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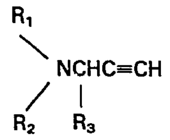
(54) Corrosion inhibitors containing N,N,1-trisubstituted prop-2-ynyl amines.

(57) A novel acetylenic amine and an aqueous composition containing said amine for inhibiting the corrosion of metals is described. The composition comprises a non-oxidizing acid, and, as a corrosion inhibitor, an effective amount of tertiary amine containing acetylenic unsaturation having the formula:



$$(R_1)(R_2)NCH(R_3)C\equiv CH$$

wherein R_1 and R_2 are independently C_1-C_8 alkyl or phenyl and R_3 is selected from the group of branched chain C_7-C_{10} alkyl, cinnamyl optionally mono- or di-substituted with halo, C_1-C_8 alkyl and/or C_1-C_8 alkoxy; mono- or di-similarly substituted phenyl or, when R_1 and R_2 are other than C_1-C_2 alkyl, then R_3 can be unsubstituted phenyl.

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CORROSION INHIBITORS CONTAINING 3-DIALKYL-3-(1-ETHYLPENTYL)PROP-1-YNE.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to compositions for inhibiting the corrosion of metals placed therein, and to novel acetylenic amines for such use as corrosion inhibitors.

2. Description of the Prior Art

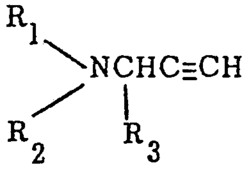
In the field of oil-welling acidizing, it is necessary to use inhibitors to prevent corrosion of the oil-well equipment by the acid solutions employed. Many different acetylenic amines have been proposed or used as corrosion inhibitors for oil-well acidization; see e.g. U.S. patents 2,997,507; 3,079,345; 3,107,221; 3,231,507; 3,268,524; 3,268,583; 3,382,179; 3,428,566; 3,496,232; 3,705,106; 3,772,208; 3,779,935; 3,802,890; 3,816,322; and 4,002,694; and the articles entitled "Ethynylation" by W. Reppe, et al. Ann. Chem. 59B, 1-224 (1955); and "Acetylenic Corrosion Inhibitors" by Foster et al., Ind. and Eng. Chem., 51, 825-8 (1959).

Nonetheless, there has been a continuing search for new materials which are highly effective in such application. More particularly, it is desired to provide new and improved corrosion inhibitors which are particularly advantageous in commercial use to prevent corrosion of metals in highly acid solutions, even after prolonged periods of use, which have a low vapor pressure and relatively high stability so that they can be employed at the high temperatures which prevail in modern deep drilling operations, which function effectively at low concentrations, and which are relatively inexpensive to make.

SUMMARY OF THE INVENTION

According to this invention, there is described herein novel acetylenic amines and aqueous compositions for inhibiting the corrosion of metals placed therein which comprises:

(a) a tertiary amine as a corrosion inhibitor having the formula:



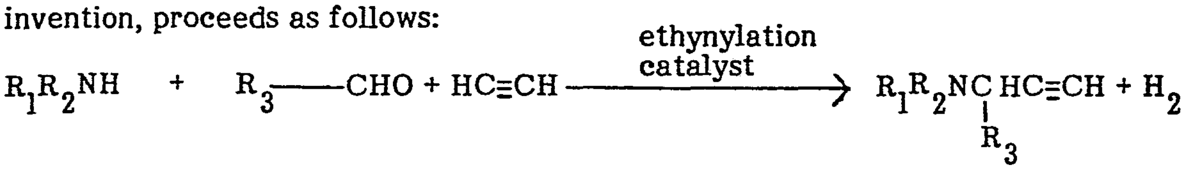
where R_1 and R_2 are independently alkyl C_1-C_8, or phenyl; and R_3 is selected from the group of C_7-C_{10} alkyl; cinnamyl, optionally substituted with halo, C_1-C_8 alkyl and/or C_1-C_8 alkoxy; mono- or di- similarly substituted phenyl or, when R_1 and R_2 are other than C_1-C_2 alkyl, then R_3 can be unsubstituted phenyl; and

(b) a non-oxidizing acid.

