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METHOD AND COMPOSITION FOR COMBATING CORROSION

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This invention concerns the protection of ferruginous materials against corrosion, particularly by fluids derived from subterranean sources. It is especially concerned with the protection of ferrous metal parts of oil or gas wells, pipelines and processing equipment against the action of corrosive agents in, or accompanying, the petroleum fluids that are contacted therewith.

The production of fluids, especially petroleum fluids, from underground sources, and the processing of such fluids, is usually attended by corrosion of the ferruginous parts, e. g. the steel parts, of the system in contact with the fluids being produced. Subterranean fluids usually contain water and often contain acidic substances such as carbon dioxide, hydrogen sulfide, organic acids, inorganic acids, salts of acids, and acidic sulfur compounds. Many of these acidic substances are soluble in water and some are volatile. Thus, the surfaces of metal parts of the wells, pipelines and processing equipment in contact with such fluids are exposed to the corrosive agents occurring in or introduced into such fluids from underground sources.

Many suggestions have been made for preventing such corrosion. It has been proposed to inject various alkaline substances, amino compounds, nitrogenous compounds and other chemicals into the well or process system in order to react with and neutralize the acidic corrodants in the produced fluid. None of these methods and anti-corrosive agents have been entirely satisfactory. Some, such as solids, are difficult to charge to the production system; some are relatively insoluble in the produced fluid or react therewith to cause formation of an insoluble precipitate. Even the least objectionable of such agents are only partially or briefly, i. e. temporarily, effective in preventing the corrosion.

The principal object of this invention is to provide an improved method and composition for combating, i. e. preventing or inhibiting, such corrosion and thus prolonging the useful life of ferruginous materials in contact with fluids, especially petroliferous fluids, obtained from subterranean sources. Other objects and advantages will be apparent from the following description.

It has now been found that mixtures of the several types of organic nitrogen compounds hereinafter described are effective, when applied to ferrous metal surfaces that are to be contacted with the aforementioned petroleum fluids, in preventing or greatly curtailing corrosion of the metals by the substances normally present in the fluids. The corrosion inhibiting compositions of the invention can be applied before, or during contact of the petroleum fluids with the metals.

The corrosion inhibiting compositions of the invention comprise a mixture of organic nitrogen compounds consisting essentially of from 25 to 65 percent by weight of one or more members of a group of organic nitrogen compounds hereinafter designated as group "A"; from 2 to 30 percent of one or more members of another such group "B"; and from 20 to 60 percent of one or more organic nitrogen compounds belonging to the group re-

ferred to below as "C." All of the proportions just given are expressed as percent of the combined weight of the organic nitrogen compounds present belonging to all three of these groups. The following is a description of the organic nitrogen compounds of the respective groups "A," "B" and "C."

GROUP A

Each member of this group is a quaternary ammonium halide, i. e. quaternary ammonium chloride, bromide or iodide, wherein all of the organic substituents are hydrocarbon radicals containing up to 18 carbon atoms, at least one of such radicals being an aliphatic hydrocarbon radical containing from 8 to 18 carbon atoms and each of two of such radicals being lower alkyl radicals having from 1 to 3 carbon atoms. Such quaternary ammonium halides have the general formula



wherein R₁ represents a monovalent hydrocarbon radical, such as an alkyl, alkenyl, alkadienyl, or arylalkyl radical, containing from 1 to 18 carbon atoms; R₂ represents an aliphatic hydrocarbon radical, such as an alkyl, alkenyl or alkadienyl radical, containing from 8 to 18 carbon atoms; R₃ and R₄ represent the same or different lower alkyl radical, such as the methyl, ethyl, propyl or isopropyl radical, X represents a halogen atom, i. e. chlorine, bromine or iodine. Particularly preferred examples of such quaternary ammonium halides are the aliphatic trimethyl ammonium chlorides and the aliphatic benzyl dimethyl ammonium chlorides wherein the aliphatic substituent is a long chain alkyl, alkenyl or alkadienyl radical, e. g. octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, octadecenyl, or octadecadienyl radical, and mixtures thereof.

