar to the alkoxyalkylamines of the formula IV, or adding an amount of base equimolar to the alkoxyalkylamines of the formula IV
15 after the reaction.

Bases which are employed are alkali metal hydroxides, alkaline earth metal hydroxides, alkanolamines of the formula $\text{NR}^5\text{R}^6\text{R}^7$ or mixtures thereof.

- 20 The base is usually employed in an amount equimolar to the alkanolamines.

- The preparation of the alkenylsuccinic acid anhydrides used as starting materials is carried out by reaction of olefins and maleic anhydride and is known. Preferred olefins are oligomers of ethylene, propylene and butylene, and olefins having an internal double bond. For
25 example, n-dodecenylsuccinic anhydride can be prepared by reaction of n-dodec-1-ene with maleic anhydride at temperatures of 150 to 230°C under a pressure of 3 to 10 bar in the presence of suitable free radical
30 inhibitors. The alkenylsuccinic acid anhydrides thus obtained can be employed for the preparation of the compounds according to the invention either after purification by distillation or recrystallization or directly.



The alkoxyalkylamines, for example 2-hydroxyethylamine, can be prepared by addition of acrylonitrile onto alcohols and subsequent hydrogenation.

5 The salts of alkenylsuccinic acid alkoxyalkyl-half-amides of the formula Ia and/or Ib according to the invention, if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formula IIa and/or IIb and/or alkenylsuccinic acid imides of the formula III are used as metalworking auxiliaries, in particular as
10 anticorrosion agents and an emulsifier in aqueous and/or oil-containing formulations or metalworking fluids.

The invention likewise relates to aqueous and/or oil-containing formulations for working metals, in particular for use as cooling lubricants, which comprise the above-
15 mentioned salts of alkenylsuccinic acid alkoxyalkyl-half-amides of the formula Ia and/or Ib, if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formula IIa and/or IIb and/or alkenylsuccinic acid imides of the formula III.

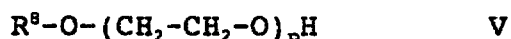
20 The alkenylsuccinic acid alkoxyalkyl-half-amide salts of the formula Ia and/or Ib prepared by the processes described above, if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formula IIa and/or IIb and/or alkenylsuccinic acid imides
25 of the formula III, form a clear solution in water and, with mineral oil, give formulations which are readily emulsifiable in water. These compounds are employed in concentrated form as emulsifiers and anticorrosion agents in oil-containing and/or aqueous formulations. The
30 concentration of the alkenylsuccinic acid alkoxyalkyl-half-amide salts of the formula Ia and/or Ib, if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formula IIa and/or IIb and/or alkenylsuccinic acid imides of the formula III, in the
35 formulation is higher than that during use and is usually 10 to 80 % by weight. The formulation is diluted with



water for cutting or non-cutting shaping, such as, for example, in drilling, cutting, drawing and milling fluids. To prepare the formulations, the products according to the invention are either stirred into the
5 required amount of water or mixed with mineral oil or mineral oil/water. The resulting aqueous or oil-containing formulations are usually diluted or emulsified with water before use. The dilution ratio is in general 1 : 10 to 1 : 100. The use concentration of the alkenylsuccinic
10 acid alkoxyalkyl-half-amide salts in metalworking fluids, for example drilling, cutting, drawing and milling fluids, is in general about 0.1 to 10 % by weight, preferably 2 to 10 % by weight. The concentration mentioned relates both to the use of the products in water
15 and to their use in mineral oil/water emulsions during metalworking. Metalworking fluids are also to be understood as meaning cooling lubricants.

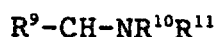
The alkenylsuccinic acid alkoxyalkyl-half-amide salts are employed as an emulsifier with corrosion protection in
20 aqueous metalworking fluids containing mineral oil and as an anticorrosion agent in aqueous metalworking fluids which are free from mineral oil. They are suitable for mixing with customary mineral oils, in particular with naphthene-based and paraffin-based mineral oils and
25 mineral oils on a mixed basis.

The formulations or metalworking fluids can comprise additional auxiliaries for optimizing the emulsifying properties and the corrosion protection. Auxiliaries which are particularly advantageous for this purpose are
30 oxyethylates of the formula V



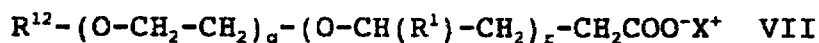
in which R^8 is C_{10} - C_{22} alkyl, C_{10} - C_{22} alkenyl or alkylphenyl having a total of 10 to 20 carbon atoms and p is a number from 2 to 10.

35 Fatty acid alkanolamides of the formula VI



VI

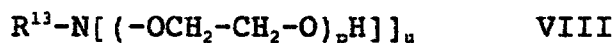
in which R^9 is C_{10} - C_{22} alkyl or C_{10} - C_{22} alkenyl and R^{10} and R^{11} are identical or different and are hydrogen or hydroxy-(C_1 - C_6)-alkyl, in particular 2-hydroxyethyl or 2-hydroxypropyl, can also be employed as auxiliaries. Further suitable auxiliaries are ether-carboxylic acids of the formula VII



in which

R^{12} is a branched or unbranched, saturated or unsaturated C_8 - C_{22} alkyl or C_8 - C_{22} alkenyl radical and q and r independently of one another can assume values from 0 to 10, with the proviso that the sum of q and r is at least 1 and X is hydrogen or an alkali metal atom or alkaline earth metal atom.

Auxiliaries which are likewise suitable are alkoxyated primary amines of the formula VIII



in which

R^{13} is C_{12} - C_{20} -alkyl, or alkenyl, preferably C_{16} - C_{18} -alkyl, p is a number from 2 to 10, preferably 4 to 6, and u is the number 1 or 2, with the proviso that if u is 1 a hydrogen atom is located on the free bond of the nitrogen atom.

Other suitable auxiliaries are also fatty acid polyglycol esters, in particular of saturated or unsaturated fatty acids having 10 to 22 carbon atoms in the alkyl chain and 1 to 10 ethylene oxide units, such as oleic acid having 4 to 6 ethylene oxide units. The formulations in general comprise these auxiliaries individually or in mixtures in amounts of in each case about 20 to 40 % by weight. The formulations for this purpose furthermore can comprise



customary additives, such as foam suppressants or suitable perservatives.

The terms used below for characterization, such as acid number, amine number, base nitrogen and iodine color
5 number, are determined or ascertained as follows:

Determination of the acid number:

To determine the acid number, stated in mg of KOH/g of substance, 0.1 to 0.5 g of the sample is weighed into a
150 ml glass beaker and dissolved in 60 to 80 ml of
10 ethanol and the solution is titrated with 0.1 N ethanolic potassium hydroxide solution. The end point is indicated potentiometrically (apparatuses: Metrohm Titroprocessor 682, Dosimat 665 with combined pH glass electrode).

15 Ascertaining the base nitrogen and the amine number:

To ascertain the base nitrogen, stated in % of N, 0.1 to 0.5 g of the sample is weighed into a 150 ml glass beaker and dissolved in 60 to 80 ml of glacial acetic acid and the solution is titrated with 0.1 N perchloric acid in
20 glacial acetic acid. The end point is indicated potentiometrically (apparatuses: Metrohm Titroprocessor 682, Dosimat 665 with combined pH glass electrode).

The amine number, stated in mg of KOH/g of substance, is calculated from the value for the base nitrogen from the
25 formula:

$$\text{amine number [mg of KOH/g]} = \% \text{ of base N} \times 5.61/0.140067$$

The iodine color number denotes the concentration of free iodine in an iodine/potassium iodide solution (in mg of
30 iodine per 100 ml of iodine/potassium iodide solution) and serves to characterize the color or transparency of this solution and liquids of a similar type. The basis for the determination of the iodine color number is the iodine color scale (comparison tubes). Literature:



DIN 53403.