The compounds of the invention are made by a catalytic reaction, followed by purification, such as by molecular distillation of the crude reaction product under vacuum, or liquid chromatography.

DETAILED DESCRIPTION OF THE INVENTION

The catalytic ethynylation reaction between a secondary amine, an aldehyde and acetylene, to produce the desired acetylenic amines of this invention, proceeds as follows:



$$R_1R_2NH + R_3\text{—}CHO + HC{\equiv}CH \xrightarrow[\text{catalyst}]{\text{ethynylation}} R_1R_2N\underset{\substack{|\\R_3}}{C}HC{\equiv}CH + H_2$$

where R_1, R_2 and R_3 are as defined above.

Specific examples of aldehyde reactions employed in this invention include 2-ethylhexanal, benzaldehyde, cinnamaldehyde, 2,4-dichlorobenzaldehyde, 4-methylbenzaldehyde, 4-ethoxybenzaldehyde, 2-chlorobenzaldehyde, 2,4-dichlorocinnamaldehyde, 2-chlorocinnamaldehyde, 2-methoxycinnamaldehyde, 4-ethylcinnamaldehyde, etc.

The reaction is carried out in the presence of an ethynylation catalyst, such as is used for commercial preparation of butynediol; see, e.g. U.S. patents 3,920,759; 4,117,248; and 4,119,790. The preferred catalyst is a complex cuprous acetylide prepared from a precursor containing about 5-35% by weight of copper, and 2-3% by weight of bismuth, as the oxides, on a magnesium silicate carrier. However, many other ethynylation catalysts and carriers known in the art may be used as well.

The ethynylation reaction can be run under either low or high pressure conditions, i.e. a partial pressure of acetylene, as is used for butynediol, generally from about 0.1 atmosphere to 20 or more atmospheres, either in a stirred reactor with a slurried catalyst, or in a fixed bed, through which the acetylene and the solution are passed.

The ethynylation process preferably is carried out in the presence of a solvent in which the reactants are at least partially soluble. An organic solvent which is inert to the reaction may be used advantageously; preferably it is also volatile so that it can be easily separated from the reaction product by distillation. Alcohols, hydrocarbons and other organic solvents such as a ketone, e.g. methylethylketone or acetone, or an amide, e.g. dimethyl formamide may be used for this purpose. A preferred organic solvent is either dry or aqueous methanol or isopropanol.

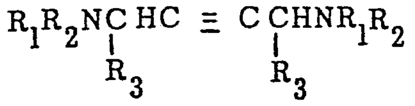
Water also is a suitable solvent; however, water does not completely dissolve the reactants, and it wets the catalyst, which interferes with intimate contact with the organic reactants. Consequently, ethynylation reaction rate is slower in water than in an organic solvent which forms a single liquid phase. However, mixtures of an organic solvent and water may be used, most suitably those which give a single reacting liquid phase.

In a typical synthesis, a charge is made of the reactants in relatively stoichiometric proportions of the secondary amine and aldehyde in an alcoholic solvent. The charge then is heated to a temperature of about 70° to 115°C., preferably 85° to 105°C., and acetylene is introduced and maintained at the desired pressure. The reaction is effected over a period of from less than 1 to 36 hours, generally for a period of from about 0.2 to 8 hours.

The crude reaction product then is separated from the catalyst, where necessary, stripped of solvent by rotary evaporation under reduced pressure and the crude reaction mixture is purified by fractional distillation under vacuum. Gas chromatographic (GC) assay indicates that the isolated compounds have a purity of at least 85%, and usually 95% or more. Some decomposition of the compound may occur, however, at the temperature of the assay.

