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PROCESS OF INHIBITING CORROSION AND CORROSION INHIBITING COMPOSITIONS

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7 Claims. (Cl. 252—8.55)

This invention relates to the retarding of corrosion of metals and more particularly to corrosion inhibiting compositions for use in preventing the corrosion of iron, steel, and ferrous alloys.

An object of the invention is to provide a new and improved process for inhibiting corrosion of metal equipment in oil and gas wells.

Another object of the invention is to provide a method of preventing corrosion of pipe or equipment which is in contact with a corrosive oil-containing medium in oil wells, refineries or the like.

Still a further object of the invention is to provide a method of inhibiting corrosion of metals in systems which are subject to contact by various corrosive agents such as carbon dioxide, aqueous or non-aqueous solutions of carbon-dioxide, hydrogen sulfide, aqueous or non-aqueous solutions of hydrogen sulfide, brines, weak inorganic acids and organic acids.

An additional object of the invention is to provide new and improved corrosion inhibiting compositions which are readily absorbed by metal surfaces. Other objects will appear hereinafter.

In accordance with the invention, it has been found that new and improved results in inhibiting corrosion, particularly in inhibiting the corrosion of ferrous metals in oil and gas well equipment, are obtained by applying to the metals a corrosion inhibitor which can be described as a quaternary salt of a compound from the group consisting of compounds having the general formula

$$\mathrm{R{-}\underset{\substack{\| \\ O}}{C}(NHC_xH_{2x})_mNH_2}$$

and compounds having the general formula

$$\mathrm{NH_2(C_xH_{2x}NH)_m\underset{\substack{\| \\ O}}{C}{-}R{-}\underset{\substack{\| \\ O}}{C}(NHC_yH_{2y})_nNH_2}$$

wherein *x*, *y*, *m* and *n* are the same or different whole numbers, and R is the non-carboxy portion of a fatty acid containing at least 12 carbon atoms.

The compounds to be quaternized are preferably produced by heating to a temperature of at least 260° C. under conditions facilitating the elimination of an aqueous distillate, a mixture comprising an alkylene polyamine and an organic acid from the group consisting of fatty acids and dimeric derivatives of fatty acids, said fatty acids having at least 12 carbon atoms.

The quaternary salt of the aforementioned compound is generally produced by admixing with the compound an alkyl ester of a mineral acid, preferably by admixing with the compound lower alkyl esters of a strong acid, such as the lower alkyl halides, sulfonates and sulfates, e.g., diethyl sulfate, in an amount in excess of molecular requirements. Employing an excess of diethyl sulfate as the quaternizing agent, the reaction is believed to be as follows:

$$\mathrm{R{-}\underset{\substack{\| \\ O}}{C}(NHC_nH_{2n})_xNH_2+2(C_2H_5)_2SO_4 \longrightarrow}$$

$$\mathrm{R{-}\underset{\substack{\| \\ O}}{C}(C_2H_5NC_nH_{2n})_x\underset{\substack{| \\ HSO_4}}{N}(C_2H_5)_3+H_2SO_4}$$

wherein R is the non-carboxy portion of a detergent-forming fatty acid containing 12 or more carbon atoms, and *n* and *x* are whole numbers. However, in the above representative reaction, it is not certain that all of the nitrogen groups are ethylated; nor is it certain that only one of the ethylated nitrogen groups is quaternized.

The simplest polyamines employed for the practice of the invention are those containing two primary amino groups connected by a carbon chain, e.g., ethylene diamine, 1,2-propylene diamine, trimethylene diamine, butylene diamine, amylene diamine, hexamethylene diamine, decamethylene diamine, etc.

The alkylene polyamines which are preferably employed in preparing the corrosion inhibitors of the present invention include, for example, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, dipropylenetriamine, tripropylenetetramine, and higher homologues thereof, including still residues that remain after the preparation of these materials. These starting materials can be described generally as polyalkylene polyamines because they contain two or more alkylene groups separated from each other by nitrogen atoms.

The terminal amino groups of the alkylene polyamines are preferably primary amino groups and any intermediate amino groups (or imino groups) are preferably secondary. In an amidification reaction the acylation of the polyamine can take place either at the primary or secondary groups, but acylation preferentially occurs at the primary groups until these groups are acylated. When the primary amino groups are blocked by the acyl groups or other groups, acylation or amidification occurs at the secondary amino groups.