The following embodiment examples illustrate the present invention without limiting it:

Examples:

5 Example 1

Preparation of $C_{12/14}$ -alkenylsuccinic acid 3-butoxypropyl-half-amide triethanolammonium salt

10 A mixture of 127.5 g (1.0 mol) of 3-n-butoxypropylamine, 149.1 g (1.0 mol) of triethanolamine and 30 g of water was initially introduced into a 1 l three-necked flask with a stirrer, internal thermometer and reflux condenser, and 279.2 g (hydrolysis number: 401.9 mg of KOH/g; 1 mol) of technical grade $C_{12/14}$ -alkenylsuccinic acid anhydride (chain distribution of the starting olefin mixture: 65 % by weight of dodecene, 35 % by weight of tetradecene) were metered in over a period of 0.5 hours (exothermic reaction). The internal temperature was limited to not more than 50°C by periodic cooling. When the addition had ended, the mixture was subsequently stirred at 50°C for a further 2 hours. At this point in time, the reaction mixture contained about 67 % of $C_{12/14}$ -alkenylsuccinic acid 3-n-butoxypropyl-half-amide triethanolammonium/3-butoxypropylammonium salt and about 33 % of $C_{12/14}$ -alkenylsuccinic acid triethanolamine ester 3-n-butoxypropylammonium/triethanolammonium salt (determined by base N determination).

25 The reaction mixture was rendered alkaline by addition of 48 g (0.6 mol) of a 50 % strength sodium hydroxide solution. 642.1 g of a pale brown-yellow liquid having an iodine color number of 30 to 40, an amine number (determined potentiometrically) of 171 mg of KOH/g, an acid number of 46 mg of KOH/g and a viscosity of 1.9 Pas (Brookfield, 28°C, 10 revolutions per minute) were obtained.



Example 2

Preparation of $C_{12/14}$ -alkenylsuccinic acid 3-methoxypropyl-half-amide triethanolammonium salt

44.6 g (0.5 mol) of 3-methoxypropylamine were initially
5 introduced into the apparatus described in Example 1 at
30°C and 139.6 g (hydrolysis number: 401.9 mg of KOH/g;
0.5 mol) of technical grade $C_{12/14}$ -alkenylsuccinic acid
anhydride (chain distribution of the starting olefin
mixture: 65 % by weight of dodecene, 35 % by weight of
10 tetradecene) were added dropwise in the course of
30 minutes (exothermic reaction), the internal
temperature being kept at not more than 50°C by periodic
cooling. When the addition had ended, the mixture was
subsequently stirred at 50°C for a further 2 hours
15 (conversion according to control of the base N > 98 %)
and was neutralized by addition of 74.5 g (0.5 mol) of
triethanolamine. Finally, the reaction mixture was
rendered alkaline by addition of 39 g of a 30 % strength
sodium hydroxide solution (pH (1 % in demineralized
20 water): 8.4). 296 g of a dark yellow liquid having an
iodine color number of 20, an amine number (potentio-
metric determination) of 151 mg of KOH/g and an acid
number of 50.6 mg of KOH/g were obtained.

Example 3

25 Preparation of $C_{12/14}$ -alkenylsuccinic acid 3-butoxypropyl-
amide methyldiethanolammonium salt

55.8 g (0.2 g) of technical grade n- $C_{12/14}$ -alkenylsuccinic
acid anhydride were added dropwise to a mixture of 25.5 g
(0.2 mol) of 3-butoxypropylamine, 23.8 g (0.2 mol) of N-
30 methyl-diethanolamine and 6 g of demineralized water in
the course of 30 minutes, starting at 30°C (exothermic
reaction), the internal temperature being kept at 50°C by
periodic cooling, and the mixture was subsequently
stirred at 50°C for 2 hours. At this point in time, the



reaction mixture contained, according to analysis (base N) about 86 % of n-C_{12/14}-alkenylsuccinic acid 3-butoxypropyl-half-amide triethanolammonium/3-butoxypropylammonium salt and about 14 % of n-C_{12/14}-alkenylsuccinic acid triethanolamine ester 3-butoxypropylammonium/triethanolammonium salt. When the reaction had ended, the mixture was rendered alkaline with 9.6 g of 50 % strength sodium hydroxide and 119.1 g of a yellowish viscous liquid having an iodine color number of 20, an amine number of 168 mg of KOH/g and an acid number of 51 mg of KOH/g were thus obtained.

Example 4

Preparation of C_{12/14}-alkenylsuccinic acid 3-methoxypropylamide triethanolammonium salt

3-Methoxypropylamine was added dropwise to 139.8 g (0.5 mol) of n-C_{12/14}-alkenylsuccinic acid anhydride in the course of 0.5 hours, with periodic cooling, such that the internal temperature did not exceed 50°C, and the mixture was subsequently stirred for 1 hour and neutralized with a mixture of 75.6 g of triethanolamine and 14.2 g of water to give, after post-reaction for 1 hour at 50°C, a reaction mixture having a half-amide/ester ratio of 93.7 (analysis by base N). After the mixture had been rendered alkaline with 24 g of 50 % strength sodium hydroxide solution, 291.6 g of a dark yellow liquid having an amine number of 160 mg of KOH/g, an acid number of 46 mg of KOH/g and a viscosity of 2.3 Pas were obtained.

Example 5

Preparation of tripropylsuccinic acid 3-methoxypropylamide triethanolammonium salt

111.5 g (0.5 mol) of technical grade tripropenylsuccinic anhydride were added dropwise to a mixture of 44.6 g (0.5 mol) of 3-methoxypropylamine, 74.5 g (0.5 mol) of



triethanolamine and 13.6 g of water in the course of 0.5 hours, starting at 30°C, with periodic cooling, such that the internal temperature did not exceed 50°C, and the mixture was then subsequently stirred at this temperature for a further 2 hours. At this point in time, the reaction mixture contained about 63 % of half-amide and 37 % of half-ester. After the mixture had been rendered alkaline with 24 g of 50 % strength sodium hydroxide solution, 266.2 g of a pale yellow viscous liquid having an amine number of 206 mg of KOH/g and an acid number of 56 mg of KOH/g were obtained.

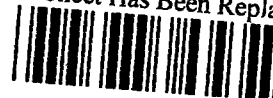


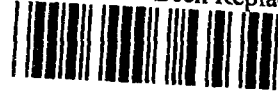
Table 1: Applications properties of alkenylsuccinic acid
3-alkoxypropylamides

Example	1	2	3	4	5
Appearance of 3 % strength aqueous solutions: distilled water immediately after 24 hrs	clear clear	clear trans- parent	clear clear	clear clear	clear clear
Foam height ¹⁾ immediately after 5 mins	> 50 > 50	> 50 > 50	> 50 > 50	> 50 20	> 50 12
20°dH immediately after 24 hrs Foam height ¹⁾ immediately after 5 mins	clear clear > 50 3	trans- parent trans- parent 50 45	clear clear > 50 > 50	clear clear > 50 trace of marginal foam	cloudy cloudy 45 2
Corrosion protection a.) Herbert test (DIN 51360/1) distilled H ₂ O 1.0 % 20°dH 3.0 % b.) Filter paper test (DIN 51360/2) distilled H ₂ O 1.5 % 20°dH 3.0 %	RO/SO RO/SO 0 0	RO/SO RO/SO 1 0	RO/SO RO/SO 0 0	RO/SO RO/SO 0 0	RO/SO RO/SO 1 0
Emulsifiability	spon- taneous	spon- taneous	spon- taneous	spon- taneous	spon- taneous

Notes on Table 1:

- 1) To determine the foaming properties, in each case 50 ml of 3 % strength aqueous solutions of the test products were introduced into a graduated 100 ml measuring cylinder and the cylinder was closed with a glass stopper and shaken vigorously 20 x in the horizontal direction. The evaluation was carried out after the waiting periods stated by measuring the amount of foam in ml.

