

Description

The present invention relates to a method of stabilizing a corrosion inhibitor in an acidizing treatment of a subterranean formation or well bore employing selected compounds which substantially reduce the potential for precipitate formation from the corrosion inhibitor upon acid spending of the acidic solution.

Acidizing and fracturing treatments using aqueous acidic solutions commonly are carried out in hydrocarbon-containing subterranean formations penetrated by a well bore to accomplish a number of purposes, one of which is to increase the permeability of the formation. The increase in formation permeability normally results in an increase in the recovery of hydrocarbons from the formation.

In acidizing treatments, aqueous acidic solutions are introduced into the subterranean formation under pressure so that the acidic solution flows into the pore spaces of the formation. The acidic solution reacts with acid-soluble materials contained in the formation which results in an increase in the size of the pore spaces and an increase in the permeability of the formation.

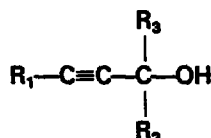
In fracture acidizing treatments, one or more fractures are produced in the formation and the acidic solution is introduced into the fracture to etch flow channels in the fracture face. The acid also enlarges the pore spaces in the fracture face and in the formation.

A problem associated with acidizing subterranean formations is the corrosion by the acidic solution of the tubular goods in the well bore and the other equipment used to carry out the treatment. The expense of repairing or replacing corrosion damaged equipment is extremely high. The corrosion problem is exacerbated by the elevated temperatures encountered in deeper formations.

Various methods have been proposed to decrease the corrosion problem related to acidizing treatments. However, the corrosion inhibitors employed generally are effective only at temperature levels below about 250°F (121°C). It would be desirable to provide a composition and method for acid treating a subterranean formation which overcomes at least some of the corrosion problem resulting from contact of the aqueous acidic treating solutions with ferrous and other metals while preventing further problems caused by precipitation of various compounds from the acidic solutions upon acid spending.

We have now found a way of acidizing a subterranean formation employing an acidic solution containing a stabilized corrosion inhibitor which substantially reduces the corrosive effect of the acid on ferrous and other metals without significantly reducing the effectiveness of the acidic solution in treating the subterranean formation and which substantially prevents precipitation of solids from the corrosion inhibitor upon acid spending.

According to the present invention, there is provided a method of inhibiting the corrosivity of a corrosive acid in contact with a metal at elevated temperatures, which comprises adding to said corrosive acid an inhibiting effective amount of a corrosion inhibitor composition comprising: at least one acetylenic alcohol having the general formula



wherein R_1 , R_2 and R_3 are each selected from hydrogen, alkyl, phenyl, substituted phenyl and hydroxy-alkyl radicals, at least one aromatic quaternary ammonium compound, at least one aromatic hydrocarbon compound which exhibits high oil-wetting characteristics; at least one antimony compound capable of activation by the other constituents of said corrosion inhibitor composition whereby the corrosivity of said corrosive acid in contact with said ferrous metal is reduced; and, at least one stabilizer selected from reactive fluoride-containing compounds, compounds having alpha-hydroxy or beta-hydroxy organic acid functional groups, or polyhydroxy compounds having from 3 to 9 carbon atoms, present in an amount effective for preventing substantial precipitation of said antimony compound from at least partially spent acid solutions containing said corrosion inhibitor.

In general, the acidizing solution is introduced into a subterranean formation through a well bore at a flow rate and pressure sufficient to permit the acid to dissolve formation materials or foreign material in the vicinity of the well bore. The acidic solution can comprise, for example, a solution of hydrochloric acid, or mixtures of hydrochloric acid with hydrofluoric acid, acetic acid, formic acid or formic and hydrofluoric acid, sulfuric acid, formic acid, acetic acid, mixtures thereof and the like.

The inhibitor composition of the invention broadly comprises a corrosion-reducing effective amount of one or more acetylenic alcohols, an aromatic quaternary ammonium compound, an aromatic hydrocarbon having high oil-wetting characteristics, an antimony compound and a stabilizer. Any antimony compound can be used which is capable of activation by the other constituents of the inhibitor. The stabilized corrosion inhibitor is particularly effective in reducing the corrosive effects of acidic solutions in contact with ferrous metals where the temperature at which the metal and acid are in contact is between about 150°F and 500°F (65°C and 260°C).

The stabiliser comprises at least one reactive fluoride-containing compound, or compound having an alpha-hydroxy or beta-hydroxy organic acid functional group, or a non-organic acid polyhydroxy

compound having from 3 to 9 carbon atoms. The fluoride-containing compound can comprise, for example, hydrofluoric acid, ammonium bifluoride, sodium fluoride, potassium fluoride, ammonium fluoride transition metal fluorides, rare earth fluorides, alkaline earth fluorides and the like. The fluoride source can comprise substantially any compound which is capable of solubilization in the presence of the antimony compound and other constituents of the corrosion inhibitor without adversely affecting the operability of the corrosion inhibitor in the acid. The compounds having alpha-hydroxy or beta-hydroxy organic acid functional groups can comprise, for example, citric acid, citric acid salts, tartaric acid, tartaric acid salts, glycolic acid, glycolic acid salts, lactic acid, lactic acid salts, 3-hydroxy-propionic acid, 3-hydroxy-butanoic acid, 3,4-dihydroxy-1,6-hexanedioic acid, and the like.