The purified compound may be characterized by its IR and NMR spectra. The IR spectrum shows the presence of a strong sharp C-H stretching absorption band at about 3320 cm^{-1}, attributable to the ethynyl group, and an absence of carbonyl absorption in the region of 1600-1700 cm^{-1}. Where the aldehyde reactant is a benzaldehyde or cinnamaldehyde, the NMR spectrum of the product shows distinctive absorptions related to the $>\overset{1}{C}H\overset{2}{C}\equiv\overset{3}{C}H$ portion of the molecule. The C-1 proton is evident by a doublet at 3.1-5.2 δ due to coupling of the C-3 proton with the C-1 proton. The C-3 proton also shows up as a doublet for the same reason; however, at 2.0-3.0 δ. In the case where 2-ethylhexanal is employed as the aldehyde reactant, the NMR spectrum of the product shows distinctive absorptions related to the $>\overset{4}{C}H\overset{1}{C}H\overset{2}{C}\equiv\overset{3}{C}H$ portion of the molecule. The C-1 proton is evident by a 4-CH doublet of doublets at 3.1-3.2 δ due to coupling of the C-3 proton with both the C=1 and C=4 protons. The C-3 proton also shows up as a doublet by coupling with the C-1 proton; however, at 2.0-2.2 δ. In addition, the NMR spectrum of the compounds herein reveals the absence of both an aldehyde proton absorption, which is present in the starting material at 9-10 δ, and any N-H absorption.

The crude ethynylation reaction product is a complex mixture which, in the case of ethylhexanal, contains predominately 3-dialkylamino-3-phenylethenylprop-1-yne, 3-dialkylamino-3-phenylprop-1-yne or the phenyl substituted derivatives thereof or corresponding N-phenylamino derivatives, depending on the reactants selected. In the case of ethylhexanal reactant, the product contains predominately the two diastereoisomers of the 3-dialkylamino-3-(1-ethylpentyl)prop-1-yne, in the ratio of about 3:1 to 4:1 of each other. In addition, the products of these reactions may contain some of the corresponding di-compound, having the formula:



$$R_1R_2N\underset{R_3}{\underset{|}{C}}HC \equiv C\underset{R_3}{\underset{|}{C}}HNR_1R_2$$

and also some 3-dialkylaminobutyne, e.g. $R_1R_2NCH(CH_3)C\equiv CH$, and, depending upon reaction conditions, unreacted starting materials, and lesser amounts of other materials.

The reaction product itself may be used as a corrosion inhibitor without purification or isolation of the predominate compound therein. This option is particularly attractive from a commercial standpoint, because of the economic feature, and, indeed, the crude reaction product often performs as well or better under more severe testing conditions than does the purified compound. This effect may be due to the presence of by-products in the reaction product which may act as a synergist with the predominate compound.

The corrosion-inhibiting compositions of the invention may be used at varying concentrations. What is an effective amount in a particular application will depend upon local operating conditions. For example, the temperature and other characteristics of the acid corrosion system will have a bearing upon the amount of inhibitor to be used. The higher the temperature and/or the higher the acid concentration, the greater is the amount of corrosion inhibitor required to give optimum results. In general, however, it has beenfound that the corrosion inhibitor composition of the invention should be employed at a concentration of between 0.01 and 2%, preferably between 0.01% and 1.2%, by weight of the aqueous acidic solution, although higher concentrations can be used when conditions make them desirable. An inhibitor concentration between 0.05% and 0.75% by weight is of the most general use, particularly at elevated temperatures, e.g. in the neighborhood of 200°F.

The acidic solution itself can be dilute or concentrated as desired, and can be of any of the specific concentrations customarily used in treating metals, e.g. ferrousmetals, or for operations involving contact of acidic solutions with such metals in oil-well acidizing. Generally the acid content is about 5 to 80%, and, in most operations of the character indicated, acid concentrations of 10-15% by weight are employed. Non-oxidizing inorganic acids are the most common acids used.

The invention will now be described in more detail by the following example which is for illustration only, and not by way of limitation.

EXAMPLES 1-4

A charge is made to a 1-l. stirred autoclave consisting of 1 mole (129 g) of dibutylamine, 1 mole of the aldehyde shown in Table I, 25 g of a 35 wt. % Cu-containing catalyst, prepared as described in U.S. 4,119,790, as a powder, and 350 ml of isopropanol.

The reactor is purged well with nitrogen, released to atmospheric pressure, and the reactants are heated to 95°C. The vapor pressure at this point is recorded. Acetylene then is admitted at a pressure of 100 psig above the recorded pressure. The amount of acetylene furnished to the reaction is measured by the loss in weight of the supply cylinder.