Information on the test procedure:



- 14 -

The tests were carried out on formulations comprising:

- 18 % of emulsifier mixture
- 4 % of nonylphenol ethoxylate
- 2 % of water
- 5 78 % of naphthene-based mineral oil

Emulsifier mixture:

- 37 % of product according to the example
- 32 % of oleyl alcohol + 2EO (ethylene oxide)
- 31 % of tall oil fatty acid diethanolamide



Patent claims:

1. A salt of an alkenylsuccinic acid alkoxyalkyl-half-amide of the formula Ia or Ib

Ia

Ib



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if appropriate as a mixture with a salt of an alkenylsuccinic acid half-ester amine of the formula IIa or IIb

IIa

IIb



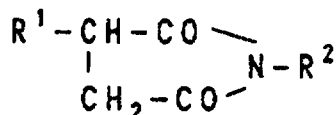
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and/or an alkenylsuccinic acid imide of the formula III



III

in which

10

R^1 is $\text{C}_6\text{-C}_{30}$ -alkenyl or $\text{C}_6\text{-C}_{30}$ -alkyl, preferably $\text{C}_9\text{-C}_{18}$ -alkenyl or $\text{C}_9\text{-C}_{18}$ -alkyl, in which R^1 can be straight-chain or branched;

R^2 is $-(\text{CH}_2)_n\text{-O-(A)}_m\text{-R}^3$, where

A is $-\text{CH}_2\text{-CH}_2\text{-O-}$ or $-\text{CH(R}^4\text{)-CH}_2\text{-O-}$, in which

15

R^3 is $\text{C}_1\text{-C}_{18}$ -alkyl, and in which R^3 can be straight-chain or branched,

R^4 is hydrogen or methyl,

n is a number from 1 to 6,

m is a number from 0 to 8 and

20

M^+ is an alkali metal or alkaline earth metal cation





or an ammonium ion of the formula $\text{HNR}^5\text{R}^6\text{R}^7$, in which R^5 , R^6 and R^7 are identical or different and are hydrogen, $\text{C}_1\text{-C}_6$ -alkyl or hydroxy- $(\text{C}_1\text{-C}_6)$ -alkyl,

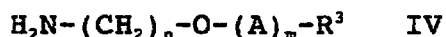
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in particular

2-hydroxyethyl and 2-hydroxypropyl.

2. A compound as claimed in claim 1, wherein a salt of an alkenylsuccinic acid half-ester amide of the formula IIa or IIb and an alkenylsuccinic acid imide of the formula III are present in a concentration of up to 40 % by weight, preferably up to 20 % by weight, as a mixture with a salt of an alkenylsuccinic acid alkoxyalkyl-half-amide of the formula Ia or Ib.

3. A process for the preparation of a salt of an alkenylsuccinic acid alkoxyalkyl-half-amide of the formula Ia or Ib, if appropriate as a mixture with a salt of an alkenylsuccinic acid half-ester amine of the formula IIa or IIb and/or an alkenylsuccinic acid imide of the formula III, which comprises reacting an alkenylsuccinic acid anhydride with an alkoxyalkylamine of the formula IV



in which

R^3 is $\text{C}_1\text{-C}_{18}$ -alkyl, in which R^3 can be straight-chain or branched,

n is a number from 1 to 6 and

m is a number from 0 to 8,

in a molar ratio of 1 : 0.7 to 2.5, preferably 1 : 0.8 to 1.2, at temperatures of 20 to 120°C, preferably 60 to 100°C, and carrying out this reaction in the presence of an amount of base which is equimolar to the alkoxyalkylamine of the formula IV, or adding an amount of base equimolar to the alkoxyalkylamine of the formula IV after the





reaction.

4. The process as claimed in claim 3, wherein an alkali metal hydroxide, alkaline earth metal hydroxide, alkanolamine of the formula $NR^5R^6R^7$ or a mixture thereof is employed as the base.
5. The process as claimed in claim 3, wherein 2-hydroxyethylamine and/or 2-hydroxypropylamine are employed as the alkoxyalkylamine of the formula IV.
6. An aqueous or oil-containing formulation for working metals, in particular for use as a cooling lubricant, which comprises a salt of an alkenylsuccinic acid alkoxyalkyl-half-amide of the formula Ia or Ib, if appropriate as a mixture with a salt of an alkenylsuccinic acid half-ester amine of the formula IIa or IIb and/or an alkenylsuccinic acid imide of the formula III, as claimed in claim 1.
7. A formulation as claimed in claim 6, which comprises a compound as claimed in claim 1 in a concentration of 10 to 80 % by weight.
8. An aqueous or oil-containing metalworking fluid for working metals, in particular for use as a cooling lubricant, which comprises a salt of an alkenylsuccinic acid alkoxyalkyl-half-amide of the formula Ia or Ib, if appropriate as a mixture with a salt of an alkenylsuccinic acid half-ester amine of the formula IIa or IIb and/or an alkenylsuccinic acid imide of the formula III, as claimed in claim 1.
9. An aqueous and/or oil-containing metal working liquid as claimed in claim 8, which comprises compounds as claimed in claim 1 in a concentration of 0.1 to 10 % by weight, preferably 2 to 10 % by





weight.

10. A formulation as claimed in claim 6, which comprises as additional auxiliaries an oxyethylate of the formula V

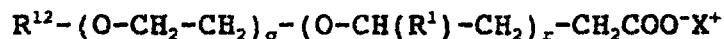


in which R^8 is C_{10} - C_{22} -alkyl, C_{10} - C_{22} alkenyl or alkylphenyl having a total of 10 to 20 carbon atoms and p is a number from 2 to 10, and/or a fatty acid alkanolamide of the formula VI

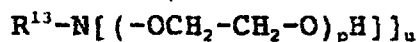


in which R^9 is C_{10} - C_{22} -alkyl or C_{10} - C_{22} -alkenyl and R^{10} and R^{11} are identical or different and are hydrogen or hydroxyl- (C_1-C_6) -alkyl, in particular 2-hydroxyethyl or 2-hydroxypropyl, and/or

15 an ether-carboxylic acid of the formula VII



in which R^{12} is a branched or unbranched, saturated or unsaturated C_8 - C_{22} -alkyl or C_8 - C_{22} -alkenyl radical and q and r independently of one another have values from 0 to 10, with the proviso that the sum of q and r is at least 1, and X is hydrogen, an alkali metal atom or an alkaline earth metal atom,
20 an alkoxyated primary amine of the formula VIII



25 in which

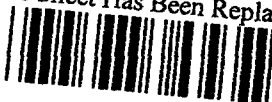
R^{13} is C_{12} - C_{20} -alkyl, or alkenyl, preferably C_{16} - C_{18} -alkyl,

p is a number from 2 to 10, preferably 4 to 6, and

u is the number 1 or 2, with the proviso that if u

30 is 1, a hydrogen atom is located on the free bond





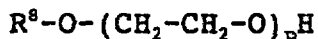
of the nitrogen atom,
and/or

5 a fatty acid polyglycol ester, in particular of a saturated or unsaturated fatty acid having 10 to 22 carbon atoms in the alkyl chain and 1 to 10 ethylene oxide units, preferably oleic acid having 4 to 6 ethylene oxide units.

10 11. A formulation as claimed in claim 10, which comprises the auxiliaries in a concentration of 20 to 40 % by weight.