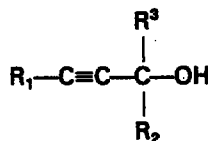
The non-organic acid polyhydroxy compounds can comprise, for example, sorbitol, glycerol, glucose, mannose, ribitol, erythritol, mannitol, perseitol, iditol, altritol, xylitol, and the like.

The stabilizer is preferably admixed with the corrosion inhibitor in a molar ratio of generally about one mole of either fluoride ion, alpha-hydroxy or beta-hydroxy organic acid functional groups, non-organic acid polyhydroxy compounds or an admixture thereof per mole of antimony present in the corrosion inhibitor. Larger quantities of the stabilizer may be utilized and, preferably, an amount slightly in excess of the molar concentration of the antimony which is present is utilized. It is to be understood that smaller quantities of the stabilizer also may be used but that the stabilizing effect is reduced.

The stabilizer is effective at preventing the precipitation of antimony from spent acid solutions containing the corrosion inhibitor at ambient temperature and at elevated temperature levels.

The antimony compound which is employed in the present invention can comprise any antimony compound which is activated by the other constituents of the corrosion inhibitor to cause the corrosion inhibitor to substantially reduce the corrosive effect of the acid in the aqueous acidic solution on ferrous metals, copper, brass, duplex metals and the like in contact with the acidic solution. The antimony compound can comprise, for example, antimony trioxide, antimony pentoxide, antimony trichloride, antimony pentachloride, potassium pyroantimonate and other alkali metal salts thereof, antimony adducts of ethylene glycol, solutions containing ethylene glycol, water and the oxidized product of hydrogen peroxide and antimony trioxide or any other trivalent antimony compound and the like.

The acetylenic alcohols employed in the present invention may suitably include substantially any of the acetylenic compounds having the general formula:



wherein R_1 , R_2 and R_3 are hydrogen, alkyl, phenyl, substituted phenyl or hydroxy-alkyl radicals. Preferably, R_1 comprises hydrogen. Preferably, R_2 comprises hydrogen, methyl, ethyl or propyl radicals. Preferably R_3 comprises an alkyl radical having up to 10 carbon atoms.

Some examples of acetylenic alcohols which can be employed in accordance with the present invention are, for example, methyl butynol, methyl pentynol, hexynol, ethyl octynol, propargyl alcohol, benzylbutynol, ethynylcyclohexanol and the like. Preferred alcohols are hexynol, propargyl alcohol, methyl butynol and ethyl octynol.

The quaternary ammonium compounds employed in the present invention comprise aromatic nitrogen compounds which may be illustrated by alkyl pyridine-N-methyl chloride quaternary, alkyl pyridine-N-benzyl chloride quaternary, quinoline-N-methyl chloride quaternary, quinoline-N-benzyl chloride quaternary, isoquinoline quaternaries, benzoquinoline quaternaries, chloromethyl naphthalene quaternaries of the above, admixtures of the compounds and the like.

The hydrocarbon compound can comprise substantially any aromatic compound which exhibits high oil-wetting characteristics. The aromatic hydrocarbon compound can comprise, for example, xylenes, saturated biphenyl-xylenes admixtures, heavy aromatic naphtha, heavy aromatic solvent, tetralene, tetrahydroquinoline, tetrahydronaphthalene and the like.

The acetylenic alcohol, aromatic hydrocarbon and quaternary amine are present in the corrosion inhibitor in an amount sufficient to effect an activation of the antimony compound whereby the composition can significantly reduce the corrosive effect of an acid on a ferrous metal or other metal in comparison to the reduction in corrosive effect resulting from the use of the individual components or admixtures of less than all the components. Preferably, the acetylenic alcohol is present in the corrosion inhibitor in an amount sufficient to comprise at least five percent by volume of the inhibitor composition. Most preferably, the acetylenic alcohol comprises from about 5 to about 35 percent of the composition. Preferably, the ratio of the volume of acetylenic alcohol to the volume of aromatic hydrocarbons is at least about 0.05:1.0. Most preferably, the ratio of acetylenic alcohol to aromatic hydrocarbon is in the range of from about 0.08:1.0 to about 1.66:1.0. Preferably, a sufficient quantity of the antimony compound is added to obtain a solution having a concentration of from about 0.007 to about 0.04 molar. The antimony compound may be admixed with the other constituents of the corrosion inhibitor composition to form a premixed inhibitor or it may be formulated in situ in an acidic solution by the addition of a sufficient

quantity of the antimony compound and a quantity of the other constituents which may be premixed. The quaternary amine and any additional additives constitute the remainder of the corrosion inhibitor.

