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3,661,981

CORROSION INHIBITORS

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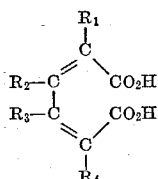
5 Claims 10

ABSTRACT OF THE DISCLOSURE

This specification discloses compositions and methods for inhibiting corrosion normally caused by oil well fluids. The compositions comprise a major amount of an amine salt wherein the amine is



wherein R is selected from the group consisting of aliphatic and cycloaliphatic hydrocarbon radicals having 12 to 30 carbon atoms and the acid is



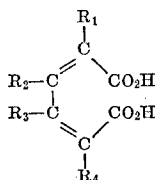
wherein R₁, R₂, R₃ and R₄ are selected from the group consisting of CH₃ and H.

CROSS REFERENCE TO RELATED APPLICATION

This application is a division of copending application Ser. No. 565,701, filed July 18, 1966, by Samuel E. Jolly and entitled Corrosion Inhibitors now Patent No. 3,523,894, issued Aug. 11, 1970.

This invention relates to new compositions and to the inhibiting of corrosion of metal equipment used in connection with the production and transportation of oil well fluids, and more particularly, to inhibiting the corrosion normally caused by well fluids such as mixtures of crude oil and brine.

More specifically this invention relates to corrosion inhibiting compositions containing N-alkyl trimethylene diamine salts of acids having the general structure;



wherein R₁, R₂, R₃ and R₄ are CH₃ or H, and to processes

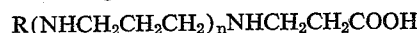
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of inhibiting corrosion in oil wells using such compositions.

Protection of metal surfaces from corrosion is an important factor in many fields of technology. One manner of providing such protection is by use of a corrosion inhibitor which forms an adsorbed protective film on a metal surface, which film resists attack of the surface by corrosive agents in fluids with which the surface would otherwise come in direct contact. The present invention provides a highly effective corrosion inhibitor for such use.

One application of corrosion inhibition which is of great importance in petroleum production is the inhibition of corrosion normally caused by oil well fluids such as mixtures of crude oil and brine. Corrosion of metal tubing, casing, pumps and other equipment used in producing oil from wells is a particularly difficult problem in petroleum production. The mixtures of crude oil and brine which are produced in most wells are highly corrosive to the metals of which such equipment is commonly constructed, particularly when the brine contains hydrogen sulfides, carbon dioxide or other acidic materials.

Amine salts of acids have been proposed as oil well corrosion inhibitors. For example, U.S. Pat. No. 3,054,750 discloses using acids having the formula:

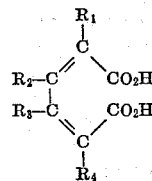


where R is a hydrocarbon radical having 12 to 30 carbon atoms, and n is an integer from 0 to 5. R is preferably aliphatic or cycloaliphatic. In a preferred embodiment R is the hydrocarbon residue of petroleum naphthenic acids. Also proposed by this patent are salts of these acids and N-alkyl trimethylene diamines having the formula;



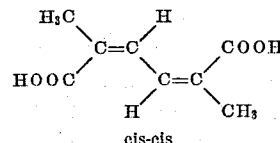
where R is a hydrocarbon of 12 to 30 carbon atoms.

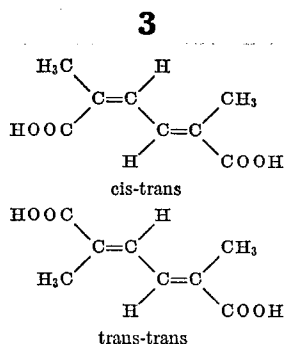
It has now been found that oil well corrosion inhibitor compositions exhibiting improved properties over the compositions of Pat. No. 3,054,750 comprise the N-alkyl trimethylene diamine salts of acids having the general structure;



wherein R₁, R₂, R₃, and R₄ are CH₃ or H. Surprisingly it has been found that these compositions exhibit improved corrosion protection over those known in the art, as will be shown infra.

The preferred salt of this invention is that of α,α'-dimethylmuconic acid (DMMA) which can exist in three isomeric forms, cis-cis, cis-trans, and trans-trans, which can be depicted by the following structural formulas:





The three isomeric dimethylmuconic acids are white crystalline powders with the physical properties listed in Table I.

