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(54) **COMPOSITION COMPRISING 2-ALKYL CARBOXYLIC ACID SALTS AND USE THEREOF AS ANTI-CORROSION ADDITIVE**

(57) The present invention concerns a composition comprising a 2-alkyl carboxylic acids salts and an oil component and optionally water as well as the use of 2-alkyl carboxylic acids salts as an anti-corrosion additive, in particular in aqueous metal working fluids.

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Description**Introduction**

[0001] The present invention relates to a composition comprising at least a 2-alkyl carboxylic acids salts and an oil component. Further the use of 2-alkyl carboxylic acids salts as anti-corrosion additive is disclosed such as in aqueous metal working fluids.

Background of the Invention

[0002] In the past one of the most commonly used acids for the purpose of providing anti-corrosion properties in metalworking fluid formulations was boric acid. Boric acid is an easily available and cheap compound. In recent years however, boric acid came under attack as a potential hazard to human, animal and plant health. The compound was subsequently classified as a Substance of Very High Concern (SVHC) by the EU. A need therefore exists in the marketplace to find alternatives for boric acid.

[0003] Carboxylic acids and carboxylic acid salts are widely used in metalworking fluids, biofuels and general lubricant application for a great variety of very different purposes depending on the structure such as emollients, anticorrosion additives, raw materials for esters, coupling agents, antimicrobial agent (see EP 0742004B1 or DE 19516705 A1), and detergency and lubricity improvers.

[0004] Carboxylic acid salts including long carbon chain carboxylic acid salts, are compounds obtained by the neutralisation of the corresponding organic acids with, for example, amines, alkanolamines or sodium compounds. The organic acids may comprise linear, branched, cyclic or aromatic hydrocarbyl groups. US 5507861 for example teaches the use of odd-numbered, monocarboxylic acids in corrosion inhibiting compositions. US 4588513 describes the use of dicarboxylic acids or salts thereof as corrosion inhibitors and US 8168575 discloses neutralised fatty acid salts, both linear and branched, as anti-staining agents for non-ferrous metals, with no reference to anti-corrosion properties.

[0005] There exists, however, a continuing need to develop corrosion inhibitors that are superior to the well-known corrosion inhibitors in particular in aqueous compositions for metalworking, lubricants or fuels.

Summary of the Invention

[0006] The object of the present invention is to provide compositions for metalworking fluids, lubricants and fuels as lubricity, emulsification, detergency and anticorrosion. In particular, this invention relates to compositions comprising neutralised or partially neutralised 2-alkyl branched carboxylic acids comprising in total 10 or 11 carbon atoms and their uses as lubricity improver, anticorrosion additive, emollient, and/or detergency improver.

[0007] The present invention is defined by the subject matter of the independent claims. Preferred embodiments are subject matter of the dependent claims or disclosed herein below.

[0008] The composition according to the invention comprises

- (a) at least one 2-alkyl branched carboxylic acid having in total 10 or 11 carbon atoms partially or completely neutralised by a neutralising agent and
- (b) an oil component

wherein the ratio between (a), calculated as 2-alkyl branched carboxylic acid, and (b) is 1 to 2 and higher (weight/weight) such as 1 to 4 to 1 : 200.

[0009] 2-alkyl branched carboxylic acids comprise only one branching. The alkyl group is a methyl, ethyl, propyl or butyl group. Preferred are 2-alkyl branched carboxylic acids salts that are mixtures of the respective salts with at least three of the following alkyl groups: methyl, ethyl, propyl or butyl branches.

[0010] The 2-alkyl branched carboxylic acids of the present invention may be used in mixtures comprising also linear fatty acid salts. It was surprisingly found that compositions comprising 2-alkyl-branched carboxylic acid salts with 10 or 11 carbon atoms exhibit significantly enhanced anticorrosion and wetting abilities when compared to the state of the art linear carbon chain fatty acid salts.

[0011] The specific nature of the branching of the carbon chains described for the compounds illustrated by the invention was shown to provide a significant benefit.

[0012] The compounds described for the current invention contain 2-alkyl branching, or mixtures of these branched compounds together with linear compounds, with no quaternary carbons present. This property provides specific advantages with regard to biodegradability.

[0013] The compounds disclosed in the invention also perform significantly better with regard to corrosion inhibition when compared to the current state of the art linear and geminally-branched fatty acid salts. Furthermore, it was sur-

prisingly found that the compositions of the invention provide enhanced corrosion inhibition properties even in neutral pH environments such as pH 7 to 8.