Additional additives which can be present in the corrosion inhibitor can comprise, for example, a solvent such as an alkanol to assist in maintaining the constituents of the corrosion inhibitor as a homogeneous admixture.

Alkanols which can be employed in the present invention are, for example, methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, heptyl, octyl and the higher liquid members of these aliphatic alcohols. Preferably, the quantity of alkanol employed is that which merely is sufficient to maintain the constituents in homogeneous admixture as excess quantities have no demonstrable effect on the effectiveness of the corrosion inhibitor. Preferably, the alkanol comprises less than about fifteen percent by volume of the corrosion inhibitor composition to avoid unnecessary dilution of the inhibitor composition.

The corrosion inhibitor also can include a nonionic surfactant which facilitates dispersion of the corrosion inhibitor in the aqueous acidic solution.

The non-ionic surfactant can comprise an ethoxylated oleate, tall oils or ethoxylated fatty acids. The 8 to 20 moles of ethylene oxide adducts of octyl phenol, nonyl phenol, tridecyl phenol and the like are preferred. Sufficient non-ionic surfactant is admixed with the other constituents of the corrosion inhibitor to facilitate dispersion of the corrosion inhibitor in the aqueous acidic solution. Preferably, the surfactant comprises less than about 20 percent by volume of the corrosion inhibitor composition to avoid unnecessary dilution of the inhibitor composition.

The method of the present invention is carried out in one embodiment by first admixing the aqueous fluid with the acid to provide an acidic solution of a desired concentration. The corrosion inhibitor then is admixed with the solution in an amount sufficient to substantially reduce the corrosion rate of the acid on ferrous metals in contact with the acid. When the corrosion inhibitor is generated in situ in the acidic solution, preferably the acetylenic alcohol, aromatic hydrocarbon quaternary ammonium compound and other additives are admixed prior to addition of the antimony compound. The stabilizer may be admixed with the acidic solution either before or after addition of the antimony compound. The amount of corrosion inhibitor utilized in the practice of the invention can vary over a substantial range. Preferably, the inhibitor is present in an amount of from about 1% to 3% by volume of the acidic solution. The quantity of corrosion inhibitor will depend upon the concentration of the acid employed and the temperature at which the acidic solution will contact the metal surfaces.

The aqueous acidic solution of the present invention can be prepared by any suitable tank equipped with suitable mixing means well known to individuals skilled in the art. The solution may be transferred either at a controlled rate directly into the well bore or into a convenient storage tank for injection down the well bore.

The aqueous acidic solution is introduced into the subterranean formation whereby either foreign material in the well bore or in the formation or formation materials are dissolved to thereby increase the permeability of the formation. The increased permeability permits better flow of hydrocarbon fluids through the formation and into its well bore. The pumping rate and pressure utilized will depend upon the characteristics of the formation and whether or not fracturing of the formation is desired. After the aqueous acidic solution has been injected, the well may be shut in and allowed to stand for a period of several hours or more depending on the type of said employed and the formation treated. If there is pressure on the well, pressure then can be released and the spent or at least partially spent aqueous acidic solution, containing salts formed by the reaction of the acid, is permitted to flow back into the well bore and is pumped or flowed to the surface for appropriate disposal. The stabilizer contained within the at least partially spent acid substantially prevents the precipitation of any antimony compounds within the subterranean formation. The well then can be placed on production or used for other purposes.

To further illustrate the effectiveness of the stabilizer of the present invention in preventing the precipitation of antimony compounds from the corrosion inhibitor employed in the aqueous acidic solution, but not by way of limitation, the following Examples are provided.

Example I

To determine the effectiveness of the stabilizer of the present invention as a constituent of the corrosion inhibitor, the following tests were performed. An acidic aqueous solution is prepared by adding a sufficient quantity of concentrated hydrochloric acid to water to form a 15 percent HCl solution. A corrosion inhibitor composition is prepared in accordance with the present invention as hereinbefore described by admixing the following constituents: a quaternary ammonium compound, a heavy aromatic hydrocarbon compound, acetylenic alcohol, a surfactant comprising an ethoxylated phenol and a surfactant comprising an alkanol. A quantity of the various antimony compounds identified in Table I, hereafter, then is admixed with samples of the acidic solution and co-mixed with the other constituents of the corrosion inhibitor. The antimony compound is present in an amount to produce a solution containing a 0.04 molar concentration. A quantity of Iceland Spar chips (calcium carbonate) is admixed with a portion of the sample solution to spend a significant portion of the acid present in the sample to determine if a precipitate would form in the solution upon acid spending. The results are set forth in Table I. A quantity of the stabilizer identified in the Table I then was admixed with the remaining sample solution in an amount sufficient to provide a 0.04 molar concentration in the sample solution. A quantity of Iceland Spar chips are admixed with the

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stabilized corrosion inhibitor solution to spend at least a significant portion of the acid present. The results of the acid spending are set forth in Table I, below.