After about 12-24 hrs., corresponding to the absorption of 1 mole of acetylene (26 g), the reactor is cooled and the product is discharged. The reaction mixture is filtered to remove catalyst and stripped of solvent by rotary evaporation. The weight % of crude reaction product, indicated in Table I, is obtained by gas chromatographic analysis. The crude mixture can then be purified by vacuum distillation under conditions reported in Table I and gas chromatographic assays indicates the weight % of purified product (also reported).

TABLE I

Example No.	Aldehyde Reactant	Wt. % Crude Product	Distillation °C./mm Hg	Wt. % Purif. Product	Remarks
1.	140 g. 2-chlorobenzaldehyde	65% 3-dibutylamino-3-(2-chlorophenyl)prop-1-yne	130-140/0.1	$\sim$84%	The IR spectra shows a sharp band at 3340 cm^{-1}; and the NMR spectrum contains distinctive doublets at 5.1 and 2.9 in addition to absorptions associated with the butyl and 2-chlorophenyl groupings.
2.	105.5 g benzaldehyde	50% 3-dibutylamino-3-phenylprop-1-yne	130-140/0.1	$\sim$84%	-
3.	130 g. cinnamaldehyde	50% 3-dibutylamino-3-phenylethenylprop-1-yne	130-140/0.1	$\sim$77%	-
4.	128 g. 2-ethylhexanal	75% combined diastereoisomers of 3-butylamino-3-(1-ethylpentyl)prop-1-yne	118/2.5	$\sim$87% combined isomers	-

EXAMPLES 5-14

Using the same procedure as described in Example 1 except that a charge of the dialkylamine and substituted benzaldehyde appropriate for the desired acetylenic amines is used, the following compounds listed below are obtained. Their purity by GC analysis, boiling point, and distinctive absorptions in the IR (cm^{-1}) and NMR (δ) associated with $>\text{CHC}\equiv\text{CH}$ are indicated.

(5) Dimethylamino-3-(4-chlorophenyl)-prop-1-yne; 84%; ir 3320 cm^{-1}; nmr 4.55(d) and 2.6(d).

(6) Dibutylamino-3-(4-methylphenyl)-prop-1-yne; 94.7%, 160°/1 mm. ir; 3330 cm^{-1}; nmr 4.8 and 2.3(d).

(7) Dibutylamino-3-(4-methoxyphenyl)-prop-1-yne; 95.3%; 137°/0.5 mm; ir 3320 cm^{-1}; nmr 4.78(d) and 2.45(d).

(8) Dibutylamino-3-(2,4-dichlorophenyl)-prop-1-yne; and ir 3320 cm^{-1}; nmr 5.08(d) and 2.9(d).

(9) Dibutylamino-3-(4-chlorophenyl)-prop-1-yne; 87%; 131°/0.8 mm; ir 3320 cm^{-1}; nmr 4.8(d) and 2.4(c).

(10) Dimethylamine and 4-chlorobenzaldehyde; dimethylamino-3-(4-chlorophenyl) prop-1-yne.

(11) Dibutylamine and 4-methoxybenzaldehyde; dibutylamino-3-(4-methoxyphenyl) prop-1-yne.

(12) Dibutylamine and 2,4-dichlorobenzaldehyde; dibutylamino-3-(2,4-dichlorophenyl) prop-1-yne.

(13) Dibutylamine and 4-chlorobenzaldehyde; dibutylamino-3-(4-chlorophenyl) prop-1-yne.

(14) Dihexylamine and 2-chlorobenzaldehyde; dihexylamino-3-(2-chlorophenyl) prop-1-yne.

d = doublet

c = complex

It is to be understood that other compounds of this invention are prepared by substitution of the appropriate aldehyde and/or secondary amine starting material in examples 1-4 above. Accordingly, for example the N,N-diphenyl substituted acetylenic amine products are produced by using N,N-diphenyl-amine as the starting material; the N,N-dipropyl acetylenic amine products are prepared by employing N,N-dipropyl amine reactant; the N-methyl-N-phenyl acetylenic amine products are obtained from N-methyl-N-phenylamine reactant; etc.