[0014] The compositions described herein can contain no or little amounts of water (concentrates) or after dilution substantial amounts of water.

[0015] According to one embodiment the composition comprises

(a) 0.05 to 5 weight %, preferably 0.5 to 2.5 weight %, of the partially or completely neutralised 2-alkyl branched carboxylic acid;

(b) 1 to 15 wt.%, preferably 2 to 10 wt.% of the oil component; and

(c) 70 to 99 wt.%, preferably 85 to 98 wt.% water.

[0016] In case the 2-alkyl carboxylic acids (or their salts) are mixed with linear or midchain branched carboxylic acids (or their salts), such as C8- to C22- fatty acids, the 2-alkyl branched carboxylic acids represent from 40 to 100 weight percent of the total mixture, each calculated relative to the carboxylic acid.

[0017] The fatty acids or fatty acid mixtures are neutralised by neutralising agents such as amines, alkanolamines and caustic compounds. The neutralising agent is selected from the group consisting of an alkali metal or an amine, including an alkanol amine or an alkane amine, and mixtures thereof. Partially means for example that more than 90% or more than 98% of the acid groups are neutralized.

[0018] The compounds described by the present invention do not contain any quaternary carbons, which leads to the added advantage of good biodegradability properties above the prior art compounds such as neodecanoic acid salts.

[0019] The compounds were surprisingly found to display excellent anticorrosion behaviour in an pH environment between 7 and 11, particularly and unexpectedly in the neutral pH range, as well as enhanced wetting properties when compared to the state of the art.

[0020] Other features and advantages of the present invention will become apparent from the following experimental part.

Experimental Part

[0021] The following acids were used for evaluation purposes or as comparative examples:

Table 1

ISOCARB 11	Branched undecanoic acids (mixture of 2-butylheptanoic acid, 2-propyloctanoic acid, 2-ethylnonanoic acid, 2-methyldecanoic acid)
Undecanoic Acid	Linear undecanoic acid
ISOCARB L11	Mixture of linear undecanoic acid (50%) and ISOCARB 11 (50%)
Versatic Acid	Neo-decanoic acid
MARLOWET 4539	Isononanol, ethoxylated and propoxylated (>2.5 EO/PO) and carboxymethylated
MARLOWET 4541	Alcohols, C12-14 (even numbered), ethoxylated (>2.5 moles EO) and carboxymethylated
CORFREE M1	Mixture of undecanoic acid, dodecanoic acid and sebacic acid
IRGACOR L 190 Plus	(2,4,6-Tri-(6-aminocaproic acid)-1,3,5-triazine)

[0022] The following - non-limiting examples and results will illustrate the preparation and test methods followed and demonstrate the advantages obtained.

Anti-corrosion behaviour:

[0023] The test method DIN 51360 part 2 was used for all examples to determine the anti-corrosion behaviour of the different acid salt solutions.

Example 1:

[0024] The acids evaluated (see table 2) were neutralised to a pH value of 8 with monoethanolamine (MEA) to form the corresponding active salts. Hard water (see preparation method in DIN 51360 part 2) was used to prepare dilutions of 2 weight %. Dry-turned grey cast iron flakes were put on a circular filter paper and soaked with 2 ml of the diluted sample solution. After 2 hours, the corrosion grade on the filter paper was evaluated according to the guidelines provided

in the test method (DIN 51360 part 2).

Table 2:

	Acid [weight %]	Active Salt [pH]	Corrosion Grade after 2 h
ISOCARB L11 (branched + linear)	2	8	0
Neodecanoic acid (branched)	2	8	4
Marlowet 4539 (linear)	2	8	4
Marlowet 4541 (linear)	2	8	4
ISOCARB 11 (branched)	2	8	0
Undecanoic acid (linear)	2	8	2

[0025] It is clear that, under pH 8 conditions, the solutions containing the 2-alkyl branched carbon chain ISOCARB 11 MEA salt as well as the 50:50 branched : linear ISOCARB L11 salts, showed superior anti-corrosion performance when compared to the MARLOWET 4539, MARLOWET 4541 or undecanoic acid MEA salt as well as the geminally-branched neodecanoic acid MEA salt.

Example 2:

[0026] ISOCARB 11 (100% branched) and undecanoic acid (100% linear) were neutralised to pH values of 8, 8.5 and 9 respectively with monoethanolamine (MEA) to form the corresponding active salts. Hard water (see preparation method in DIN 51360 part 2) was used to prepare dilutions of 1, 1.5 and 2 weight%. Dry-turned grey cast iron flakes were put on circular filter papers and soaked with 2 ml of the diluted sample solutions. After 2 hours, the corrosion grade on the filter papers were evaluated according to the guidelines provided in the test method (DIN 51360 part 2).