TABLE I

Sample No.	Antimony compound present	Stabilizer present	Fluid sample	
			15% HCl	Spent 15% HCl
1	Sb ₂ O ₃	—	S ¹	ppt ²
2	Sb ₂ O ₃	HF	S	S
3	Sb ₂ O ₃	Tartaric Acid	S	S
4	Sb ₂ O ₅ ³	—	S	ppt
5	Sb ₂ O ₅ ³	HF	S	S
6	Sb ₂ O ₅ ³	Tartaric Acid	S	S
7	SbCl ₃	—	S	ppt
8	SbCl ₃	HF	S	S
9	SbCl ₃	Tartaric Acid	S	S
10	SbCl ₅	—	S	ppt
11	SbCl ₅	HF	S	S
12	SbCl ₅	Tartaric Acid	S	S

¹ S: soluble

² ppt: precipitate formed

³ Sb₂O₅: solution heated to 325°F (163°C) to effect dissolution of antimony compound then cooled to ambient

The data set forth above clearly illustrate the effectiveness of the stabilizer of the present invention in substantially preventing the precipitation of insoluble antimony-containing compounds from at least partially spent acidic solutions containing the same.

Example II

To determine the effectiveness of the stabilizer of the present invention as a constituent of the corrosion inhibitor in the presence of acidic solutions containing hydrogen sulfide, the following tests were performed. A corrosion inhibitor composition and acidic solution are prepared as in Example I. Various samples are prepared containing the antimony compound and stabilizer in an amount sufficient to provide a 0.04 molar concentration as identified in Table II. A quantity of a 5 percent hydrogen sulfide containing solution then is admixed with the sample solutions to determine whether or not a precipitate will form in the solution. The solutions are substantially spent by the addition of Iceland Spar chips. The results of the tests are set forth in Table II, below.

TABLE II

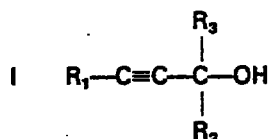
Sample No.	Antimony compound present	Stabilizer present	H ₂ S containing fluid sample	
			15% HCl	Spent 15% HCl
1	Sb ₂ O ₃	—	ppt	ppt
2	Sb ₂ O ₃	HF	S	clouding ¹
3	Sb ₂ O ₅	—	S	ppt
4	Sb ₂ O ₅	HF	S	clouding ¹

¹ No significant precipitate occurred, clouding occurred after standing for 24 hours

The results set forth above clearly illustrate the effectiveness of the stabilizer in substantially preventing precipitation of acid-soluble antimony compounds from substantially spent acid solutions.

In our European specification No. 130006, we have described and claimed corrosion inhibitor composition for reducing the corrosivity of a corrosive acid in contact with a ferrous metal at elevated temperatures, which composition comprises:

(i) at least one acetylenic alcohol having the general formula



wherein R_1 , R_2 and R_3 are each a hydrogen, alkyl, phenyl, substituted phenyl or hydroxy-alkyl radical; and

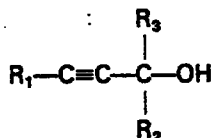
(ii) at least one quaternary ammonium compound which is an aromatic nitrogen compound; and

(iii) at least one aromatic hydrocarbon compound which exhibits high oil-wetting characteristics; and

(iv) at least one antimony compound capable of activation by the other constituents of said corrosion inhibitor composition whereby the corrosivity of said corrosive acid in contact with said ferrous metal is reduced, said antimony compound(s) being selected from antimony trioxide, antimony pentoxide, antimony trichloride, antimony sulfide, antimony pentachloride, alkali metal salts of antimony tartrate, antimony tartrate, antimony trifluoride, alkali metal salts of pyroantimonate, antimony adducts of ethylene glycol, and solutions containing ethylene glycol, water and the oxidized product of hydrogen peroxide and at least one trivalent antimony compound; and wherein the ratio of the volume of acetylenic alcohol(s) to the volume of aromatic hydrocarbon(s) is at least 0.05:1, and wherein the acetylenic alcohol(s) comprise(s) at least 5% by volume of the inhibitor composition.

Claims

1. A method of inhibiting the corrosivity of a corrosive acid in contact with a metal at elevated temperatures, which comprises adding to said corrosive acid an inhibiting effective amount of a corrosion inhibitor composition comprising: at least one acetylenic alcohol having the general formula:



wherein R_1 , R_2 and R_3 are each selected from hydrogen, alkyl, phenyl, substituted phenyl and hydroxy-alkyl radicals; at least one aromatic quaternary ammonium compound; at least one aromatic hydrocarbon compound which exhibits high oil-wetting characteristics; at least one antimony compound capable of activation by the other constituents of said corrosion inhibitor composition whereby the corrosivity of said corrosive acid in contact with said ferrous metal is reduced; and, at least one stabilizer selected from reactive fluoride-containing compounds, compounds having alpha-hydroxy or beta-hydroxy organic acid functional groups, or polyhydroxy compounds having from 3 to 9 carbon atoms, present in an amount effective for preventing substantial precipitation of said antimony compound from at least partially spent acid solutions containing said corrosion inhibitor.

