

Corrosion inhibitors having increased biological degradability and minimized toxicity

The present invention relates to a process for inhibiting corrosion on and in devices for extraction and transport of hydrocarbons in mineral oil extraction and processing by adding a salt of a nitrogen base and an N-substituted 5-oxopyrrolidine-3-carboxylic acid to the corrosive system.

In industrial processes in which metals come into contact with water or else with oil-water biphasic systems, there is the risk of corrosion. This is particularly marked when the aqueous phase, as in the case of mineral oil extraction and processing processes, has a high salt content or is acidic as a result of dissolved (acidic) gases such as carbon dioxide or hydrogen sulfide. The exploitation of a deposit and the processing of mineral oil are therefore impossible without specific additives to protect the equipment used.

Although suitable anticorrosives for mineral oil extraction and processing have been known for some time, they will be unacceptable in the future for offshore applications for reasons of environmental protection.

As typical prior art corrosion inhibitors, amides, amidoamines or imidazolines of fatty acids and polyamines have exceptionally good oil solubility and are therefore present only in a low concentration in the corrosive water phase owing to poor partitioning equilibria. Accordingly, these products have to be used in high dosage in spite of their poor biodegradability.

Quaternary alkylammonium compounds (quats) are alternative prior art anticorrosives which, as well as the corrosion-inhibiting properties, may also possess biostatic properties. In spite of an improved water solubility, the quats, for example compared to the imidazolines, exhibit a significantly reduced film persistence and therefore likewise lead to effective corrosion protection only in a relatively high dosage. The high algal toxicity and the moderate biodegradability are restricting the use of quats ever more to ecologically insensitive fields of use.

US-2 757 125 describes salts of N-alkyl-4-carboxy-2-pyrrolidones, which are used as antibacterial components in cosmetic formulations or detergents. The use of these compounds as corrosion inhibitors in the oilfield chemicals sector is not described.

US-2 908 711 and US-3 035 907 describe oil-soluble reaction products of amines or diamines and itaconic acids, which can be used as antirust additives in fuels or mineral oils.

US-3 218 264 discloses oil-soluble pyrrolidonecarboxylic acid-amine salts and the uses thereof as corrosion inhibitors in lubricant oils and greases. The amines used for salt formation are oil-soluble in accordance with the invention.

US-3 224 968 likewise describes oil-soluble amine salts of pyrrolidonecarboxylic acids, which find use as antirust additives in lubricant oils. Again, oil-soluble amines (preferably C₁₂-C₂₀-alkyl-substituted) are used for amine salt formation. US-3 224 975 describes the free pyrrolidonecarboxylic acids for the same use.

GB-A-1 323 061 discloses pyrrolidone derivatives and the use thereof in functional fluids, for example hydraulic fluids. The compounds used have C₁-C₅-alkyl substituents or C₆-C₁₀-aryl substituents on the pyrrolidone nitrogen. In hydraulic fluids, the compounds exhibit anticorrosive properties, also in combination with aliphatic amines.

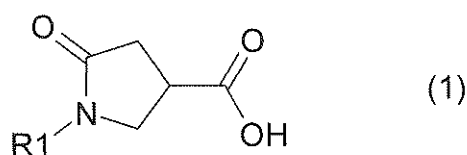
EP-A-0 069 512 describes water-soluble salts of N-substituted 2-pyrrolidone-4-carboxylic acids as humectants.

It was an object of the present invention to find novel corrosion inhibitors which, combined with constant good or improved corrosion protection, and in addition to good water solubility, also give improved biodegradability and lower toxicity compared to the prior art corrosion inhibitors.

It has now been found that, surprisingly, water-soluble or water-dispersible salts of specific cyclic amines and of an N-substituted 5-oxopyrrolidine-3-carboxylic acid exhibit excellent action as corrosion inhibitors, and also good biodegradability and reduced toxicity.