12. A formulation as claimed in claim 6, which comprises a foam suppressant and/or preservative.

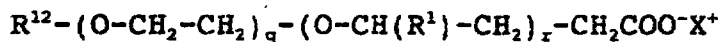
15 13. A metalworking fluid as claimed in claim 8, which comprises as additional auxiliaries an oxyethylate of the formula V



20 in which R^8 is C_{10} - C_{22} -alkyl, C_{10} - C_{22} alkenyl or alkylphenyl having a total of 10 to 20 carbon atoms and p is a number from 2 to 10, and/or a fatty acid alkanolamide of the formula VI



25 in which R^9 is C_{10} - C_{22} -alkyl or C_{10} - C_{22} -alkenyl and R^{10} and R^{11} are identical or different and are hydrogen or hydroxyl-(C_1 - C_6)-alkyl, in particular 2-hydroxyethyl or 2-hydroxypropyl, and/or an ether-carboxylic acid of the formula VII



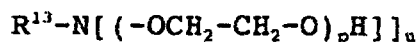
30 in which R^{12} is a branched or unbranched, saturated or unsaturated C_8 - C_{22} -alkyl or C_8 - C_{22} -alkenyl radical and q and r independently of one another have values





from 0 to 10, with the proviso that the sum of q and r is at least 1, and X is hydrogen, an alkali metal atom or an alkaline earth metal atom, an alkoxyated primary amine of the formula VIII

5



in which

R^{13} is C_{12} - C_{20} -alkyl, or alkenyl, preferably C_{16} - C_{18} -alkyl,

10 p is a number from 2 to 10, preferably 4 to 6, and u is the number 1 or 2, with the proviso that if u is 1, a hydrogen atom is located on the free bond of the nitrogen atom,

and/or

15 a fatty acid polyglycol ester, in particular of a saturated or unsaturated fatty acid having 10 to 22 carbon atoms in the alkyl chain and 1 to 10 ethylene oxide units, preferably oleic acid having 4 to 6 ethylene oxide units.

20 14. The use of a salt of an alkenylsuccinic acid alkoxy-alkyl-half-amide of the formula Ia or Ib, if appropriate as a mixture with a salt of an alkenylsuccinic acid half-ester amine of the formula IIa or IIb and/or an alkenylsuccinic acid imide of the formula III as a metalworking auxiliary, in particular as an anticorrosion agent and emulsifier in
25 an aqueous and/or oil-containing formulation or metalworking auxiliary.





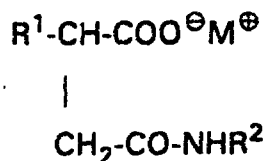
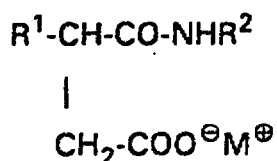
Abstract

Alkenylsuccinic acid derivatives as metalworking auxiliaries

The present invention relates to salts of alkenylsuccinic acid alkoxyalkyl-half-amides of the formula Ia and/or Ib

Ia

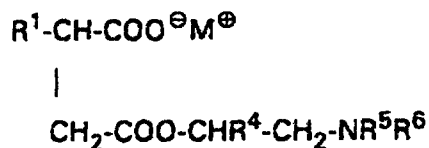
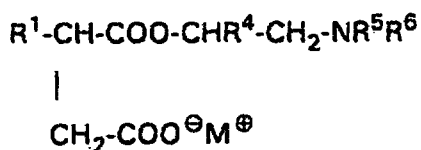
Ib



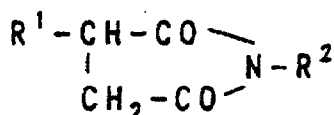
if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formula IIa and/or IIb

IIa

IIb

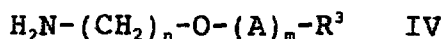


and/or alkenylsuccinic acid imides of the formula III



in which R¹, R², A, R³, R⁴, n, m and M^{*} have the meaning given in the description.

The invention also relates to a process for the preparation of salts of alkenylsuccinic acid alkoxyalkyl-half-amides of the formula Ia and/or Ib, if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formula IIa and IIb and/or alkenylsuccinic acid imides of the formula III, which comprises reacting alkenylsuccinic acid anhydrides with alkoxyalkylamines of the formula IV



in which R^3 , n , m and A have the meaning given in the description, and carrying out this reaction in the presence of an amount of base equimolar to the alkoxy-
5 alkyamines of the formula IV, or adding an amount of base equimolar to the alkoxyalkylamines of the formula IV after the reaction.

The invention furthermore relates to aqueous and/or oil-containing formulations for working metals, which
10 comprise the abovementioned salts of alkenylsuccinic acid alkoxyalkyl-half-amides of the formula Ia and/or Ib, if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formula IIa and/or IIb and/or alkenylsuccinic acid imides of the formula III,
15 and their use as anticorrosion agents, cooling lubricants and metalworking auxiliaries.

REPLACEMENT SHEETS		SC
☒ Description	: paged .1. to paged .4.	
☒ Claim(s)	: paged .5. to paged .8.	
☐ Drawing(s)	: paged to paged	
☒ Abstract	: paged .21. to paged .22.	
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Description

Alkenylsuccinic acid derivatives as metalworking auxiliaries

- 5 The use of metalworking auxiliaries extends to numerous working processes for pre- and after-treatment of metals. The field of work comprises cutting and non-cutting shaping of metal components. Drilling and cutting oils are employed for cutting shaping, and milling and drawing oils are employed for non-cutting shaping.
- 10 Anticorrosion agents and emulsifiers in emulsifiable metalworking fluids should meet the following requirements:
1. pronounced corrosion protection properties with respect to ferrous metals
 - 15 2. emulsifying power with respect to mineral oils, possibly also in combination with selected nonionic compounds
 3. low tendency to foam or rapid collapse of foam
 4. prevention of the growth of microorganisms
- 20 These requirements are only partly met by the compounds which are already known.
- 25 Salts of C₆-C₁₂-alkenylsuccinic acid half-amides and their use as anticorrosion agents are known from EP-A-127 132. However, these compounds do not exhibit an adequate emulsifying power, which leads to inadequate service lives of the emulsion to be used. Furthermore, emulsions comprising these compounds tend to foam, which is a disadvantage in particular during working processes such as grinding, when the emulsions are exposed to high
- 30 mechanical influences.

Alkanolamine salts of C₆-C₁₂-alkenylsuccinic acid half-amides, where a primary amine having a C₁-C₁₀-alkyl chain is employed for half-amide formation, are described in DE-A-33 00 874.

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DE-A-33 41 013 describes C_6 - C_{10} -alkenylsuccinic acid half-amides, where secondary amines having 1 to 10 carbon atoms are employed for the half-amide formation.

The abovementioned requirements also cannot be met in full by the use of these compounds.

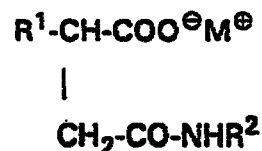
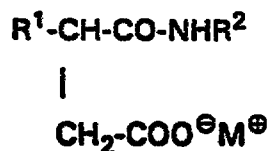
The object of the invention is to provide derivatives of alkenylsuccinic acids which combine the properties described above.

Surprisingly, it has now been found that this object can be achieved by salts of alkenylsuccinic acid half-amides which contain alkoxyalkylamines as the amine component, if appropriate as a mixture with salts of alkenylsuccinic acid half-amides which contain an alcoholamine as the ester group, and alkenylsuccinic acid imides.

The invention relates to salts of alkenylsuccinic acid alkoxyalkyl-half-amides of the formula Ia and/or Ib

Ia

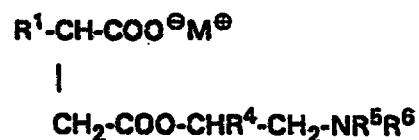
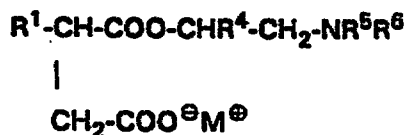
Ib



if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formula IIa and/or IIb

IIa

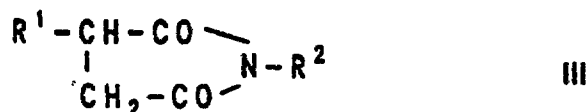
IIb



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and/or alkenylsuccinic acid imides of the formula III



in which

- 5 R^1 is C_6 - C_{30} -alkenyl or C_6 - C_{30} -alkyl, preferably C_6 - C_{18} -alkenyl or C_6 - C_{18} -alkyl, in which R^1 can be straight-chain or branched;
- R^2 is $-(\text{CH}_2)_n-\text{O}-(\text{A})_m-\text{R}^3$, where
- A is $-\text{CH}_2-\text{CH}_2-\text{O}-$ or $-\text{CH}(\text{R}^4)-\text{CH}_2-\text{O}-$, in which
- R^3 is C_1 - C_{18} -alkyl, and in which R^3 can be straight-chain or branched,
- 10 R^4 is hydrogen or methyl,
- n is a number from 1 to 6,
- m is a number from 0 to 8 and
- M^+ is an alkali metal or alkaline earth metal cation or an ammonium ion of the formula $\text{HNR}^5\text{R}^6\text{R}^7$, in which R^5 , R^6 and R^7 are identical or different and are hydrogen, C_1 - C_6 -alkyl or hydroxy- $(\text{C}_1$ - C_6)-alkyl,
- 15 in particular
2-hydroxyethyl and 2-hydroxypropyl.