Table 3:

Active salt [weight %]	Corrosion grade after 2 hours					
	pH 8		pH 8.5		pH 9	
	(A)	(B)	(A)	(B)	(A)	(B)
1.5	1	2	0	3	0	4
2	0	2	0	2	0	2
(A) = ISOCARB 11 (branched) / (B) = Undecanoic acid (linear)						

[0027] The 2-alkyl-branched ISOCARB 11 MEA salt showed enhanced corrosion inhibiting behaviour when compared to the linear undecanoic acid MEA salt at the various dilutions prepared, as well as at the three pH values evaluated.

Example 3:

[0028] The acids evaluated were neutralised to various pH values (see table 4) with monoethanolamine (MEA) to form the corresponding active salts. Hard water (see preparation method in DIN 51360 part 2) was used to prepare dilutions of one weight%.

[0029] Dry-turned grey cast iron flakes were put on a circular filter paper and soaked with 2 ml of the diluted sample solution. After 2 hours, the degree of staining on the filter paper was evaluated according to the guidelines provided in the test method (DIN 51360 part 2).

Table 4:

	Corrosion Grade after 2 hours			
	pH 7.3	pH 8.2	pH 8.7	pH 9.0
ISOCARB 11 (branched)	0	-	-	0
Neodecanoic acid (branched)	-	-	4	3
CORFREE M1 (linear)	-	-	-	4
IRGACORL 190 Plus (branched)	-	4	-	1

[0030] These experiments clearly show enhanced corrosion inhibiting properties for the 2-alkyl branched ISOCARB

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11 MEA salt when compared to the geminally-branched neodecanoic acid MEA salt at the pH values evaluated. In addition, comparison of the ISOCARB 11 salt with two industry-accepted standards (linear CORFREE M1 and linear IRGACORL 190 Plus) MEA salts clearly demonstrate the advantage of the claimed invention.

Example 4:

[0031] The acids evaluated were neutralised to various pH values (see table 5) with monoisopropanolamine (MIPA) to form the corresponding active salts. Hard water (see preparation method in DIN 51360 part 2) was used to prepare dilutions of 1 weight%.

[0032] Dry-turned grey cast iron flakes were put on a circular filter paper and soaked with 2 ml of the diluted sample solution. After 2 hours, the degree of staining on the filter paper was evaluated according to the guidelines provided in the test method (DIN 51360 part 2).

Table 5:

	Corrosion Grade after 2 hours		
	pH 8.1	pH 8.4	pH 9.1
ISOCARB 11 (branched)	-	1	0
CORFREE M1 (linear)	4	-	1
IRGACORL 190 Plus (branched)	-	4	3

[0033] The one weight % dilutions of fatty acid MIPA salts were prepared and the results clearly show enhanced corrosion inhibiting properties of the 2-alkyl branched ISOCARB 11 salts when compared to the two industry-accepted standards (linear CORFREE M1 and linear IRGACORL 190 Plus).

Example 5:

[0034] The acids evaluated were neutralised to different pH values (see table 6) with monoisopropanolamine (MIPA) to form the corresponding active salts. Hard water (see preparation method in DIN 51360 part 2) was used to prepare dilutions of 2 weight%.

[0035] Dry-turned grey cast iron flakes were put on a circular filter paper and soaked with 2 ml of the diluted sample solution. After 2 hours, the degree of staining on the filter paper was evaluated according to the guidelines provided in the test method (DIN 51360).

Table 6:

	Corrosion Grade after 2 hours	
	pH 8.0	pH 8.2
ISOCARB 11 (branched)	-	0
CORFREE M1 (linear)	-	1
IRGACORL 190 Plus (branched)	4	-

[0036] In this case, two weight % dilutions of fatty acid MIPA salts were prepared. The results again show promising corrosion inhibiting properties for 2-alkyl branched ISOCARB 11 and ISOCARB 12 MIPA salts, when compared to the two industry-accepted standards (linear CORFREE M1 and branched IRGACORL 190).

Example 6:

[0037] Table 7 shows a metalworking fluid formulation package (emulsifiable concentrate) based on mineral oil.