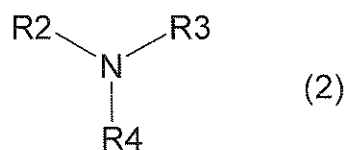
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The invention therefore provides for the use of salts of compounds of the formula (1)



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with amines of the formula (2)



15 in which

R1 is C₈- to C₃₀-alkyl or C₈- to C₃₀-alkenyl

R2 is hydrogen, C₁- to C₆-alkyl or a heteroatom-containing organic radical having 1 to 8 carbon atoms, and

R3, R4 with inclusion of the nitrogen atom form a cycle having 5 to 7 ring

20 atoms, where this cycle, in addition to carbon atoms, may optionally contain an oxygen atom or a nitrogen atom or both,

as water-soluble or water-dispersible corrosion inhibitors.

25 The invention further provides salts of compounds of the formula (1) and amines of the formula (2).

The invention further provides a process for inhibiting corrosion at metal surfaces, especially of ferrous metals, by adding at least one salt of compounds of the formula (1) and amines of the formula (2) to a corrosive system which is in contact

with the metal surfaces.

The invention further provides for the use of the compounds of the formulae (1) and (2) as metalworking agents. In this context, the inventive compounds give very good corrosion protection even in the case of severe mechanical stress, such as in the course of grinding, cutting and drilling of metal workpieces.

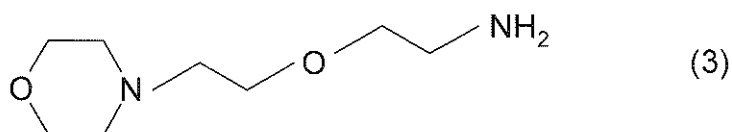
Corrosive systems in the context of this invention are preferably liquid/liquid or liquid/gaseous polyphasic systems consisting of water and hydrocarbons which comprise corrosive constituents, such as salts and acids, in free and/or dissolved form. The corrosive constituents may also be gaseous, for instance hydrogen sulfide and carbon dioxide.

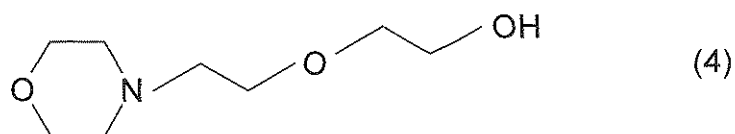
Hydrocarbons in the context of this invention are organic compounds which are constituents of mineral oil/natural gas, and the conversion products thereof.

Hydrocarbons in the context of this invention are also volatile hydrocarbons, for example methane, ethane, propane, butane. For the purposes of this invention, they also include the further gaseous constituents of mineral oil/natural gas, for instance hydrogen sulfide and carbon dioxide.

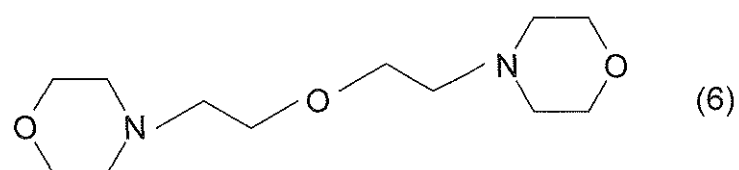
The amines of the formula 2 are preferably distillation residues from morpholine production (morpholine process residues), which are substance mixtures of CAS number 68909-77-3.

Distillation residues from morpholine production (CAS 68909-77-3) are a residue from the reaction of diethylene glycol and ammonia. It consists predominantly of derivatives based on morpholine, such as [(aminoethoxy)ethyl]morpholine, [(hydroxyethoxy)ethyl]morpholine, 3-morpholinone and 4,4'-(oxydi-2,1-ethanediyl)bis[morpholine], i.e. compounds of the formulae 3-6:





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The compound of the formula 2 is preferably selected from the compounds of the formulae 3 to 6.