The organic acids suitable for the purpose of this invention are fatty acids having at least 12 carbon atoms or the dimeric derivatives thereof. Mixtures of fatty acids may also be used. An example of such a mixture is crude tall oil in which the fatty acids comprise 45% to 60% by weight and include, oleic, linoleic and dilinoleic acids, the remainder being largely natural carbocyclic resin acids, principally abietic acid. Castor oil is another material containing suitable fatty acids.

The dimeric derivatives of fatty acids suitable for the purpose of this invention are the condensation products or dimers of two molecules of fatty acid. Any mixtures of the dimers with the monomeric acids or mixtures of dimeric acids are also suitable. Dimers of suitable fatty acids are obtained, for example, as a by-product from the production of sebacic acid. Dimeric acids suitable for use as starting materials in the practice of the invention can be prepared by any of the methods described in Goebel, U.S. 2,482,761, or Landis, U.S. 2,632,695. Especially suitable polymer acids for the purpose of the invention are polymerized di-unsaturated mono-carboxy acids, e.g., dilinoleic acid, and the dimeric acids obtained by the dry distillation of castor oil in the presence of sodium hydroxide.

The fatty acid chlorides, glycerides and other esters of the fatty acids may be used in place of the free fatty acids, but this is not usually done in commercial practice.

Generally the condensation of the polyamine with the fatty acid is effected by gradually heating a mixture of the two compounds to a certain temperature and then holding the mixture at this temperature until the equivalent quantity of water has been eliminated. However, for the purpose of this invention it is essential to amidify all of the carboxy groups present in the reaction mixture. Accordingly, an excess of polyamine and a final reaction temperature of at least 260° C. is employed.

The relative proportions of the polyamine and the fatty acid employed in making the intermediate compounds,

while in excess of a mol ratio of N:COOH of 1:1, usually do not exceed a mol ratio of N:COOH of 20:1.

The invention is further illustrated but is not limited by the following examples in which quantities are stated in parts by weight unless otherwise indicated. Some of the starting materials employed in these examples are defined as follows:

Polyamine H Special is a mixture of 75% polyalkylene polyamine homologues higher than tetraethylenepentamine and 25% of diethylenetriamine.

Technical diethylenetriamine is a mixture of 85% diethylenetriamine and 15% higher polyalkylene polyamine homologues.

VR–1 acid is a mixture of polybasic acids, with an average molecular weight of about 1,000. It has an average of slightly less than two carboxylic acid groups per molecule. It is a by-product acid, and is a dark amber, rather viscous liquid. A typical sample of VR–1 acid gave the following analysis:

Acid number	150
Iodine number	36
Saponification number	172
Unsaponifiable matter ——percent——	3.7, 3.5
Moisture content ——do——	0.86

Dimer acids are a commercial form of a dimeric polymer consisting essentially of dilinoleic acid. The method used in their preparation is set forth in the Journal of the American Oil Chemists' Society, 24, 65 (March 1947). Specifications are as follows:

Neutral equivalent	290–310.
Iodine value	80–95.
Color	Gardner 12 max.
Dimer content	Approximately 85%.
Trimer and higher	Approximately 12%.
Monomer	Approximately 3%.

Hardesty 401 fatty acid is a by-product from the production of sebacic acid which contains between 40% and 50% dimer acids. The molecular weight as determined from the saponification number is around 300. The material contains approximately 75% to 80% of free fatty acid and has an iodine number of 50 and a saponification of 180.

Hardesty D75 acid is a dimerized fatty acid derived from the manufacture of sebacic acid. It differs from Hardesty 401 fatty acid in that most of the monobasic acids have been removed. It is essentially a clear dimerized fatty acid with an average equivalent weight of about 300.