The corresponding cinnamyl substituted products of this invention are obtained by substituting for cinnamaldehyde in Example 3 the following compounds

2-chlorocinnamylaldehyde
2,4-dichlorocinnamaldehyde
2-ethylcinnamaldehyde
4-methoxycinnamaldehyde

and other homologous cinnamaldehyde reactants. Similarly substituted benzaldehyde reactants provide the correspondingly substituted products.

The most preferred inhibitors of this invention are the dialkylamino halogenated phenyl prop-1-ynes and dibutylamino alkylpentylprop-1-ynes.

EXAMPLES 16-61

The compounds of the present invention were tested in the usual way to determine their effectiveness as corrosion inhibitors. In such tests, strips of 1020 carbon steel of the dimensions 2.5" x 1.0" x 0.20" were first degreased with methylethyl ketone and then descaled by soaking in 10% hydrochloric acid solution containing approximately 0.1% propargyl alcohol. The coupons then were cleaned with a brush and thoroughly rinsed with water. After rinsing, the coupons were soaked in 2% sodium carbonate solution, rinsed successively with water and acetone and air dried. The surface dimensions of the cleaned coupons were determined with the vernier scale and the coupons were allowed to dry in a desiccator. Before use the coupons were weighed on an analytical balance.

The tests were carried out in a 4 oz. jar containing a weighed amount of the inhibitor. The total solution weight was taken to 100.0 g with the addition of hydrochloric acid solutions at concentrations noted in Table II. The coupon then was placed in the mixture and the jar loosely capped and placed in a 80^{o}C. oil bath. After the designated hours, the jar was removed from the oil bath and the contents were allowed to attain ambient conditions. The coupon was removed from the acid solution, thoroughly washed with water, 2% sodium carbonate solution, again with water, and finally rinsed with acetone. After air drying the coupon was kept in a desiccator before weighing and the net weight loss was calculated by the established procedure.

Controls also were run using no inhibitor whatsoever, and, for comparative purposes, with other related compounds.

The test results are presented in following Table II where a lower value of weight loss represent better corrosion inhibition.

TABLE II

EFFECTIVENESS OF COMPOUNDS OF INVENTION AS CORROSION INHIBITORS

Ex.	Inhibitor Tested	Conditions of Test	Wt. Loss (%)
		0.4% Inhibitor; 15% HCl and 16 hrs.	
16	3-Dibutylamino-3-(1-ethylpentyl)prop-1-yne		0.21** 0.16
17	3-(N-Methyl-N-phenylamino)-3-(1-ethylpentyl)prop-1-yne		0.20
18	3-Dihexylamino-3-(1-ethylpentyl)prop-1-yne		1.05
19	3-Dimethylamino-3-(1-ethylpentyl)prop-1-yne		0.25
20	3-Dibutylamino-3-phenylethenylprop-1-yne		0.03** 0.40
21	3-Dibutylamino-3-cyclohexylprop-1-yne*		1.25
22	3-Dibutylaminoprop-1-yne*		1.90
23	3-Dibutylamino-3-methylprop-1-yne*		1.18** 1.82
24	3-Dibutylamino-3-propylprop-1-yne*		3.15
25	3-Dimethylamino-3-(1-methylethyl)prop-1-yne*		4.50
26	3-Dibutylamino-3-phenylprop-1-yne		0.28** 0.04
27	3-Dihexylamino-3-phenylprop-1-yne		0.07** 0.06
28	3-Dimethylamino-3-phenylprop-1-yne*		1.40**
29	3-Diethylamino-3-phenylprop-1-yne*		3.28** 0.53
30	3-Dibutylamino-3-(2-chlorophenyl)prop-1-yne		0.03
31	3-Dibutylamino-3-(4-chlorophenyl)prop-1-yne		0.03
32	3-Dibutylamino-3-(4-methylphenyl)prop-1-yne		0.06
33	3-Dibutylamino-3-(4-methoxyphenyl)prop-1-yne		0.07
34	3-Dibutylamino-3-(2,4-dichlorophenyl)prop-1-yne		0.04
35	3-Dimethylamino-3-(4-chlorophenyl)prop-1-yne		0.08
36	3-Dimethylamino-3-(phenyl)prop-1-yne*		0.87
37	No Inhibitor		26.50
		0.2% Inhibitor; 15% HCl; 16 hrs.	
38	3-Dibutylamino-3-(4-chlorophenyl)prop-1-yne		0.06