20 The alkenylsuccinic acid half-ester amine salts of the formula IIa and IIb and the alkenylsuccinic acid imides of the formula III can occur as by-products during preparation of the alkenylsuccinic acid alkoxyalkyl-half-amide salts of the formula Ia and Ib and are usually present in concentrations of 0 to 40 % by weight, preferably 0 to 20 % by weight, as a mixture with the alkenylsuccinic acid alkoxyalkyl-half-amide salts of the formula Ia and Ib.

30 The invention likewise relates to a process for the preparation of salts of alkenylsuccinic acid alkoxyalkyl-half-amides of the formula Ia and/or Ib, if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formulae IIa and/or IIb and/or alkenylsuccinic acid imides of the formula III, which

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comprises reacting alkenylsuccinic acid anhydrides with alkoxyalkylamines of the formula IV



in which

- 5 R^3 is C_1 - C_{18} -alkyl, in which R^3 can be straight-chain or branched,
 n is a number from 1 to 6 and
 m is a number from 0 to 8,
10 in a molar ratio of 1 : 0.7 to 2.5, preferably 1 : 0.8 to 1.2, at temperatures of 20 to 120°C, preferably 60 to 100°C, and carrying out this reaction in the presence of an amount of base which is equimolar to the alkoxyalkylamines of the formula IV, or adding an amount of base equimolar to the alkoxyalkylamines of the formula IV
15 after the reaction.

Bases which are employed are alkali metal hydroxides, alkaline earth metal hydroxides, alkanolamines of the formula $\text{NR}^5\text{R}^6\text{R}^7$ or mixtures thereof.

- 20 The base is usually employed in an amount equimolar to the alkanolamines.

- 25 The preparation of the alkenylsuccinic acid anhydrides used as starting materials is carried out by reaction of olefins and maleic anhydride and is known. Preferred olefins are oligomers of ethylene, propylene and butylene, and olefins having an internal double bond. For example, n-dodecenylsuccinic anhydride can be prepared by reaction of n-dodec-1-ene with maleic anhydride at temperatures of 150 to 230°C under a pressure of 3 to 10 bar in the presence of suitable free radical
30 inhibitors. The alkenylsuccinic acid anhydrides thus obtained can be employed for the preparation of the compounds according to the invention either after purification by distillation or recrystallization or directly.

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The alkoxyalkylamines, for example 2-hydroxyethylamine, can be prepared by addition of acrylonitrile onto alcohols and subsequent hydrogenation.

5 The salts of alkenylsuccinic acid alkoxyalkyl-half-amides of the formula Ia and/or Ib according to the invention, if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formula IIa and/or IIb and/or alkenylsuccinic acid imides of the formula III are used as metalworking auxiliaries, in particular as
10 anticorrosion agents and an emulsifier in aqueous and/or oil-containing formulations or metalworking fluids.

The invention likewise relates to aqueous and/or oil-containing formulations for working metals, in particular for use as cooling lubricants, which comprise the above-
15 mentioned salts of alkenylsuccinic acid alkoxyalkyl-half-amides of the formula Ia and/or Ib, if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formula IIa and/or IIb and/or alkenylsuccinic acid imides of the formula III.

20 The alkenylsuccinic acid alkoxyalkyl-half-amide salts of the formula Ia and/or Ib prepared by the processes described above, if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formula IIa and/or IIb and/or alkenylsuccinic acid imides
25 of the formula III, form a clear solution in water and, with mineral oil, give formulations which are readily emulsifiable in water. These compounds are employed in concentrated form as emulsifiers and anticorrosion agents in oil-containing and/or aqueous formulations. The
30 concentration of the alkenylsuccinic acid alkoxyalkyl-half-amide salts of the formula Ia and/or Ib, if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formula IIa and/or IIb and/or alkenylsuccinic acid imides of the formula III, in the
35 formulation is higher than that during use and is usually 10 to 80 % by weight. The formulation is diluted with

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water for cutting or non-cutting shaping, such as, for example, in drilling, cutting, drawing and milling fluids. To prepare the formulations, the products according to the invention are either stirred into the
5 required amount of water or mixed with mineral oil or mineral oil/water. The resulting aqueous or oil-containing formulations are usually diluted or emulsified with water before use. The dilution ratio is in general 1 : 10 to 1 : 100. The use concentration of the alkenylsuccinic
10 acid alkoxyalkyl-half-amide salts in metalworking fluids, for example drilling, cutting, drawing and milling fluids, is in general about 0.1 to 10 % by weight, preferably 2 to 10 % by weight. The concentration mentioned relates both to the use of the products in water
15 and to their use in mineral oil/water emulsions during metalworking. Metalworking fluids are also to be understood as meaning cooling lubricants.

The alkenylsuccinic acid alkoxyalkyl-half-amide salts are employed as an emulsifier with corrosion protection in
20 aqueous metalworking fluids containing mineral oil and as an anticorrosion agent in aqueous metalworking fluids which are free from mineral oil. They are suitable for mixing with customary mineral oils, in particular with naphthene-based and paraffin-based mineral oils and
25 mineral oils on a mixed basis.

The formulations or metalworking fluids can comprise additional auxiliaries for optimizing the emulsifying properties and the corrosion protection. Auxiliaries which are particularly advantageous for this purpose are
30 oxyethylates of the formula V



in which R^s is C_{10} - C_{22} alkyl, C_{10} - C_{22} alkenyl or alkylphenyl having a total of 10 to 20 carbon atoms and p is a number from 2 to 10.

35 Fatty acid alkanolamides of the formula VI

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VI

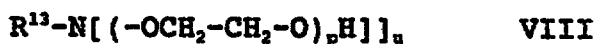
in which R^9 is $C_{10}-C_{22}$ alkyl or $C_{10}-C_{22}$ alkenyl and R^{10} and R^{11} are identical or different and are hydrogen or hydroxy-(C_1-C_6)-alkyl, in particular 2-hydroxyethyl or
 5 2-hydroxypropyl, can also be employed as auxiliaries. Further suitable auxiliaries are ether-carboxylic acids of the formula VII



in which

10 R^{12} is a branched or unbranched, saturated or unsaturated C_8-C_{22} alkyl or C_8-C_{22} alkenyl radical and q and r independently of one another can assume values from 0 to 10, with the proviso that the sum of q and r is at least 1 and X is hydrogen or an alkali metal atom or alkaline
 15 earth metal atom.

Auxiliaries which are likewise suitable are alkoxyated primary amines of the formula VIII



in which

20 R^{13} is $C_{12}-C_{20}$ -alkyl, or alkenyl, preferably $C_{16}-C_{18}$ -alkyl,
 p is a number from 2 to 10, preferably 4 to 6, and
 u is the number 1 or 2, with the proviso that if u is 1 a hydrogen atom is located on the free bond of the nitrogen atom.