Example I

2580 pounds of crude tall oil and 1375 pounds of polyamine H Special are charged into a stainless steel vessel equipped with a means of heating and agitation, and a trap for removing water collected during azeotropic distillation. The reaction mass is agitated while gradually heating. At a temperature of 130°–140° C. extreme care is exercised, for the presence of any contaminating water in the reactants will cause severe foaming in the vessel. Heating is continued to 260°–275° C. and held at that point for at least thirty minutes until about 32 gallons of aqueous distillate is secured. The reaction product is represented by the formula:

$$R-\underset{\underset{O}{\|}}{C}(NHC_xH_{2x})_mNH_2$$

wherein R is the non-carboxy portion of a fatty acid obtained from tall oil, and x and m are the same or different whole numbers. The reaction mass is then cooled to about 90° C. At this point 2120 pounds of diethyl sulfate are added gradually in small portions of 100 to 200 pounds each, being certain that the reaction temperature is maintained below 120° C. After the addition of diethyl sulfate has been completed, the temperature of the mass is raised to 140° C. and held at that point for one hour. After cooling to 90° C., 4050 pounds of water and 2900 pounds of methanol are added and the product stirred to uniformity to yield the finished product.

Example II

In a three-necked reaction flask there is added 300 parts by weight of tall oil and 105 parts by weight of a technical grade diethylenetriamine. The reaction flask is provided with a means of agitation, heating, and a water trap to remove aqueous distillate as it forms throughout the course of the reaction. Temperature is gradually raised and at 160° C. an aqueous distillate begins to form. After four hours at a maximum temperature of 255° C. a total of 32 ccs. of aqueous distillate was secured. The reaction product is represented by the formula:

$$R-\underset{\underset{O}{\|}}{C}(NHC_2H_4)_2NH_2$$

wherein R is the non-carboxy portion of a fatty acid obtained from tall oil. After cooling to approximately 90° C., 250 grams of diethyl sulfate were added in small portions while maintaining the reaction temperature below 100° C. After addition was complete the temperature was raised to 135°–140° C. and held for one hour. After cooling to approximately 90°, 375 grams of water and 250 grams of methanol were added with stirring to yield the finished product.

Example III

Following the procedure of Example II, 60 grams of anhydrous ethylene diamine are used in place of the technical grade diethylenetriamine. Prior to quaternizing the reaction product is represented by the formula:

$$R-\underset{\underset{O}{\|}}{C}NHC_2H_4NH_2$$

wherein R is the non-carboxy portion of a fatty acid obtained from tall oil.

Example IV

Following the procedure of Example II, 80 grams of a 90% to 95% propylene diamine are used in place of the technical grade diethylenetriamine. Prior to quaternizing the reaction product is represented by the formula:

$$R-\underset{\underset{O}{\|}}{C}NHC_3H_6NH_2$$

wherein R is the non-carboxy portion of a fatty acid obtained from tall oil.

Example V

Following the procedure of Example II, 190 grams of tetraethylenepentamine are used in place of the technical grade diethylenetriamine. Prior to quaternizing the reaction product is represented by the formula:

$$R-\underset{\underset{O}{\|}}{C}(NHC_2H_4)_4NH_2$$

wherein R is the non-carboxy portion of a fatty acid obtained from tall oil.

Example VI

Following the procedure of Example II, 280 grams of oleic acid were used in place of the crude tall oil. Prior to quaternizing the reaction product is represented by the formula:

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7\underset{\underset{O}{\|}}{C}(NHC_2H_4)_2NH_2$$

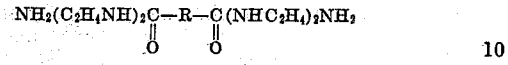
Example VII

Following the procedure of Example II, 312 grams of castor oil are used in place of the crude tall oil. Prior to quaternizing the reaction product is represented by the formula given in Example II except that R is the non-

carboxy portion of a fatty acid obtained from castor oil.

Example VIII

Following the procedure of Example II, 300 grams of Hardesty D75 acid were used in place of the tall oil. Prior to quaternizing the reaction product is represented by the formula:



wherein R is the non-carboxy portion of a dimerized fatty acid derived from the manufacture of sebacic acid.

Example IX

Following the procedure of Example II, 500 grams of Rohm & Haas VR–1 acid are used in place of the crude tall oil.

Example X

Following the procedure of Example II, 300 grams of Emery's dimerized fatty acid are used in place of the crude tall oil.

Example XI

Following the procedure of Example II, 300 grams of Hardesty's No. 401 fatty acid are used in place of the crude tall oil.

Example XII

Following the procedure of Example II a mixture of 150 grams of Hardesty D75 acid and 75 grams of crude tall oil were used in place of the crude tall oil alone.

The compositions prepared in Examples I–XII were found to be highly surface active. They were not only effective as corrosion inhibitors but also had a bactericidal action.