2. A method according to claim 1, wherein the or each stabilizer is selected from hydrofluoric acid, lactic acid, glycolic acid, citric acid, tartaric acid, alkali metal fluorides, alkaline earth fluorides, rare earth fluorides, transition metal fluorides, ammonium fluoride, ammonium bifluoride, alkali metal salts of citric, tartaric, lactic and glycolic acid, 3,4-dihydroxy-1,6-hexanedioic acid, 3-hydroxyl-propionic acid and 3-hydroxyl-butanoic acid, sorbitol, glycerol, mannitol, perseitol, glucose, mannose, xylitol, alritol, iditol, ribitol and erythritol.

3. A method according to claim 1 or 2, wherein the molar ratio of the stabilizer to the antimony compound present in said composition is at least about 1.

4. A method according to claim 1, 2 or 3, wherein said corrosion inhibitor composition contains a solvent effective amount of an alkanol, and/or a non-ionic surfactant.

5. A method according to any of claims 1 to 4, wherein the volumetric ratio of said acetylenic alcohol to said hydrocarbon having high oil-wetting characteristics is in the range of from about 0.08:1 to about 1.66:1.

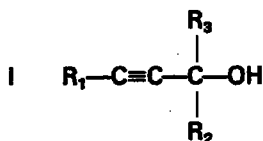
6. A method according to any of claims 1 to 5, wherein said corrosion inhibitor composition is present in said acidic solution in an amount of at least about 0.5 percent by volume of said acidic solution.

7. A method according to any of claims 1 to 6, wherein the or each antimony compound is selected from antimony trioxide, antimony pentoxide, antimony trichloride, antimony pentachloride, alkali metal

The results set forth above clearly illustrate the effectiveness of the stabilizer in substantially preventing precipitation of acid-soluble antimony compounds from substantially spent acid solutions.

In our European specification No. 130006, we have described and claimed corrosion inhibitor composition for reducing the corrosivity of a corrosive acid in contact with a ferrous metal at elevated temperatures, which composition comprises:

(i) at least one acetylenic alcohol having the general formula



wherein R_1 , R_2 and R_3 are each a hydrogen, alkyl, phenyl, substituted phenyl or hydroxy-alkyl radical; and

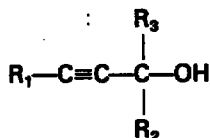
(ii) at least one quaternary ammonium compound which is an aromatic nitrogen compound; and

(iii) at least one aromatic hydrocarbon compound which exhibits high oil-wetting characteristics; and

(iv) at least one antimony compound capable of activation by the other constituents of said corrosion inhibitor composition whereby the corrosivity of said corrosive acid in contact with said ferrous metal is reduced, said antimony compound(s) being selected from antimony trioxide, antimony pentoxide, antimony trichloride, antimony sulfide, antimony pentachloride, alkali metal salts of antimony tartrate, antimony tartrate, antimony trifluoride, alkali metal salts of pyroantimonate, antimony adducts of ethylene glycol, and solutions containing ethylene glycol, water and the oxidized product of hydrogen peroxide and at least one trivalent antimony compound; and wherein the ratio of the volume of acetylenic alcohol(s) to the volume of aromatic hydrocarbon(s) is at least 0.05:1, and wherein the acetylenic alcohol(s) comprise(s) at least 5% by volume of the inhibitor composition.

Claims

1. A method of inhibiting the corrosivity of a corrosive acid in contact with a metal at elevated temperatures, which comprises adding to said corrosive acid an inhibiting effective amount of a corrosion inhibitor composition comprising: at least one acetylenic alcohol having the general formula:



wherein R_1 , R_2 and R_3 are each selected from hydrogen, alkyl, phenyl, substituted phenyl and hydroxy-alkyl radicals; at least one aromatic quaternary ammonium compound; at least one aromatic hydrocarbon compound which exhibits high oil-wetting characteristics; at least one antimony compound capable of activation by the other constituents of said corrosion inhibitor composition whereby the corrosivity of said corrosive acid in contact with said ferrous metal is reduced; and, at least one stabilizer selected from reactive fluoride-containing compounds, compounds having alpha-hydroxy or beta-hydroxy organic acid functional groups, or polyhydroxy compounds having from 3 to 9 carbon atoms, present in an amount effective for preventing substantial precipitation of said antimony compound from at least partially spent acid solutions containing said corrosion inhibitor.

2. A method according to claim 1, wherein the or each stabilizer is selected from hydrofluoric acid, lactic acid, glycolic acid, citric acid, tartaric acid, alkali metal fluorides, alkaline earth fluorides, rare earth fluorides, transition metal fluorides, ammonium fluoride, ammonium bifluoride, alkali metal salts of citric, tartaric, lactic and glycolic acid, 3,4-dihydroxy-1,6-hexanedioic acid, 3-hydroxyl-propionic acid and 3-hydroxyl-butanoic acid, sorbitol, glycerol, mannitol, perseitol, glucose, mannose, xylitol, altritol, iditol, ribitol and erythritol.