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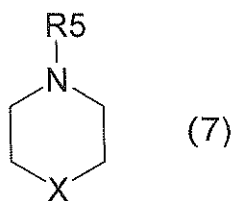
In formula (1), R1 is preferably an alkyl or alkenyl group having 8 to 24 carbon atoms, especially an alkyl or alkenyl group having 8 to 18 carbon atoms. R1 is more preferably an octyl, cocoyl or oleyl radical.

15 R2 is preferably hydrogen or may contain an organic radical having 1 to 4 carbon atoms and optionally oxygen or nitrogen atoms. In a particularly preferred embodiment, R2 is $-\text{CH}_2-\text{CH}_2-\text{OH}$.

20 R3 and R4 contain, in addition to the nitrogen atom shown in formula 2, carbon atoms, and optionally an oxygen atom or a further nitrogen atom or both. The total number of ring atoms is preferably six.

In a further preferred embodiment of the invention, the compound of the formula (2) is a cyclic amine of the formula (7)

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in which

R5 is hydrogen or an optionally heteroatom-containing C₁ to C₆ alkyl radical,
and

5 X is C, O or N.

The inventive compounds can be used alone or in combination with other known corrosion inhibitors. In general, a sufficient amount of the inventive corrosion inhibitor will be used that sufficient corrosion protection is obtained under the
10 given conditions.

Preferred use concentrations of the corrosion inhibitors based on the pure inventive salts are 5 to 5000 ppm, preferably 10 to 1000 ppm, especially 15 to 150 ppm.

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The N-substituted 5-oxopyrrolidine-3-carboxylic acids are prepared as described in detail in the prior art, by reacting itaconic acid with primary amines, and can be performed as described in EP-A-0 069 512, US-3 224 975 and US-4 127 493.

20 The purity of the N-substituted 5-oxopyrrolidine-3-carboxylic acids thus obtained is generally 80-100%, in particular 88-98% and especially 90-95%.

The inventive salts of the formulae (1) and (2) are prepared by a neutralization reaction, either in substance or in a suitable solvent system, preferably mixtures of
25 water and an alcohol. This preferably involves dissolving the amine of the formula (2) in the solvent and adding the N-substituted 5-oxopyrrolidine-3-carboxylic acid while stirring.

Examples:

General method for the preparation of N-substituted 5-oxopyrrolidine-3-carboxylic acid ammonium salts

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A standard stirred apparatus is initially charged with 1 mol of amine and heated to 50°C while stirring. Then 1 mol of itaconic acid is added in portions and the reaction mixture is heated gradually to 180°C. As the reaction advances, 1 mol of water of reaction is distilled off. Subsequently, the N-substituted 5-oxopyrrolidine-3-carboxylic acid is converted to the N-substituted 5-oxopyrrolidine-3-carboxylic acid ammonium salt by adding an equimolar amount of the corresponding amine. The product obtained is characterized by acid number (AN) and basic nitrogen (bas. N). Percentages are percentages by weight based on the weight of the inventive salt.

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Example 1

N-cocoyl-5-oxopyrrolidine-3-carboxylic acid, ammonium salt with morpholine process residues

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196 g of coconut amine, 130 g of itaconic acid and 127 g of morpholine process residues, were used to obtain 435 g N-cocoyl-5-oxopyrrolidine-3-carboxylic acid, ammonium salt with morpholine process residues with AN = 123 mg KOH/g and bas. N = 3.2%.

Example 2

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N-oleyl-5-oxopyrrolidine-3-carboxylic acid, ammonium salt with morpholine process residues

265 g of oleylamine, 130 g of itaconic acid and 127 g of morpholine process residues were used to obtain 506 g of N-oleyl-5-oxopyrrolidine-3-carboxylic acid, ammonium salt with morpholine process residues with

30

AN = 110 mg KOH/g and bas. N = 2.8%.