GROUP B

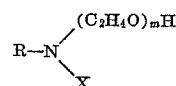
This group consists of tertiary alkyl primary amines having from 18 to 24 carbon atoms and the rosin amines. Such amines have the general formula



wherein R— is a highly branched aliphatic hydrocarbon monovalent radical having from 18 to 24 carbon atoms. In the tertiary alkyl primary amines, the radical R— has the general formula $t-C_nH_{2n+1}$ —wherein n is an integer from 18 to 24 and the acyclic carbon chain contains at least one tertiary carbon atom. In the rosin amines the radical R— represents a highly branched polycyclic terpene hydrocarbon radical such as the abietyl, dihydroabietyl, tetrahydroabietyl, and dehydroabietyl radical; the term "rosin amine" signifies any primary amine or mixture thereof prepared in known manner from various rosins, modified rosins or rosin acids, such as wood rosin, gum rosin, dehydrogenated rosin, hydrogenated rosin, heat-treated rosin, isomerized rosin, polymerized rosin, abietic acid, dehydroabietic acid, dihydroabietic acid, tetrahydroabietic acid, etc., whereby the carboxyl group of the rosin or rosin acid is converted to a $-CH_2NH_2$ group.

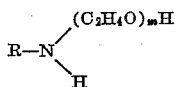
GROUP C

Each member of this group is a polyethylene glycol-amine which is the condensation product of from 8 to 21 moles of ethylene oxide per mole of amine with an amine of group B. These compounds, which can be described as polyglycol ethers of a mono- or di-ethanol amine, have the general formula

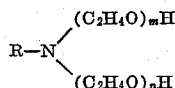


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wherein R— represents any of the hydrocarbon radicals previously described as represented by R— in group B supra; X represents hydrogen or the radical $-(C_2H_4O)_nH$; and m and n represent integers whose sum is 8 to 21. Included in this group C are the products corresponding to polyglycol ethers of a mono-ethanol amine



in which m represents an integer from 8 to 21, and the products corresponding to polyglycol ethers of a diethanol amine



in which m and n are integers, the sum of which is 8 to 21, the symbol R— being as aforesaid.

Examples of mixtures illustrative of preferred inhibitor compositions of this invention are the following:

(1) An inhibitor composition containing, on the basis of their combined weight:

(a) From 35 to 60 per cent of a mixture comprising the quaternary ammonium chlorides hexadecyl-, octadecyl-, octadecenyl-, and octadecadienyl trimethyl ammonium chlorides;

(b) From 10 to 25 per cent of a rosin amine mixture comprising abietylamine, dihydroabietylamine, tetrahydroabietylamine, and dehydroabietylamine; and

(c) From 25 to 40 per cent of a polyethylene glycol ether of ethanol rosin amine, corresponding to the product of condensation of one mole of a rosin amine mixture comprising abietylamine, dihydroabietylamine, tetrahydroabietylamine and dehydroabietylamine with 11 moles of ethylene oxide.

(2) An inhibitor composition containing, on the basis of their combined weight:

(a) From 30 to 60 per cent of a mixture comprising the quaternary ammonium chlorides octyl-, decyl-, dodecyl-, tetradecyl-, hexadecyl- and octadecyl benzyl dimethyl ammonium chloride;

(b) From 2 to 25 per cent of a rosin amine mixture comprising abietylamine, dihydroabietylamine, tetrahydroabietylamine and dehydroabietylamine; and

(c) From 25 to 50 per cent of a polyethylene glycol ether of ethanol rosin amine, corresponding to the product of condensation of one mole of a rosin amine mixture comprising abietylamine, dihydroabietylamine, tetrahydroabietylamine and dehydroabietylamine with 11 moles of ethylene oxide.