3. A method according to claim 1 or 2, wherein the molar ratio of the stabilizer to the antimony compound present in said composition is at least about 1.

4. A method according to claim 1, 2 or 3, wherein said corrosion inhibitor composition contains a solvent effective amount of an alkanol, and/or a non-ionic surfactant.

5. A method according to any of claims 1 to 4, wherein the volumetric ratio of said acetylenic alcohol to said hydrocarbon having high oil-wetting characteristics is in the range of from about 0.08:1 to about 1.66:1.

6. A method according to any of claims 1 to 5, wherein said corrosion inhibitor composition is present in said acidic solution in an amount of at least about 0.5 percent by volume of said acidic solution.

7. A method according to any of claims 1 to 6, wherein the or each antimony compound is selected from antimony trioxide, antimony pentoxide, antimony trichloride, antimony pentachloride, alkali metal



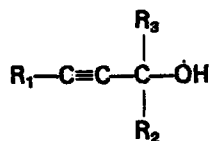
salts of pyroantimonate, antimony adducts of ethylene glycol, and solutions containing ethylene glycol, water and the oxidized product of hydrogen peroxide and at least one trivalent antimony compound.

8. A stabilized acidic composition containing antimony compounds comprising:

(a) an aqueous ferrous metal corrosive acid; and

(b) a corrosion inhibitor composition comprising:

at least one acetylenic alcohol having the general formula



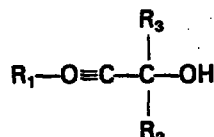
wherein R_1 , R_2 and R_3 are each selected from hydrogen, alkyl, phenyl, substituted phenyl and hydroxy-alkyl radicals; the alcohol being present in an amount of from 5 to 35 percent by volume of said corrosion inhibitor; at least one aromatic quaternary ammonium compound; at least one aromatic hydrocarbon compound which exhibits high oil-wetting characteristics present in an amount whereby the volumetric ratio of said acetylenic alcohol to said hydrocarbon compound is in the range of 0.08:1 to 1.66:1; at least one antimony compound capable of activation by the other constituents of said corrosion inhibitor composition whereby the corrosivity of said corrosive acid in contact with said ferrous metal is reduced; and at least one stabilizer selected from reactive fluoride-containing compounds, compounds having alpha-hydroxy or beta-hydroxy organic acid functional groups or polyhydroxy compounds having from 3 to 9 carbon atoms, present in an amount effective for preventing substantial precipitation of said antimony compound from at least partially spent acid solutions containing said corrosion inhibitor.

9. A composition according to claim 8, wherein the or each said antimony compound is selected from antimony trioxide, antimony pentoxide, antimony trichloride, antimony pentachloride, alkali metal salts of pyroantimonate, antimony adducts of ethylene glycol, and solutions containing ethylene glycol, water and the oxidized product of reaction between hydrogen peroxide and at least one trivalent antimony compound.

10. A corrosion inhibitor composition as defined hereinabove in any of claims 1 to 5, 8 or 9.

Patentansprüche

1. Verfahren zur Verhinderung der Korrosion eines Metalls durch Kontakt mit einer korrosiven Säure bei erhöhten Temperaturen, bei dem der korrosiven Säure eine die Korrosion wirksam verhindernde Menge einer Korrosionsverhindererzusammensetzung zugefügt wird, enthaltend wenigstens einen Acetylenalkohol der allgemeinen Formel



worin R_1 , R_2 und R_3 jeweils aus Wasserstoff, Alkylradikalen, Phenylradikalen, substituierten Phenylradikalen und Hydroxyalkylradikalen ausgewählt sind; wenigstens eine aromatische quaternäre Ammoniumverbindung; wenigstens eine aromatische Kohlenwasserstoffverbindung mit guten Öl-Benetzungseigenschaften; wenigstens eine Antimonverbindung, die durch die anderen Bestandteile der Korrosionsverhindererzusammensetzung aktivierbar ist, wodurch die Korrosion von eisenhaltigen Metallen durch Kontakt mit der korrosiven Säure verringert wird; und wenigstens einen Stabilisator, ausgewählt aus Verbindungen mit reaktivem Fluorid, Verbindungen mit organischen α -Hydroxy- oder β -Hydroxy-Säuregruppen als funktionelle Gruppen, oder Polyhydroxyverbindungen mit 3 bis 9 Kohlenstoffatomen, in ausreichender Menge, um wirksam eine wesentliche Ausfällung der jeweiligen Antimonverbindung aus wenigstens teilweise verbrauchten Säurelösungen zu verhindern, die den Korrosionsverhinderer enthalten.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der oder jeder Stabilisator ausgewählt wird aus Fluorwasserstoffsäure, Milchsäure, Glykolsäure, Zitronensäure, Weinsäure, Alkalimetallfluoriden, Erdalkalifluoriden, Fluoriden seltener Erden, Übergangsmetallfluoriden, Ammoniumfluorid, Ammoniumbifluorid, Alkalimetallsalzen von Zitronensäure, Weinsäure, Milchsäure und Glykolsäure, 3,4-Dihydroxy-1,6-hexandicarbonsäure, 3-Hydroxypropionsäure und 3-Hydroxybuttersäure, Sorbitol, Glycerin, Mannitol, Perseitol, Glucose, Mannose, Xylitol, Altritol, Iditol, Ribitol und Erythritol.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Molverhältnis von Stabilisator zu Antimonverbindung in der Korrosionsverhindererzusammensetzung wenigstens ungefähr 1 beträgt.