TABLE II CONT'D

EFFECTIVENESS OF COMPOUNDS OF INVENTION AS CORROSION INHIBITORS

Ex.	Inhibitor Tested	Conditions of Test	Wt. Loss (%)
		0.4% Inhibitor; 37.5% HCl; 4 hrs.	
39	3-Dibutylamino-3-(2-chlorophenyl)prop-1-yne		0.17
40	3-Dibutylamino-3-(4-chlorophenyl)prop-1-yne		0.29
41	3-Dibutylamino-3-(4-methylphenyl)prop-1-yne		0.55
42	3-Dibutylamino-3-(4-methoxyphenyl)prop-1-yne		0.41
43	3-Dibutylamino-3-(2,4-dichlorophenyl)prop-1-yne		0.44
44	3-Dibutylamino-3-phenylethenylprop-1-yne		0.17**
45	3-Dibutylamino-3-(2-chlorophenyl)prop-1-yne		0.06
46	3-Diethylamino-3-(2-chlorophenyl)prop-1-yne		0.17
47	3-Dihexylamino-3-(2-chlorophenyl)prop-1-yne		0.33
48	3-Dimethylamino-3-(4-chlorophenyl)prop-1-yne		0.49
49	No Inhibitor		50.94
		0.4% Inhibitor; 37.5% HCl; 16 hrs.	
50	3-Dibutylamino-3-(2-chlorophenyl)prop-1-yne		0.19
51	3-Dibutylamino-3-(4-chlorophenyl)prop-1-yne		1.30
52	3-Dibutylamino-3-(4-methylphenyl)prop-1-yne		0.85
53	3-Dibutylamino-3-(4-methoxyphenyl)prop-1-yne		1.07
54	3-Dibutylamino-3-(phenyl)prop-1-yne*		4.23
55	3-Dimethylamino-3-(4-chlorophenyl)prop-1-yne		10.83
56	3-Dimethylamino-3-(phenyl)prop-1-yne*		14.55
57	3-Dibutylamino-3-phenylprop-1-yne		7.06** 4.26
58	3-Dihexylamino-3-phenylprop-1-yne		47.25#** 44.90#
59	3-Dimethylamino-3-phenylprop-1-yne*		13.12** 7.89
60	3-Diethylamino-3-phenylprop-1-yne*		13.31** 8.31
61	No Inhibitor		54.90

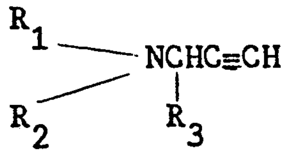
* Comparative tests
** Pure Compound
\# Decomposition Occurs

As is seen from the data in Table II, the compounds of the invention exhibit excellent corrosion inhibition for metal in aqueous acid solution. These compounds perform substantially better than the corresponding dialkylamino compounds which are unsubstituted or which contain lower alkyl substitutions, either straight chain, branched chain or cyclic. This result is attributable primarily to the long chain alkyl group and its branching groups at the 1-position.

While the invention has been described with reference to certain embodiments thereof, it will be understood that modifications and changes may be made which are within the skill of the art and the scope of this invention.

CLAIMS:-

1. A compound of the formula:



$$\begin{matrix} R_1 \\ & \searrow \\ & & NCHC{\equiv}CH \\ & \nearrow & | \\ R_2 & & R_3 \end{matrix}$$

wherein R_1 and R_2 are independently alkyl C_1-C_8, or phenyl and R_3 is a branched chain C_7-C_{10} alkyl; cinnamyl, optionally substituted with halo, C_1-C_8 alkyl or C_1-C_8 alkoxy; mono- or di- similarly substituted phenyl or, when R_1 and R_2 are other than C_1-C_2 alkyl, then R_3 can be unsubstituted phenyl.

2. A compound according to Claim 1 wherein both R_1 and R_2 are the same.

3. A compound according to Claim 2 wherein both R_1 and R_2 are butyl and R_3 is halogenated phenyl, phenyl or phenylethenyl.