Table 7:

Component	[% weight]	Function
Mineral Oil	51	Base oil
Methyl Ester Sulphurized	10	Extreme Pressure (EP) additive

(continued)

	Component	[% weight]	Function
	MARLON OS 85	10	Emulsifier
5	Petroleum sulphonate Na salt	5	Surfactant
	MARLOX RT 42	4	Coupling agent
	ISOCARB 11	4	Anticorrosion and Stabiliser
	Di Ethanol Amine	12	Alkaline agent
10	DIONIL TR 23	0.5	Defoamer
	EDTA	0.5	Calcium sequestering agent
	Oxazolidine	3	Preservative
	(total)	100	
15	(with MARLON OS 85 = MIPA LAS, MARLOX RT 42 = Alkyl Polyglycol Ether, DIONIL TR 23 = Hexanol-Alkoxyat (2EO + 3PO))		

Claims

- 20 1. A composition comprising
- (a) at least one 2-alkyl branched carboxylic acid having in total 10 or 11 carbon atoms partially or completely neutralised by a neutralising agent and
- 25 (b) an oil component.
- wherein the ratio between (a), calculated as 2-alkyl branched carboxylic acid, and (b) is 1 to 2 and higher (w/w).
2. The composition of claim 1 wherein the 2-alkyl branched carboxylic acid has in total 11 carbon atoms.
- 30 3. The composition of at least one of the preceding claims wherein the alkyl group in the 2-alkyl branched carboxylic acid is one or more of methyl, ethyl, propyl and butyl, preferably a mixture of methyl, ethyl, propyl and butyl.
4. The composition of at least one of the preceding claims wherein the neutralising agent is selected from the group consisting of an alkali metal or an amine, including an alkanol amine or an alkane amine, and mixtures thereof,
- 35 wherein the amine preferably comprises one, two or three groups selected independently from each other from the group consisting of linear or branched alkyl groups and linear or branched hydroxy-alkyl groups, each having 1 to 6 carbon atoms, preferably 2 to 4 carbon atoms.
5. The composition of at least one of the preceding claims wherein the oil component is a selected from one or more of:
- 40 - hydrocarbons,
- triglyceride esters of C8- to C24- carboxylic acids, in particular C12- to C18-carboxylic acids,
- di-, tri- or polyhydroxy compounds, including polyhydroxy compounds having ether groups, partially or completely esterified with a C6- to C32-carboxylic acid and/or a C6- to C32-hydroxy carboxylic acid,
45 - a C10- to C15- alkylbenzoates,
- a di(C6-C20)ethers,
- esters (>C20), and
- silicon oils, in particular polydimethyl siloxane,
preferably with a viscosity of from 10 to 12500 cSt at 25°C, most preferably from 10 to 350 cSt., each at 25°C.
- 50 6. The composition of at least one of the preceding claims comprising
- (a) 0.05 to 5 weight %, preferably 0.5 to 2.5 weight %, of the partially or completely neutralised 2-alkyl branched carboxylic acid;
- 55 (b) 1 to 15 wt.%, preferably 2 to 10 wt.% of the oil component; and
(c) 70 to 99 wt.%, preferably 85 to 98 wt.% water.
7. The composition of at least one of the preceding claims further comprising a surfactant and/or an emollient.

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8. The composition of at least one of the preceding claims further comprising one or more of the following additives: an extreme pressure additive, a calcium sequestering agent and a biocide.

5 9. The composition of at least one of the preceding claims having a pH of 5 to 11, preferably of 6.5 to 9 and most preferably of 7 to 8.

10. Use of the composition of at least one of the preceding claims in metal working, in cutting and non-cutting shaping operations of non-metals, as a lubricant or as a spray-on anticorrosion coating.

10 11. Use of the composition of least one of claims 1 to 9 as a corrosion inhibitor.

12. Use of at least one 2-alkyl branched carboxylic acid having in total 10 or 11 carbon atoms partially or completely neutralised by a neutralising agent

15 a) in an aqueous composition comprising an oil component as a corrosion inhibitor, or
b) in an aqueous composition comprising an oil component in metal working or in cutting and non-cutting shaping operations of non-metals.

20 13. The use of claim 12 wherein the neutralising agent is selected from the group consisting of an alkali metal or an amine, including an alkanol amine or an alkane amine, and mixtures thereof, wherein the amine preferably comprises one, two or three groups selected independently from each other from the group consisting of linear or branched alkyl groups and linear or branched hydroxy-alkyl groups, each having 1 to 6 carbon atoms, preferably 2 to 4 carbon atoms.

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EUROPEAN SEARCH REPORT

Application Number
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Place of search Munich		Date of completion of the search 20 January 2016	Examiner Handrea-Haller, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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