25 Other suitable auxiliaries are also fatty acid polyglycol esters, in particular of saturated or unsaturated fatty acids having 10 to 22 carbon atoms in the alkyl chain and 1 to 10 ethylene oxide units, such as oleic acid having 4 to 6 ethylene oxide units. The formulations in general
 30 comprise these auxiliaries individually or in mixtures in amounts of in each case about 20 to 40 % by weight. The formulations for this purpose furthermore can comprise

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customary additives, such as foam suppressants or suitable preservatives.

The terms used below for characterization, such as acid number, amine number, base nitrogen and iodine color number, are determined or ascertained as follows:

Determination of the acid number:

To determine the acid number, stated in mg of KOH/g of substance, 0.1 to 0.5 g of the sample is weighed into a 150 ml glass beaker and dissolved in 60 to 80 ml of ethanol and the solution is titrated with 0.1 N ethanolic potassium hydroxide solution. The end point is indicated potentiometrically (apparatuses: Metrohm Titroprocessor 682, Dosimat 665 with combined pH glass electrode).

Ascertaining the base nitrogen and the amine number:

To ascertain the base nitrogen, stated in % of N, 0.1 to 0.5 g of the sample is weighed into a 150 ml glass beaker and dissolved in 60 to 80 ml of glacial acetic acid and the solution is titrated with 0.1 N perchloric acid in glacial acetic acid. The end point is indicated potentiometrically (apparatuses: Metrohm Titroprocessor 682, Dosimat 665 with combined pH glass electrode).

The amine number, stated in mg of KOH/g of substance, is calculated from the value for the base nitrogen from the formula:

$$\text{amine number [mg of KOH/g]} = \% \text{ of base N} \times 5.61/0.140067$$

The iodine color number denotes the concentration of free iodine in an iodine/potassium iodide solution (in mg of iodine per 100 ml of iodine/potassium iodide solution) and serves to characterize the color or transparency of this solution and liquids of a similar type. The basis for the determination of the iodine color number is the iodine color scale (comparison tubes). Literature:

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DIN 53403.

The following embodiment examples illustrate the present invention without limiting it:

Examples:

5 Example 1

Preparation of $C_{12/14}$ -alkenylsuccinic acid 3-butoxypropyl-half-amide triethanolammonium salt

10 A mixture of 127.5 g (1.0 mol) of 3-n-butoxypropylamine, 149.1 g (1.0 mol) of triethanolamine and 30 g of water was initially introduced into a 1 l three-necked flask with a stirrer, internal thermometer and reflux condenser, and 279.2 g (hydrolysis number: 401.9 mg of KOH/g; 1 mol) of technical grade $C_{12/14}$ -alkenylsuccinic acid anhydride (chain distribution of the starting olefin mixture: 65 % by weight of dodecene, 35 % by weight of tetradecene) were metered in over a period of 0.5 hours (exothermic reaction). The internal temperature was limited to not more than 50°C by periodic cooling. When the addition had ended, the mixture was subsequently stirred at 50°C for a further 2 hours. At this point in time, the reaction mixture contained about 67 % of $C_{12/14}$ -alkenylsuccinic acid 3-n-butoxypropyl-half-amide triethanolammonium/3-butoxypropylammonium salt and about 33 % of $C_{12/14}$ -alkenylsuccinic acid triethanolamine ester 3-n-butoxypropylammonium/triethanolammonium salt (determined by base N determination).

20 The reaction mixture was rendered alkaline by addition of 48 g (0.6 mol) of a 50 % strength sodium hydroxide solution. 642.1 g of a pale brown-yellow liquid having an iodine color number of 30 to 40, an amine number (determined potentiometrically) of 171 mg of KOH/g, an acid number of 46 mg of KOH/g and a viscosity of 1.9 Pas (Brookfield, 28°C, 10 revolutions per minute) were obtained.

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Example 2

Preparation of $C_{12/14}$ -alkenylsuccinic acid 3-methoxypropyl-half-amide triethanolammonium salt

44.6 g (0.5 mol) of 3-methoxypropylamine were initially
5 introduced into the apparatus described in Example 1 at
30°C and 139.6 g (hydrolysis number: 401.9 mg of KOH/g;
0.5 mol) of technical grade $C_{12/14}$ -alkenylsuccinic acid
anhydride (chain distribution of the starting olefin
10 mixture: 65 % by weight of dodecene, 35 % by weight of
tetradecene) were added dropwise in the course of
30 minutes (exothermic reaction), the internal
temperature being kept at not more than 50°C by periodic
cooling. When the addition had ended, the mixture was
subsequently stirred at 50°C for a further 2 hours
15 (conversion according to control of the base N > 98 %) and
was neutralized by addition of 74.5 g (0.5 mol) of
triethanolamine. Finally, the reaction mixture was
rendered alkaline by addition of 39 g of a 30 % strength
sodium hydroxide solution (pH (1 % in demineralized
20 water): 8.4). 296 g of a dark yellow liquid having an
iodine color number of 20, an amine number (potentio-
metric determination) of 151 mg of KOH/g and an acid
number of 50.6 mg of KOH/g were obtained.

Example 3

25 Preparation of $C_{12/14}$ -alkenylsuccinic acid 3-butoxypropyl-amide methyldiethanolammonium salt

55.8 g (0.2 g) of technical grade n- $C_{12/14}$ -alkenylsuccinic
acid anhydride were added dropwise to a mixture of 25.5 g
(0.2 mol) of 3-butoxypropylamine, 23.8 g (0.2 mol) of N-
30 methyl-diethanolamine and 6 g of demineralized water in
the course of 30 minutes, starting at 30°C (exothermic
reaction), the internal temperature being kept at 50°C by
periodic cooling, and the mixture was subsequently
stirred at 50°C for 2 hours. At this point in time, the

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reaction mixture contained, according to analysis (base N) about 86 % of n-C_{12/14}-alkenylsuccinic acid 3-butoxypropyl-half-amide triethanolammonium/3-butoxypropylammonium salt and about 14 % of n-C_{12/14}-alkenylsuccinic acid triethanolamine ester 3-butoxypropylammonium/triethanolammonium salt. When the reaction had ended, the mixture was rendered alkaline with 9.6 g of 50 % strength sodium hydroxide and 119.1 g of a yellowish viscous liquid having an iodine color number of 20, an amine number of 168 mg of KOH/g and an acid number of 51 mg of KOH/g were thus obtained.

Example 4

Preparation of C_{12/14}-alkenylsuccinic acid 3-methoxypropylamide triethanolammonium salt

3-Methoxypropylamine was added dropwise to 139.8 g (0.5 mol) of n-C_{12/14}-alkenylsuccinic acid anhydride in the course of 0.5 hours, with periodic cooling, such that the internal temperature did not exceed 50°C, and the mixture was subsequently stirred for 1 hour and neutralized with a mixture of 75.6 g of triethanolamine and 14.2 g of water to give, after post-reaction for 1 hour at 50°C, a reaction mixture having a half-amide/ester ratio of 93.7 (analysis by base N). After the mixture had been rendered alkaline with 24 g of 50 % strength sodium hydroxide solution, 291.6 g of a dark yellow liquid having an amine number of 160 mg of KOH/g, an acid number of 46 mg of KOH/g and a viscosity of 2.3 Pas were obtained.

Example 5

Preparation of tripropylsuccinic acid 3-methoxypropylamide triethanolammonium salt

111.5 g (0.5 mol) of technical grade tripropenylsuccinic anhydride were added dropwise to a mixture of 44.6 g (0.5 mol) of 3-methoxypropylamine, 74.5 g (0.5 mol) of

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triethanolamine and 13.6 g of water in the course of 0.5 hours, starting at 30°C, with periodic cooling, such that the internal temperature did not exceed 50°C, and the mixture was then subsequently stirred at this temperature for a further 2 hours. At this point in time, the reaction mixture contained about 63 % of half-amide and 37 % of half-ester. After the mixture had been rendered alkaline with 24 g of 50 % strength sodium hydroxide solution, 266.2 g of a pale yellow viscous liquid having an amine number of 206 mg of KOH/g and an acid number of 56 mg of KOH/g were obtained.