4. Verfahren nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß die



Korrosionsverhindererzusammensetzung eine als Lösungsmittel wirksame Menge eines Alkanols und/oder ein nichtionisches Benetzungsmittel enthält.

5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das Volumverhältnis von Acetylenalkohol zu dem Kohlenwasserstoff mit guten Öl-Benetzungseigenschaften im Bereich von etwa 0,08 zu 1 bis zu etwa 1,66 zu 1 liegt.

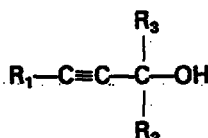
6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die Korrosionsverhindererzusammensetzung in der sauren Lösung in einer Menge von wenigstens etwa 0,5 Vol.-%, bezogen auf das Gesamtvolumen der sauren Lösung=100, enthalten ist.

7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß die oder jede Antimonverbindung ausgewählt ist aus Antimontrioxid, Antimonpentoxid, Antimontrichlorid, Antimonpentachlorid, Alkalimetallpyroantimonaten, Antimonadditionsverbindungen von Ethylenglykol, und Lösungen enthaltend Ethylenglykol, Wasser und das Oxidationsprodukt von Wasserstoffperoxid und wenigstens einer dreiwertigen Antimonverbindung.

8. Stabilisierte saure Zusammensetzung, die Antimonverbindungen enthält, enthaltend

(a) eine wäßrige, für eisenhaltige Metalle korrosive Säure; und

(b) eine Korrosionsverhindererzusammensetzung, enthaltend: wenigstens einen Acetylenalkohol der allgemeinen Formel



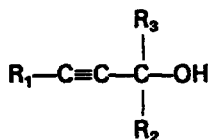
25 worin R_1 , R_2 und R_3 jeweils aus Wasserstoff, Alkylradikalen, Phenylradikalen, substituierten Phenylradikalen und Hydroxyalkylradikalen ausgewählt sind, der in einer Menge von 5 bis 35 Vol.-%, bezogen auf das Gesamtvolumen des Korrosionsverhinderers=100, vorhanden ist; wenigstens eine aromatische quaternäre Ammoniumverbindung; wenigstens eine aromatische Kohlenwasserstoffverbindung mit guten Öl-Benetzungseigenschaften, die in einer Menge entsprechend einem Volumverhältnis von Acetylenalkohol zu der aromatischen Kohlenwasserstoffverbindung im Bereich von 0,08:1 bis 1,66:1 vorhanden ist; wenigstens eine Antimonverbindung, die durch die anderen Bestandteile der Korrosionsverhindererzusammensetzung aktivierbar ist, wodurch die Korrosion von den eisenhaltigen Metallen durch Kontakt mit der korrosiven Säure verringert wird; und wenigstens einen Stabilisator, ausgewählt aus Verbindungen mit reaktivem Fluorid, Verbindungen mit organischen α -Hydroxy- oder β -Hydroxy-Säuregruppen als funktionelle Gruppen, oder Polyhydroxyverbindungen mit 3 bis 9 Kohlenstoffatomen, in ausreichender Menge, um wirksam eine wesentliche Ausfällung der jeweiligen Antimonverbindung aus wenigstens teilweise verbrauchten Säurelösungen zu verhindern, die den Korrosionsverhinderer enthalten.

9. Zusammensetzung nach Anspruch 8, dadurch gekennzeichnet, daß die oder jede Antimonverbindung ausgewählt ist aus Antimontrioxid, Antimonpentoxid, Antimontrichlorid, Antimonpentachlorid, Alkalimetallpyroantimonaten, Antimonadditionsverbindungen von Ethylenglykol, und Lösungen enthaltend Ethylenglykol, Wasser und das oxidierte Reaktionsprodukt von Wasserstoffperoxid und wenigstens einer dreiwertigen Antimonverbindung.

10. Korrosionsverhindererzusammensetzung nach einem der Ansprüche 1 bis 5, 8 oder 9.

Revendications

1. Procédé d'inhibition de l'action corrosive d'un acide corrosif en contact avec un métal à températures élevées, qui consiste à ajouter audit acide corrosif une quantité inhibitrice efficace d'une composition anticorrosive comprenant: au moins un alcool acétylénique de formule générale



où R_1 , R_2 et R_3 sont chacun choisis parmi hydrogène, alcoyle, phényle, phényle substitué et hydroxyalcoyle; au moins un composé d'ammonium quaternaire aromatique; au moins un hydrocarbure aromatique présentant de très bonnes caractéristiques de mouillabilité à l'huile, au moins un composé d'antimoine capable d'activation par les autres constituants de ladite composition anticorrosive, la corrosivité dudit acide corrosif au contact dudit métal ferreux étant ainsi réduite, et au moins un stabilisant choisi parmi des composés réactifs contenant des fluorures, composés ayant des groupes fonctionnels acides organiques α -hydroxylés ou β -hydroxylés, ou des composés polyhydroxylés de 3 à 9 atomes de carbone, présents en une quantité efficace pour prévenir une précipitation notable dudit composé



d'antimoine à partir des solutions acides au moins partiellement consommées renfermant ledit inhibiteur de corrosion.