4. A compound of Claim 3 which is 3-dibutylamino-3-(chlorophenyl) prop-1-yne.

5. A compound of Claim 2 which is 3-dibutylamino-3-(1-ethylpentyl) prop-1-yne.

6. A compound of Claim 2 which is 3-dihexylamino-3-phenyl prop-1-yne.

7. A compound of Claim 1 which is 3-N-methyl-N-phenylamino-3-(1-ethylpentyl) prop-1-yne.

8. A corrosion inhibitor for aqueous solutions of mineral acids consisting essentially of the crude reaction product obtained by the catalytic ethynylation of a secondary amine R_1 R_2 NH, and an aldehyde of the formula R_3-CHO with acetylene, wherein R_1, R_2 and R_3 are as defined in Claim 1.

9. An aqueous composition for inhititibiting the corrosion of metals placed therein comprising:

(a) an effective amount of a corrosion-inhibiting compound according to any one of Claims 1 to 7, or inhibitor according to Claim 8; and

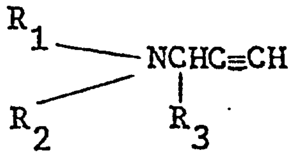
(b) a non-oxidizing acid.

10. A method of inhibiting the corrosive action of an aqueous solution of a non-oxidizing acid on a metal, comprising maintaining in said solution an effective amount of the corrosion inhibitor as defined in Claim 8 or a compound as defined in any one of Claims 1 to 7.

AMENDED CLAIMS

CLAIMS:-

1. A compound of the formula:



wherein R_1 and R_2 are independently alkyl C_1-C_8, or phenyl and R_3 is a branched chain C_7-C_{10} alkyl; cinnamyl, optionally substituted with halo, C_1-C_8 alkyl or C_1-C_8 alkoxy; mono- or di- similarly substituted phenyl or, when R_1 and R_2 are other than C_1-C_2 alkyl, then R_3 can be unsubstituted phenyl.

2. A compound according to Claim 1 wherein both R_1 and R_2 are the same.

3. A compound according to Claim 2 wherein both R_1 and R_2 are butyl and R_3 is halogenated phenyl, phenyl, methylated phenyl, methoxylated pheny or phenylethenyl.

4. A compound of Claim 3 which is 3-dibutylamino-3-(chlorophenyl) prop-1-yne.

5. A compound of Claim 2 which is 3-dibutylamino-3-(1-ethylpentyl) prop-1-yne.

AMENDED CLAIMS

6. A compound of Claim 2 which is 3-dihexylamino-3-phenyl prop-1-yne.

7. A compound of Claim 1 which is 3-N-methyl-N-phenylamino-3-(1-ethylpentyl) prop-1-yne.

8. A corrosion inhibitor for aqueous solutions of mineral acids consisting essentially of the crude reaction product obtained by the catalytic ethynylation of a secondary amine $R_1 R_2 NH$, and an aldehyde of the formula R_3-CHO with acetylene, wherein R_1, R_2 and R_3 are as defined in Claim 1.

9. An aqueous composition for inhi~~bi~~biting the corrosion of metals placed therein comprising:

(a) an effective amount of a corrosion-inhibiting compound according to any one of Claims 1 to 7, or inhibitor according to Claim 8; and

(b) a non-oxidizing acid.

European Patent Office

EUROPEAN SEARCH REPORT

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Application number

EP 82 30 4806.1

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	<u>US - A - 2 273 141</u> (W. REPPE et al.) * example 5 * --	1-7
A	<u>US - A - 2 766 285</u> (G.F. HENNION) * examples 5, 6 * --	1-7
A	<u>US - A - 2 613 208</u> (J.O. VAN HOOK et al.) * column 1, line 52 to column 3, line 18 * --	1-7
D,A	<u>US - A - 3 079 345</u> (R.F. MONROE et al.) ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl. ^{3})

C 07 C 87/24
C 07 C 87/28
C 07 C 87/29
C 07 C 93/26
C 23 F 11/14

TECHNICAL FIELDS SEARCHED (Int.Cl. ^{3})

C 07 C 87/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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A: technological background
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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

☒ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	10-12-1982	BREW

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