In the practice of this invention, the inhibitor mixtures are preferably prepared in the form of solutions in solvents or diluents for the purpose of more convenient handling. The individual components of the mixture may separately be prepared as solutions in solvents and such solutions combined to form the desired mixture, or the concentrated combined mixture may be diluted before use. Suitable solvents and diluents include water, low molecular weight alcohols, e. g. methanol, ethanol, and isopropanol, kerosene or other petroleum oils, or miscible mixtures thereof. The composition may contain as little as 10 per cent or less by weight of the active inhibitor mixture or may, in the absence of solvent or diluent, consist substantially of the active materials.

In practicing the method of the invention, the ferruginous surfaces which are exposed to corrosion by fluids from underground sources are contacted by a liquid composition comprising the inhibitor composition. This step is accomplished by causing the inhibitor mixture, or composition containing the same, to flow over the surfaces to be protected, usually by passing the inhibitor composition into the well, pipeline, processing assembly or other system in such a way that the inhibitor is carried

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into contact with all parts of the system subject to corrosion. The inhibitor composition may be passed into the system to be protected together with, or apart from, the fluids normally processed in the system. Systems to be continuously protected against corrosion need be treated only periodically although treatment may be continuous if desired.

The mechanism by which the inhibitor composition combats corrosion of iron-containing surfaces is not fully understood. The inhibitor appears to exert a pacifying action on the metal surface, since only periodic, not continuous, treatment is necessary in order to confer resistance to continuous corrosive exposure. The action is not entirely one of neutralization of acidic substances in the corrosive agents, since the quantity of inhibitor employed is not necessarily related stoichiometrically to the acids in the corrodant to be combated, and since the treatment has a residual inhibitory effect.

The corrosion inhibiting compositions of the invention are unusually efficacious in combating corrosion of the kind described. Some individual members of the described groups of compounds have previously been reported as having corrosion-inhibiting properties. However, the combinations of these substances herein disclosed have an unexpected, exalted inhibitory influence, under the conditions described, which could not have been foreseen from a consideration of the properties of the individual members. The components of the mixture cooperate in a synergistic, not merely additive, manner in inhibiting corrosion. The mechanism of this synergism is not known, but is characteristic of the particular combination of organic nitrogen compounds herein disclosed.

The following examples illustrate the invention and demonstrate some of its advantages, but are not to be construed as limiting its scope.

Example 1

An inhibitor concentrate was prepared by mixing together:

50 gallons of a 50 per cent by weight solution in isopropanol of a quaternary ammonium chloride mixture comprising, by weight, 10% hexadecyl-, 10% octadecyl-, 35% octadecenyl-, and 45% octadecadienyl-trimethyl ammonium chlorides,

9.3 gallons of a rosin amine mixture comprising abietylamine, dihydroabietylamine, tetrahydroabietylamine, and dehydroabietylamine, and

16 gallons of a polyethylene glycol ether of ethanol rosin amine, corresponding to the product of condensation of one mole of a rosin amine mixture comprising abietylamine, dihydroabietylamine, tetrahydroabietylamine and dehydroabietylamine with 11 moles of ethylene oxide.

The resulting concentrate was mixed with 25.3 gallons of water to make about 100.6 gallons of an inhibitor composition, a part of which was used to treat a producing oil well.

The well was a sour crude well which produced, per day, 15 barrels of oil, 237 barrels of brine and no gas; the fluids contained dissolved hydrogen sulfide and were highly corrosive.

Sandblasted mild steel test coupons were installed at the top of the tubing in contact with the produced oil and brine and were removed from time to time, cleaned, dried and weighed; from the weight lost from the test coupons, the degree of corrosion of the metal parts of the well system was computed as mils per year (a corrosion rate of one mil per year means a loss of weight of the test coupon corresponding to a reduction in thickness of the metal of 0.001 inch per year).