Example 3

N-octyl-5-oxopyrrolidine-3-carboxylic acid, ammonium salt with morpholine

process residues,

129 g of octylamine, 130 g of itaconic acid and 127 g of morpholine process residues, were used to obtain 369 g of N-octyl-5-oxopyrrolidine-3-carboxylic acid, ammonium salt with morpholine process residues with

5 AN = 151 mg KOH/g and bas. N = 3.8%.

Efficacy of the inventive compounds as corrosion inhibitors

10 The inventive compounds were tested as corrosion inhibitors in the Shell wheel test. Carbon steel coupons (DIN 1.1203 with surface area 15 cm²) were immersed into a saltwater/petroleum mixture (9:1.5% NaCl solution adjusted to pH 3.5 with acetic acid) and exposed to this medium at a peripheral speed of 40 rpm at 70°C for 24 hours. The dosage of the inhibitor was 50 ppm of a 40% solution of the inhibitor. The protection values were calculated from the mass decrease of the
15 coupons based on a blank value.

In the tables which follow, "comparative 1" denotes a commercial residue amine quat based on dicocoalkyldimethylammonium chloride, "comparative 2" an example from US-3 224 975 (N-oleyl-5-oxopyrrolidine-3-carboxylic acid, prior art
20 corrosion inhibitor), "comparative 3" an example from US-3 224 968 (N-oleyl-5-oxopyrrolidine-3-carboxylic acid, salt with oleylamine, prior art corrosion inhibitor) and "comparative 4" an example from GB-1 323 061 (N-butyl-5-oxopyrrolidine-3-carboxylic acid, salt with dibutylamine, prior art corrosion inhibitor).

Table 1: (Shell wheel test)

Example	Corrosion inhibitor	Ø % protection
Comparative 1	Standard quat	36
Comparative 2	N-oleyl-5-oxopyrrolidine-3-carboxylic acid	60
Comparative 3	N-oleyl-5-oxopyrrolidine-3-carboxylic acid, salt with oleylamine	55
Comparative 4	N-butyl-5-oxopyrrolidine-3-carboxylic acid, salt with dibutylamine	21
2	Compound from example 1	88
3	Compound from example 2	90
4	Compound from example 3	76

The products were also tested in the LPR test (test conditions analogous to ASTM

5 D 2776).

Table 2: (LPR test)

Example	Corrosion inhibitor	Protection after [%]		
		10 min	30 min	60 min
Comparative 1	Standard quat	54	61	74
Comparative 2	N-oleyl-5-oxopyrrolidine-3-carboxylic acid	2	10	23
Comparative 3	N-oleyl-5-oxopyrrolidine-3-carboxylic acid, salt with oleylamine	1	8	17
Comparative 4	N-butyl-5-oxopyrrolidine-3-carboxylic acid, salt with dibutylamine	4	12	25
5	Compound from example 1	90	95	99
6	Compound from example 2	88	94	99
7	Compound from example 3	75	83	90

As is evident from the above test results, the inventive products have very good
 5 corrosion properties at low dosage and are clearly superior to the efficacy of the
 prior art inhibitors.

Table 3:

Biodegradability (OECD 306) and toxicity (EC₅₀ *Skeletonema costatum*)

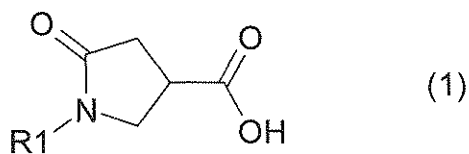
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Example	Corrosion inhibitor	Biodegradability [%]	Toxicity EC ₅₀ [mg/l]
Comparative 1	Standard quat	15	<1
8	Compound from example 1	74	>100
9	Compound from example 2	70	>100
10	Compound from example 3	83	>100

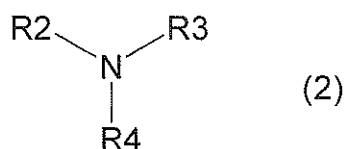
As is clearly evident from table 4, the inventive compounds exhibit better biodegradability and lower toxicity than the comparative example from the prior art.