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Table 1: Applications properties of alkenylsuccinic acid
3-alkoxypropylamides

Example	1	2	3	4	5
Appearance of 3 % strength aqueous solutions: distilled water immediately after 24 hrs	clear clear	clear trans- parent	clear clear	clear clear	clear clear
Foam height ¹⁾ immediately after 5 mins	> 50 > 50	> 50 > 50	> 50 > 50	> 50 20	> 50 12
20°dH immediately after 24 hrs Foam height ¹⁾ immediately after 5 mins	clear clear > 50 3	trans- parent trans- parent 50 45	clear clear > 50 > 50	clear clear > 50 trace of marginal foam	cloudy cloudy 45 2
Corrosion protection a.) Herbert test (DIN 51360/1) distilled H ₂ O 1.0 % 20°dH 3.0 % b.) Filter paper test (DIN 51360/2) distilled H ₂ O 1.5 % 20°dH 3.0 %	RO/50 RO/50 0 0	RO/50 RO/50 1 0	RO/50 RO/50 0 0	RO/50 RO/50 0 0	RO/50 RO/50 1 0
Emulsifiability	spon- taneous	spon- taneous	spon- taneous	spon- taneous	spon- taneous

Notes on Table 1:

- 1) To determine the foaming properties, in each case 50 ml of 3 % strength aqueous solutions of the test products were introduced into a graduated 100 ml measuring cylinder and the cylinder was closed with a glass stopper and shaken vigorously 20 x in the horizontal direction. The evaluation was carried out after the waiting periods stated by measuring the amount of foam in ml.

Information on the test procedure:

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The tests were carried out on formulations comprising:

- 18 % of emulsifier mixture
- 4 % of nonylphenol ethoxylate
- 2 % of water
- 5 78 % of naphthene-based mineral oil

Emulsifier mixture:

- 37 % of product according to the example
- 32 % of oleyl alcohol + 2EO (ethylene oxide)
- 31 % of tall oil fatty acid diethanolamide

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Patent claims:

1. A salt of an alkenylsuccinic acid alkoxyalkyl-half-amide of the formula Ia or Ib

Ia

Ib



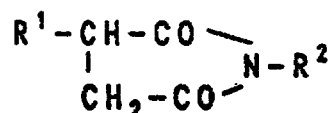
- 5 if appropriate as a mixture with a salt of an alkenylsuccinic acid half-ester amine of the formula IIa or IIb

IIa

IIb



and/or an alkenylsuccinic acid imide of the formula III



III

in which

- 10 R^1 is $\text{C}_6\text{-C}_{30}$ -alkenyl or $\text{C}_6\text{-C}_{30}$ -alkyl, preferably $\text{C}_6\text{-C}_{18}$ -alkenyl or $\text{C}_6\text{-C}_{18}$ -alkyl, in which R^1 can be straight-chain or branched;
 R^2 is $-(\text{CH}_2)_n\text{-O-(A)}_m\text{-R}^3$, where
A is $-\text{CH}_2\text{-CH}_2\text{-O-}$ or $-\text{CH(R}^4\text{)-CH}_2\text{-O-}$, in which
15 R^3 is $\text{C}_1\text{-C}_{18}$ -alkyl, and in which R^3 can be straight-chain or branched,
 R^4 is hydrogen or methyl,
n is a number from 1 to 6,
m is a number from 0 to 8 and
20 M^+ is an alkali metal or alkaline earth metal cation

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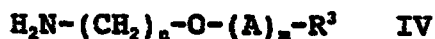


or an ammonium ion of the formula $\text{HNR}^5\text{R}^6\text{R}^7$, in which R^5 , R^6 and R^7 are identical or different and are hydrogen, $\text{C}_1\text{-C}_6\text{-alkyl}$ or hydroxy- $(\text{C}_1\text{-C}_6)\text{-alkyl}$,

5 in particular
2-hydroxyethyl and 2-hydroxypropyl.

2. A compound as claimed in claim 1, wherein a salt of an alkenylsuccinic acid half-ester amide of the formula IIa or IIb and an alkenylsuccinic acid imide of the formula III are present in a concentration of up to 40 % by weight, preferably up to 20 % by weight, as a mixture with a salt of an alkenylsuccinic acid alkoxyalkyl-half-amide of the formula Ia or Ib.

10 3. A process for the preparation of a salt of an alkenylsuccinic acid alkoxyalkyl-half-amide of the formula Ia or Ib, if appropriate as a mixture with a salt of an alkenylsuccinic acid half-ester amine of the formula IIa or IIb and/or an alkenylsuccinic acid imide of the formula III, which comprises reacting an alkenylsuccinic acid anhydride with an alkoxyalkylamine of the formula IV



in which

25 R^3 is $\text{C}_1\text{-C}_{18}\text{-alkyl}$, in which R^3 can be straight-chain or branched,

n is a number from 1 to 6 and

m is a number from 0 to 8,

30 in a molar ratio of 1 : 0.7 to 2.5, preferably 1 : 0.8 to 1.2, at temperatures of 20 to 120°C, preferably 60 to 100°C, and carrying out this reaction in the presence of an amount of base which is equimolar to the alkoxyalkylamine of the formula IV, or adding an amount of base equimolar to the alkoxyalkylamine of the formula IV after the

35



reaction.

4. The process as claimed in claim 3, wherein an alkali metal hydroxide, alkaline earth metal hydroxide, alkanolamine of the formula $\text{NR}^5\text{R}^6\text{R}^7$ or a mixture thereof is employed as the base.
5. The process as claimed in claim 3, wherein 2-hydroxyethylamine and/or 2-hydroxypropylamine are employed as the alkoxyalkylamine of the formula IV.
6. An aqueous or oil-containing formulation for working metals, in particular for use as a cooling lubricant, which comprises a salt of an alkenylsuccinic acid alkoxyalkyl-half-amide of the formula Ia or Ib, if appropriate as a mixture with a salt of an alkenylsuccinic acid half-ester amine of the formula IIa or IIb and/or an alkenylsuccinic acid imide of the formula III, as claimed in claim 1.
7. A formulation as claimed in claim 6, which comprises a compound as claimed in claim 1 in a concentration of 10 to 80 % by weight.
8. An aqueous or oil-containing metalworking fluid for working metals, in particular for use as a cooling lubricant, which comprises a salt of an alkenylsuccinic acid alkoxyalkyl-half-amide of the formula Ia or Ib, if appropriate as a mixture with a salt of an alkenylsuccinic acid half-ester amine of the formula IIa or IIb and/or an alkenylsuccinic acid imide of the formula III, as claimed in claim 1.
9. An aqueous and/or oil-containing metal working liquid as claimed in claim 8, which comprises compounds as claimed in claim 1 in a concentration of 0.1 to 10 % by weight, preferably 2 to 10 % by

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weight.

10. A formulation as claimed in claim 6, which comprises as additional auxiliaries an oxyethylate of the formula V



in which R^8 is C_{10} - C_{22} -alkyl, C_{10} - C_{22} alkenyl or alkylphenyl having a total of 10 to 20 carbon atoms and p is a number from 2 to 10, and/or a fatty acid alkanolamide of the formula VI

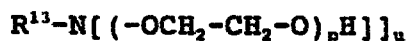


in which R^9 is C_{10} - C_{22} -alkyl or C_{10} - C_{22} -alkenyl and R^{10} and R^{11} are identical or different and are hydrogen or hydroxyl- (C_1-C_6) -alkyl, in particular 2-hydroxyethyl or 2-hydroxypropyl, and/or

15 an ether-carboxylic acid of the formula VII



20 in which R^{12} is a branched or unbranched, saturated or unsaturated C_8 - C_{22} -alkyl or C_8 - C_{22} -alkenyl radical and q and r independently of one another have values from 0 to 10, with the proviso that the sum of q and r is at least 1, and X is hydrogen, an alkali metal atom or an alkaline earth metal atom, an alkoxylated primary amine of the formula VIII



25 in which

R^{13} is C_{12} - C_{20} -alkyl, or alkenyl, preferably C_{16} - C_{18} -alkyl,

p is a number from 2 to 10, preferably 4 to 6, and

30 u is the number 1 or 2, with the proviso that if u is 1, a hydrogen atom is located on the free bond

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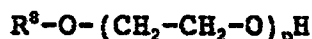
of the nitrogen atom,
and/or

5 a fatty acid polyglycol ester, in particular of a saturated or unsaturated fatty acid having 10 to 22 carbon atoms in the alkyl chain and 1 to 10 ethylene oxide units, preferably oleic acid having 4 to 6 ethylene oxide units.