TABLE I

	Cis-cis	Cis-trans	Trans-trans
Molecular weight.....	170.2	170.2	170.2
Melting point, °C.....	^a 223-224	^a 179-180	^a 332-333
Ionization constants: (at 25° C.).....	pK ₁ pK ₂	3.65 5.20	-----
Solubility, g./100 g. solution, 25.0°			
C.: water.....	0.026	0.244	0.0036
Water.....	^a 0.24	^b 1.97	^b 0.032
Ethyl alcohol.....	3.30	22.7	0.39
Ethyl acetate.....	0.185	2.17	0.39
Acetone.....	0.994	7.60	0.112
Benzene.....	0.006	0.023	0.008

^a Melting point varies with the rate of heating.

^b At 80° C.

All of the acids which fit the general formula may be prepared by the method disclosed in U.S. Pat. 3,383,289, issued May 14, 1968, which involves the fermentation of C₇ to C₁₀ methylbenzenes having 1 to 4 methyl groups to produce the corresponding unsaturated dibasic acids.

Additionally the preferred α,α'-dimethylmuconic acids may be prepared by the peracetic oxidation of p-xylene to give the cis-cis isomer as described by Elvidge et al., J. Chem. Soc., pages 1026 to 1033 (1952). This is inverted by boiling alkali to the trans-trans acid or isomerized by fulfuric acid to the lactonic acid which when esterified and treated with sodium methoxide gives the half methyl ester of cis-trans-α,α'-dimethylmuconic acid.

The diamines useful in this invention are of the formula;



wherein R is a hydrocarbon radical having 12 to 30 carbon atoms. R may be aliphatic or cycloaliphatic.

In the preparation of the amine salts, the acids and the amine are simply mixed together in the liquid or partially liquid state. Both the mono- and diacid salts may be prepared according to the relative proportion of reagents used. The temperature is maintained below 100° C. in order to avoid formation of amide linkages. Amides are avoided since they give generally inferior results as corrosion inhibitors, particularly for use in preventing corrosion normally caused by oil well fluids.

The corrosion inhibiting compositions disclosed herein are particularly useful for inhibiting corrosion of metal equipment used in production and transportation of oil well fluids, including gas well fluids and gas condensate well fluids, such corrosion being normally caused by a manner, e.g. by introducing them, either alone or distillates such as H₂S, CO₂ and lower organic acids. The inhibitors can be commingled with the well fluids in any suitable solvent such as an aromatic hydrocarbon solvent, into the well tubing or into the annulus between the tubing and the casing. The salt can alternatively be incorporated in a solid stick inhibitor containing microcrystalline wax or other suitable material. The injection practices which are known for use with other organic inhibitors are generally suitable for use with the

present inhibitor. Preferably, the salt is added to the corrosive well fluids in amounts of 25 to 1000 p.p.m. based on the well fluids, e.g. a mixture of crude oil and brine. In addition to their corrosion inhibiting properties, the salts have detergency characteristics which make them useful in maintaining metal surfaces of well production equipment in clean condition, and in removing corrosion products or scale from corroded metal surfaces.

The compositions are useful in other corrosion inhibition applications also, being generally useful in protecting ferrous metals, the protection being accomplished by means of a layer of the composition on the metal surface which is to be protected. Preferably, they are first dissolved in a protective hydrocarbon oil or other suitable solvent, and the solution is applied to the surface. Suitable operation in the latter instance is disclosed for different inhibitors in U.S. Pat. No. 2,736,658, and similar operation can be employed in the present instance. Preferred amounts of the inhibitor in the solvent are those within the approximate range from 0.01 to 1.0 weight percent, though any larger amount which is soluble in the solvent can be employed. Generally the salts of this invention are less soluble in water, hydrocarbons, alcohols, etc. than those disclosed in Pat. 3,054,750. This is advantageous because they are not as rapidly depleted by the well fluids when used as inhibitors.

The inhibitors can also be employed in greases comprising gelled hydrocarbon oils as described in the U.S. Pat. No. 2,736,658, previously cited. Preferred amounts of the inhibitor in the grease are those within the approximate range from 1 to 5 weight percent though any larger amount which is compatible with the grease can also be employed.