The quantity of the active effective corrosion inhibitor required to retard or prevent corrosion is very small, being of the order of a molecular film on the iron metal surface or other metal surface to be protected. In order to properly distribute the corrosion inhibitor on the metal surface, it is preferably dispersed in an inert solvent such as methanol, as directed in Examples I–XII. Other suitable inert solvents include SO_2 extract, isopropanol or mixtures thereof, or alcoholic or hydrocarbon liquids or homogeneous mixtures thereof.

The active effective corrosion inhibiting composition can also be prepared and used in the form of solids with or without weighting materials, wetting agents, dispersing agents, waxes and other auxiliary substances including those substances sometimes used in the preparation of the so-called solid stick corrosion inhibitors.

The invention is specially useful in combating internal corrosion attack in oil and gas wells, flow lines, and other oil production installations. Its use is also applicable in the protection of secondary recovery installations such as supply and injection wells. The process of the invention is carried out simply by bringing the corrosion inhibiting composition in contact with the metal surface of the equipment. The preferred method is to inject a corrosion inhibiting composition of the type dissolved in an inert inorganic solvent into the well annulus by means of a chemical proportioning pump continuously at the rate of one quart to two quarts of the aforesaid compositions per well per day. A ratio of 10 parts to 200 parts (preferably 50 parts) per million of the composition based on total production is usually recommended as a ratio which will bring corrosive attack under control in the down-hole treatment of oil wells. One quart of the composition per two million cubic feet of gas produced in the recommended dosage for gas wells, although the dosage should be somewhat controlled by the amount of water produced. When treatment is initiated, it is general practice to batch treat with 5 to 10 gallons of a methanol dispersed composition to take advantage of the detergent properties of the composition and also to establish a high concentration of the composition at the onset of treatment. An alternative method is to inject a slug of the material into the well periodically over one or two days. Where the corrosion inhibiting composition is prepared as a solid, it can be dropped into the well as a solid lump. Any of the other well known methods for applying corrosion inhibiting materials to oil and gas wells can be used in the practice of the invention.

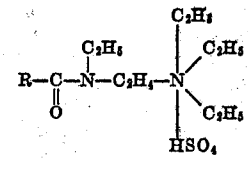
The corrosive fluids which may be treated in the practice of the invention include hydrocarbon fluids containing water such as, for example, crude petroleum as it comes from the well, petroleum distillates such as fuel oil, diesel fuels, kerosene, gasoline and mixtures of petroleum hydrocarbons and brines (e.g., mixtures of gasoline and sea water).

The compositions of the invention are especially advantageous because they are compatible with petroleum and have no adverse effect thereon. The amphoteric nature of the corrosion inhibiting compositions apparently results in better micelle formation and better adsorption at the metal surface. The chemical nature of the compositions, particularly the presence of the long chain fatty acid groups in the molecule assists in providing better adsorption and larger coverage of the metal surface which is to be protected against corrosion.

While the invention is not limited to any theory, it is thought that the unusual effectiveness of these compositions in inhibiting corrosion is due to their high oil solubility, the fact that they cause the oil to wet the metal surface and the fact that they are not lost in the water phase in the fluid containing both oil and water.

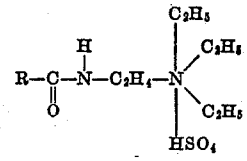
It will be understood that the invention is susceptible to some variation and modification. Thus, the quaternizing reaction can be driven more nearly to completion by removing the free acid formed. This can be accomplished by adding a basic material during the course of the reaction as, for example, sodium hydroxide or potassium hydroxide. Good results are obtained when the final pH of the reaction mixture is between 6 and 7. If the pH falls below 6 an additional quantity of the polyamine or of the amide-amine can be added in order to raise the pH. When the quaternizing action is not driven to completion some simple amine salts can be formed. For instance, in Example III when the quaternizing acition is driven to completion with respect to the primary amino group of the acylated amine and carried far enough to cause the hydrogen atom attached to the imino group to be replaced by an ethyl radical, the resultant product has the following chemical formula:

(A)

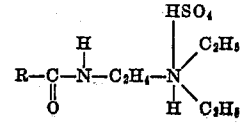


However, the possibility exists for the formation of minor amounts of compounds having the following chemical formulae:

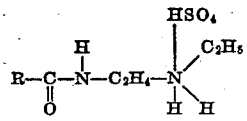
(B)



(C)



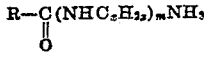
(D)



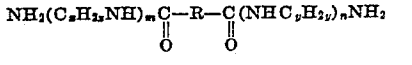
It will be apparent that when diethylenetriamine is employed in place of ethylenediamine as the polyamine a greater number of derivatives can be formed. The same is true when any other polyalkylene polyamine is substituted for an alkylene diamine because the polyalkylene polyamine contains secondary amino nitrogen atoms which are capable of reacting with the quaternizing agent.