The well was treated with the inhibitor composition prepared as described in this example. In the treatment of this well, one gallon of the inhibitor composition was further diluted with 4 gallons of water and the diluted solution was fed slowly into the annulus between the casing and the tubing while pumping the well through

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the tubing. The well was pumped for 5 hours, the fluids pumped up the tubing being pumped back into the annulus in order to distribute the inhibitor to all portions of the well system. The well was then pumped on production for the remainder of the day. Daily thereafter for a period of four weeks, one-half gallon of the diluted inhibitor, i. e. a mixture of 0.1 gallon of inhibitor composition and 0.4 gallon of water, was fed into the annulus, the well pumped in circulation for 20 minutes, and production resumed by normal pumping for the remainder of each day.

The corrosion rates in the well were computed from the loss of weight of the test coupons as follows

	Mils/year
Prior to using the inhibitor.....	3.38
During first two week of treatment.....	0.12
During second two weeks of treatment.....	0.16

These results indicate that the inhibitor treatment has effected a reduction of about 96 per cent in the rate of corrosion of the iron parts in the well.

Example 2

An inhibitor concentrate was prepared by mixing together:

67.3 gallons of a 50 per cent by weight water solution of a quaternary ammonium chloride mixture comprising octyl-, decyl-, dodecyl-, tetradecyl-, hexadecyl- and octadecyl-benzyl dimethyl ammonium chloride,

11.9 gallons of a rosin amine mixture comprising abietylamine, dihydroabietylamine, tetrahydroabietylamine, and dehydroabietylamine, and

21.9 gallons of a polyethylene glycol ether of ethanol rosin amine, corresponding to the product of condensation of one mole of a rosin amine mixture comprising abietylamine, dihydroabietylamine, tetrahydroabietylamine and dehydroabietylamine with 11 moles of ethylene oxide.

The so prepared inhibitor concentrate, diluted as described below, was used to treat a petroleum well. The well produced, per day, 24 barrels of oil, 16.6 barrels of water and 4220 cubic feet of gas containing 7.1 per cent hydrogen sulfide. Provision was made in the upper end of the tubing string for exposing test coupons of sandblasted mild steel to contact with the produced oil, water and gas.

Initial treatment of the well was made by feeding one gallon of the inhibitor concentrate diluted with 2 gallons of water into the annulus between tubing and casing. Pumping of the well was started, with the pumped fluids being passed into the annulus and back down the well in order to distribute the inhibitor to all parts of the well system. Recirculation was continued for 24 hours. The well was then put on normal production pumping. Daily thereafter, one pint of the inhibitor concentrate diluted with 3 gallons of water was fed into the annulus, the well fluids recirculated for 15 minutes and production resumed.

The corrosion rates in the well were computed from the loss of weight of the test coupons as follows:

	Mils/year
Prior to using the inhibitor.....	15.7
During first two weeks of treatment.....	8.5
During second two weeks of treatment.....	1.1
During third two weeks of treatment.....	0.8

These results indicate that the inhibitor treatment had greatly reduced the degree of corrosion of the iron parts in the well.

Example 3

The inhibitor concentrate described in Example 2 was used to combat corrosion in a recovery unit processing a sour crude oil. The treatment was initiated by feeding

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2 gallons of the inhibitor concentrate into the feed stream of the unit during the first day. Daily thereafter while the unit was in operation, one pint of the inhibitor was fed into the feed stream. The degree of corrosion of the processing unit was greatly reduced.

Example 4

A diluted inhibitor, made by mixing 15.4 gallons of the concentrated inhibitor described in Example 2 and 85.5 gallons of water, was used to treat a petroleum well producing oil and brine. The brine was analyzed and found to contain 76 parts per million of iron by weight, a portion of which was connate iron and a portion due to corrosion of iron parts in the well. The well was given an initial treatment by feeding 10 gallons of the diluted inhibitor into the annulus. On the following day, 5 gallons of the inhibitor was fed into the annulus, and on each of the succeeding days one gallon was used. Analysis of the brine produced showed the iron content in parts per million by weight to be as follows:

	P. p. m.
Before using inhibitor.....	76
After 75 days of treatment.....	36
After 138 days of treatment.....	20

These results manifest a considerable reduction in the degree of corrosion of the iron parts in the well.