The following examples illustrate the invention.

EXAMPLES I-II

Salts of N-tallow trimethylene diamines with α,α'-dimethyl-cis,cis-muconic acid were prepared. The diamines employed were a material known by the trademark "Duomeen T" and comprised a mixture of diamines having the formula RNHCH₂CH₂CH₂NH₂, where R is a hydrocarbon radical derived from tallow, the average molecular weight of the mixture of diamines being 320. Since the mixture of diamines is not pure, the combining weight of Duomeen T is about 400.

Mono-salts were prepared by admixing the diamines with the theoretical amount of acid required to neutralize one amino group of the diamines with one carboxyl group. Disalts were also prepared by using twice that ratio of the acid.

These salts were then tested as corrosion inhibitors for oil well fluids according to the following procedure: Approximately equal volumes of a severely corrosive kerosene saturated with hydrogen sulfide, and of brine containing 13.24 grams per liter of CaCl₂·2H₂O, 3.5 g./l. of Na₂SO₄, 60 g./l. of NaCl, 10.68 g./l. of MgCl₂·6H₂O, 1.0 g./l. of Na₂CO₃, and 400 to 600 p.p.m. of H₂S were placed in a bottle, together with amounts of the amine salt mixture as indicated in Table II, expressed as parts per million based on the sum of the volumes of oil and brine. A cleaned and weighed 1/8" rod of mild steel was placed in the bottle, and the latter was sealed. The liquids nearly filled the bottle, the remaining fluid being largely air. The bottle was placed on the periphery of a drum which was rotated at a rate of about 100 revolutions per minute for a period of 24 hours. The test was carried out at room temperature. The steel rod was then removed, cleaned, and weighed to determine the weight loss from corrosion by the oil and brine. This weight loss was compared with that obtained in a blank run with no inhibitor, and the percent reduction in weight loss by use of the inhibitor and the percent protection determined. The percent protection results are given in Table II, Columns A and B.

TABLE II.—SALTS

	(A)	(B)	(C)	(D)
Diamine.....	RNHCH ₂ CH ₂ CH ₂ NH ₂	RNHCH ₂ CH ₂ CH ₂ NH ₂	RNHCH ₂ CH ₂ CH ₂ NH ₂	RNHCH ₂ CH ₂ CH ₂ NH ₂
Acid.....	cis,cis DMMA	cis,cis DMMA	N-naphthenyl alanines	N-naphthenyl alanines
Mole ratio, acid to diamine.....	1:1	2:1	1:1	2:1
Percent protection				
Parts per million:				
400.....	99	99	99	96.5
200.....	99	97	99	89.5
100.....	97	90	95	87.0
80.....				84.0
75.....	94	93	88	89
67.....				59.0
50.....	85	82	86	84
25.....	78	81	84	80
				16.0
				73.0

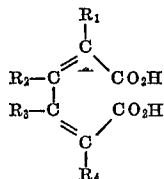
The table further shows the results obtained with the compositions prepared in Example III of U.S. Pat. 3,054,750 (indicated as C and D in Table II). Although the salts of this invention do not exhibit extraordinary film life, a comparison of results in the table does indicate that not only do the compositions of the present invention exhibit generally greater protection at a particular concentration over the N-naphthenyl alanine salts but also, surprisingly, significantly maintain their activity at extremely low concentrations. For example, at a concentration of 50 parts per million, the N-naphthenyl alanine salts exhibited percent protection of 16.0 and 73.0 while the cis, cis DMMA salts, at the same concentration showed percent protection of 85, 82, 86 and 84.

What is claimed is:

1. A composition of matter comprising an amine salt of an acid wherein the amine is



wherein R is a hydrocarbon radical having 12 to 30 carbon atoms, and the acid is



wherein R₁, R₂, R₃, and R₄ are selected from the group consisting of CH₃ and H.

2. The composition of claim 1 wherein the salt is a monosalt.

3. The composition of claim 1 wherein the salt is a disalt.

4. The composition of claim 1 wherein the salt is the monosalt of α,α'-dimethylmuconic acid.

5. The composition of claim 1 wherein the salt is the disalt of α,α'-dimethylmuconic acid.

References Cited

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