11. A formulation as claimed in claim 10, which comprises the auxiliaries in a concentration of 20 to 10 40 % by weight.

12. A formulation as claimed in claim 6, which comprises a foam suppressant and/or preservative.

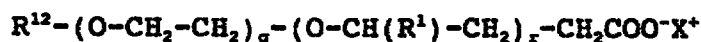
13. A metalworking fluid as claimed in claim 8, which comprises as additional auxiliaries an oxyethylate 15 of the formula V



in which R^8 is C_{10} - C_{22} -alkyl, C_{10} - C_{22} alkenyl or alkylphenyl having a total of 10 to 20 carbon atoms and p is a number from 2 to 10, and/or a fatty acid 20 alkanolamide of the formula VI



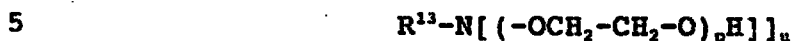
in which R^9 is C_{10} - C_{22} -alkyl or C_{10} - C_{22} -alkenyl and R^{10} and R^{11} are identical or different and are hydrogen or hydroxyl-(C_1 - C_6)-alkyl, in particular 2-hydroxy- 25 ethyl or 2-hydroxypropyl, and/or an ether-carboxylic acid of the formula VII



in which R^{12} is a branched or unbranched, saturated or unsaturated C_6 - C_{22} -alkyl or C_6 - C_{22} -alkenyl radical 30 and q and r independently of one another have values



from 0 to 10, with the proviso that the sum of q and r is at least 1, and X is hydrogen, an alkali metal atom or an alkaline earth metal atom, an alkoxyated primary amine of the formula VIII



in which

R^{13} is C_{12} - C_{20} -alkyl, or alkenyl, preferably C_{16} - C_{18} -alkyl,

10 p is a number from 2 to 10, preferably 4 to 6, and u is the number 1 or 2, with the proviso that if u is 1, a hydrogen atom is located on the free bond of the nitrogen atom,

and/or

15 a fatty acid polyglycol ester, in particular of a saturated or unsaturated fatty acid having 10 to 22 carbon atoms in the alkyl chain and 1 to 10 ethylene oxide units, preferably oleic acid having 4 to 6 ethylene oxide units.

14. 20 The use of a salt of an alkenylsuccinic acid alkoxy-alkyl-half-amide of the formula Ia or Ib, if appropriate as a mixture with a salt of an alkenylsuccinic acid half-ester amine of the formula IIa or IIb and/or an alkenylsuccinic acid imide of the formula III as a metalworking auxiliary, in particular as an anticorrosion agent and emulsifier in 25 an aqueous and/or oil-containing formulation or metalworking auxiliary.

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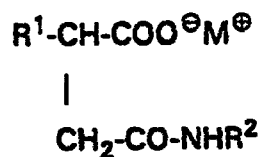
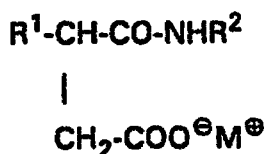
Abstract

Alkenylsuccinic acid derivatives as metalworking auxiliaries

The present invention relates to salts of alkenylsuccinic
5 acid alkoxyalkyl-half-amides of the formula Ia and/or Ib

Ia

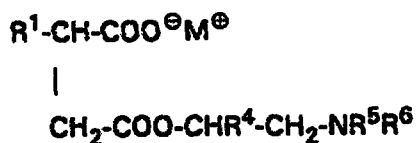
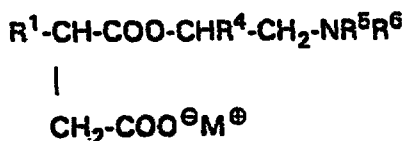
Ib



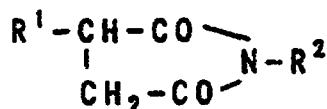
if appropriate as a mixture with salts of alkenylsuccinic
acid half-ester amines of the formula IIa and/or IIb

IIa

IIb



and/or alkenylsuccinic acid imides of the formula III



10 in which R¹, R², A, R³, R⁴, n, m and M^o have the meaning
given in the description.

The invention also relates to a process for the prepara-
tion of salts of alkenylsuccinic acid alkoxyalkyl-half-
amides of the formula Ia and/or Ib, if appropriate as a
mixture with salts of alkenylsuccinic acid half-ester
15 amines of the formula IIa and IIb and/or alkenylsuccinic
acid imides of the formula III, which comprises reacting
alkenylsuccinic acid anhydrides with alkoxyalkylamines of
the formula IV

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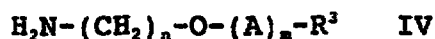


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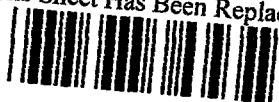
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in which R^3 , n , m and A have the meaning given in the description, and carrying out this reaction in the presence of an amount of base equimolar to the alkoxy-
5 alkyamines of the formula IV, or adding an amount of base equimolar to the alkoxyalkylamines of the formula IV after the reaction.

The invention furthermore relates to aqueous and/or oil-containing formulations for working metals, which
10 comprise the abovementioned salts of alkenylsuccinic acid alkoxyalkyl-half-amides of the formula Ia and/or Ib, if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formula IIa and/or IIb and/or alkenylsuccinic acid imides of the formula III,
15 and their use as anticorrosion agents, cooling lubricants and metalworking auxiliaries.

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TEXT OF THE ABSTRACT

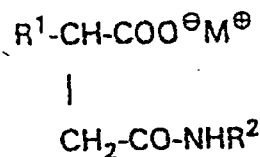
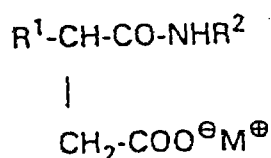
ALKENYLSUCCINIC ACID DERIVATIVES AS METALWORKING AUXILIARIES

Alkenylsuccinic acid derivatives as metalworking auxiliaries

The present invention relates to salts of alkenylsuccinic acid alkoxyalkyl-half-amides of the formula Ia and/or Ib

Ia

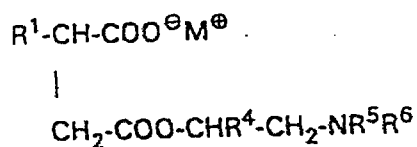
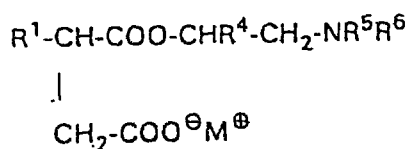
Ib



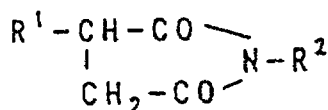
if appropriate as a mixture with salts of alkenylsuccinic acid half-ester amines of the formula IIa and/or IIb

IIa

IIb



and/or alkenylsuccinic acid imides of the formula III



in which R¹, R², A, R³, R⁴, n, m and M^{*} have the meaning given in the description.

The invention furthermore relates to aqueous and/or oil-containing formulations for working metals, which comprise the abovementioned salts and their use as anticorrosion agents, cooling lubricants and metalworking auxiliaries.