The invention is hereby claimed as follows:

1. A process for preventing corrosion of ferrous metals in contact with petroleum hydrocarbons containing corrosive agents selected from the group consisting of carbon dioxide, hydrogen sulfide, brine, weak inorganic acids and organic acids, which comprises applying to the metal a corrosion inhibiting amount of a composition comprising a quaternary salt of at least one compound from the group consisting of compounds having the general formula



and compounds having the general formula



wherein x is an integer from 2–10, inclusive, y is an integer from 2–10, inclusive and m and n are at least 1 and R is the non-carboxy portion of a fatty acid containing at least 12 carbon atoms.

2. A process for preventing corrosion of ferrous metals in contact with petroleum hydrocarbons containing corrosive agents selected from the group consisting of carbon dioxide, hydrogen sulfide, brine, weak inorganic acids and organic acids which comprises applying to the metal a corrosion inhibiting amount of a composition consisting essentially of a quaternary salt of a compound produced by reacting an alkylene polyamine with an organic acid from the group consisting of fatty acids and dimeric derivatives of fatty acids at a temperature of at least 260° C. with the removal of water from the reaction mixture until about one mol of water of reaction per mol equivalent of carboxy groups have been removed, said acids having at least 12 carbon atoms.

3. A process for preventing corrosion of ferrous metals in contact with petroleum hydrocarbons containing corrosive agents selected from the group consisting of carbon dioxide, hydrogen sulfide, brine, weak inorganic acids and organic acids which comprises applying to the metal a corrosion inhibiting amount of a composition consisting essentially of a quaternary salt of an acyclic compound produced by heating to a temperature of at least 260° C. with the removal of water from the reaction mixture until about one mol of water of reaction per mol equivalent of carboxy groups has been removed, a mixture comprising an alkylene polyamine having at least two and not more than ten carbons per alkylene group and an organic acid from the group consisting of fatty acids and dimeric derivatives of fatty acids, said acids having at least 12 carbon atoms.

4. A process for preventing corrosion of ferrous metals in contact with petroleum hydrocarbons containing corrosive agents selected from the group consisting of carbon dioxide, hydrogen sulfide, brine, weak inorganic acids and organic acids which comprises applying to the metal a corrosion inhibiting amount of a composition consisting essentially of a quaternary salt produced by heating to a temperature in the range of 260° C. to about 275° C. with the removal of water from the reaction mixture until about one mol of water of reaction per mol equivalent of carboxy groups has been removed, a mixture comprising an alkylene polyamine having at least two and not more than ten carbons per alkylene group and an organic acid from the group consisting of fatty acids and dimeric derivatives of fatty acids, said acids having at least 12 carbon atoms, and quaternizing the resulting product by admixing therewith a molar excess of an alkyl ester of a mineral acid.

5. The process according to claim 1 wherein said organic acid is a tall oil acid.

6. The process according to claim 1 wherein said organic acid is a dimerized fatty acid obtained as a by-product of the manufacture of sebacic acid.

7. A process for preventing corrosion of ferrous metals in contact with petroleum hydrocarbons containing corrosive agents selected from the group consisting of carbon dioxide, hydrogen sulfide, brine, weak inorganic acids and organic acids which comprises applying to the metal a corrosion inhibiting amount of a composition consisting essentially of a quaternary salt produced by heating to a temperature in the range of 260° C. to about 275° C. with the removal of water from the reaction mixture until about one mol of water of reaction per mol equivalent of carboxy groups has been removed, a mixture comprising a polyalkylene polyamine having 2–3 carbons per alkylene group and two primary amino groups and tall oil, and quaternizing the resulting product by admixing a molar excess of diethyl sulfate therewith at a final pH between 6 and 7.

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