2. Procédé selon la revendication 1, où le stabilisant est choisi parmi l'acide fluorhydrique, l'acide lactique, l'acide glycolique, l'acide citrique, l'acide tartrique, les fluorures de métaux alcalins ou alcalino-terreux, les fluorures des terres rares, les fluorures de métaux de transition, le fluorure d'ammonium, le difluorure d'ammonium, les sels de métaux alcalins des acides citrique, tartrique, lactique et glycolique, l'acide 3,4-dihydroxy-1,6-hexanedioïque, l'acide 3-hydroxypropionique et l'acide 3-hydroxybutanoïque, le sorbitol, le glycérol, le mannitol, le perséitol, le glucose, le mannose, le xylitol, l'altritol, l'iditol, le ribitol et l'érythritol.

3. Procédé selon la revendication 1 ou 2, où le rapport molaire du stabilisant au composé d'antimoine présent dans ladite composition est d'au moins environ 1.

4. Procédé selon les revendications 1, 2 ou 3, où ladite composition anticorrosive contient une quantité suffisante d'alcool comme solvant, et/ou un tensioactif non-ionique.

5. Procédé selon l'une quelconque des revendications 1 à 4, où le rapport volumétrique dudit alcool acétylénique audit hydrocarbure ayant de très bonnes caractéristiques de mouillabilité à l'huile se situe dans l'intervalle d'environ 0,08:1 à environ 1,66:1.

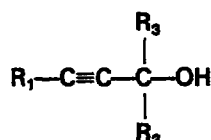
6. Procédé selon l'une quelconque des revendications 1 à 5, où ladite composition antiinhibitrice est présente dans ladite solution acide en quantité d'environ au moins 0,5% en volume de ladite solution acide.

7. Procédé selon l'une quelconque des revendications 1 à 6, où le (ou chaque) composé d'antimoine est choisi parmi: trioxyde d'antimoine, pentoxyde d'antimoine, trichlorure d'antimoine, pentachlorure d'antimoine, sels de métaux alcalins de pyroantimoniate, produits d'addition d'antimoine et d'éthylèneglycol, et solutions contenant de l'éthylèneglycol, de l'eau et du produit d'oxydation du peroxyde d'hydrogène et d'au moins un composé d'antimoine trivalent.

8. Composition acide stabilisée contenant des composés d'antimoine comprenant:

(a) un acide aqueux corrosif pour les métaux ferreux; et

(b) une composition anticorrosive comprenant: au moins un alcool acétylénique de formule générale



où R_1 , R_2 et R_3 sont chacun choisie parmi hydrogène, alcoyle, phényle, phényle substitué et hydroxylcoyle; l'alcool étant présent en quantité de 5 à 35% en volume dudit inhibiteur de corrosion; au moins un composé d'ammonium quaternaire aromatique; au moins un hydrocarbure aromatique présentant de très bonnes caractéristiques de mouillabilité à l'huile et présent en une quantité telle que le rapport volumétrique dudit alcool acétylénique audit hydrocarbure se situe dans l'intervalle 0,08:1 à 1,66:1; au moins un composé d'antimoine capable d'activation par les autres constituants de ladite composition anticorrosive, la corrosivité dudit acide corrosif au contact dudit métal ferreux étant ainsi réduite; et au moins un stabilisant choisi parmi des composés réactifs contenant des fluorures, composés ayant des groupes fonctionnels acides organiques alpha-hydroxylés ou beta-hydroxylés, ou des composés polyhydroxylés de 3 à 9 atomes de carbone, présents en une quantité efficace pour prévenir une précipitation notable dudit composé d'antimoine à partir des solutions acides au moins partiellement consommées renfermant ledit inhibiteur de corrosion.

9. Composition selon la revendication 8, où le (ou chaque) dit composé d'antimoine est choisi parmi: trioxyde d'antimoine, pentoxyde d'antimoine, trichlorure d'antimoine, pentachlorure d'antimoine, sels de métaux alcalins de pyroantimoniate, produits d'addition d'antimoine et d'éthylèneglycol, et solutions contenant de l'éthylèneglycol, de l'eau et le produit d'oxydation de la réaction entre le peroxyde d'hydrogène et au moins un composé d'antimoine trivalent.

10. Une composition antiinhibitrice telle que définie ci-dessus dans l'une quelconque des revendications 1 à 5, 8 ou 9.