Claims

1. The use of salts of compounds of the formula (1)



with amines of the formula (2)



in which

R1 is C₈- to C₃₀-alkyl or C₈- to C₃₀-alkenyl

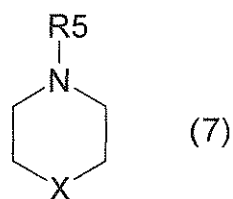
R2 is hydrogen, C₁- to C₆-alkyl or a heteroatom-containing organic radical having 1 to 8 carbon atoms, and

- 15 R3, R4 with inclusion of the nitrogen atom form a cycle having 5 to 7 ring atoms, where this cycle, in addition to carbon atoms, may optionally contain an oxygen atom or a nitrogen atom or both,
as water-soluble or water-dispersible corrosion inhibitors.

- 20 2. The use as claimed in claim 1, wherein R1 is an alkyl or alkenyl group of 8 to 18 carbon atoms.

3. The use as claimed in claim 1 and/or 2, wherein R2 is -CH₂-CH₂-OH.

- 25 4. The use as claimed in one or more of claims 1 to 3, in which the amine of the formula (2) is a compound of the formula (7)



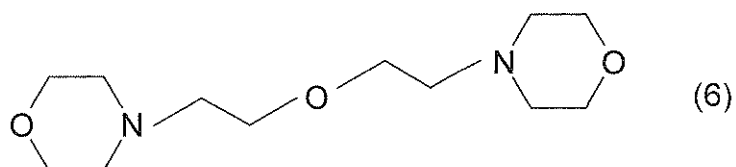
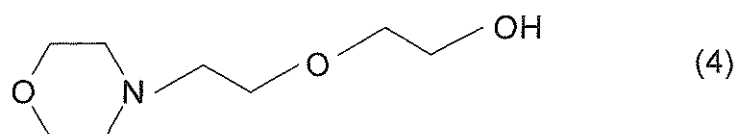
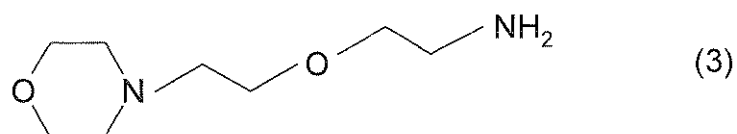
in which

R5 is hydrogen or an optionally heteroatom-containing C₁ to C₆ alkyl radical,
and

5 X is C, O or N.

5. The use as claimed in one or more of claims 1 to 3, in which the amine of
the formula 2 is a distillation residue from morpholine production.

10 6. The use as claimed in claim 5, in which the distillation residue comprises at
least one of the compounds of the formulae 3-6

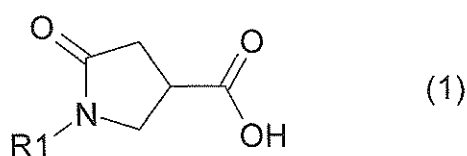


20 7. The use as claimed in one or more of claims 1 to 6 as corrosion inhibitors

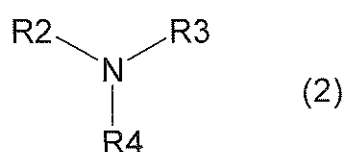
on and in devices for extraction and transport of hydrocarbons in mineral oil extraction and processing.

8. The use as claimed in one or more of claims 1 to 6 as corrosion inhibitors in metalworking assistants.

9. A salt of compounds of the formula (1)



with amines of the formula (2)



15 in which

R1 is C₈- to C₃₀-alkyl or C₈- to C₃₀-alkenyl

R2 is hydrogen, C₁- to C₆-alkyl or a heteroatom-containing organic radical having 1 to 8 carbon atoms, and

R3, R4 with inclusion of the nitrogen atom form a cycle having 5 to 7 ring atoms, where this cycle, in addition to carbon atoms, may optionally contain an oxygen atom or a nitrogen atom or both.

10. The salt as claimed in claim 9, wherein the amines of the formula 2 comprise at least one of the compounds of the formulae 3-6