Example 5

In order to show by direct comparison for purposes of contrast the corrosion-inhibiting effect of the synergistic compositions of this invention and the individual components thereof, the following tests were made under laboratory-controlled conditions.

A test-apparatus was assembled comprising a closable, generally cylindrical vessel normally in an upright position. The vessel was charged with 525 ml. of an aqueous salt brine containing sodium, calcium and magnesium chlorides and 225 ml. of a light hydrocarbon solvent, the brine forming a lower liquid layer and the hydrocarbon solvent forming an upper liquid layer, together occupying about one-half of the total capacity of the vessel and leaving a gas space. Hydrogen sulfide gas under 300 pounds per square inch pressure was charged into the gas space. Within the vessel was provided means, electrically insulated from the vessel, for mounting a test coupon, normally in the gas space and near to the cylindrical wall of the vessel. Means was provided for slowly and repeatedly tilting the vessel through an angle of about 90° whereby the test coupon was immersed first in the hydrocarbon solvent for about 6 seconds, then in the aqueous brine for about 12 seconds, and allowing the vessel to return quickly to its normal position, whereby the test coupon was exposed to the gas phase for about 112 seconds to complete a cycle of about 130 seconds. Means was also provided for maintaining a constant temperature of 185° F. in the vessel during the tests.

Sandblasted mild steel test coupons, 2¾ inches by 1 inch by ⅛ inch in size, where exposed for 72 hours in the apparatus described above, and the loss in weight of the coupons was computed from the weight of the coupons before and after the tests.

Various substances, separately and in various combinations, were added to the standard brine-hydrocarbon charge in the vessel, to the extent of 100 parts of total test agent per million parts of total fluid in the vessel, and the effect on the corrosion of the test coupons was determined.

In Table I are listed the chemical or chemicals tested, the amount of each per million parts of total fluid, and the weight-loss in grams of the test coupon under the described conditions.

TABLE I

Test No.	Chemical		Coupon Weight Loss, Grams
	Substance	p. p. m. in Total Fluid	
1.	None.		0.1917
2.	Alkyl ¹ benzyl dimethyl ammonium chloride.	100	0.0486
3.	Aliphatic ² trimethyl ammonium chloride.	100	0.0207
4.	Rosin amine.	100	0.0220
5.	Polyethylene glycol ether of ethanol rosin amine. ³	100	0.0278
6.	Polyethylene glycol ether of ethanol tertiary alkyl primary amine. ⁴	100	0.1072
7.	Test substance 2.	66%	0.0199
	Test substance 4.	11%	
	Test substance 5.	21%	
8.	Test substance 2.	50	0.0147
	Test substance 4.	5	
	Test substance 5.	45	
9.	Test substance 2.	25	0.0177
	Test substance 4.	26½	
	Test substance 5.	48¾	
10.	Test substance 2.	50	0.0131
	Test substance 4.	17½	
	Test substance 5.	32½	
11.	Test substance 3.	60	0.0181
	Test substance 5.	26	
	Test substance 4.	14	
12.	Test substance 3.	50	0.0108
	Test substance 5.	32½	
	Test substance 4.	17½	

¹ Alkyl portion is mixture of C₈H₁₇- to C₁₈H₃₇-radicals.

² A mixture comprising, by weight, approximately 10% hexadecyl-, 10% octadecyl-, 35% octadecenyl-, and 45% octadecadienyl-trimethyl ammonium chlorides.

³ Corresponding to the product of condensation of one mole of rosin amine with 11 moles of ethylene oxide.

⁴ Corresponding to the product of condensation of one mole of a mixture of tertiary C₁₈H₃₇NH₂ to C₂₄H₄₉NH₂ primary amines with 21 moles of ethylene oxide.

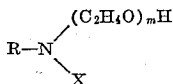
In the table, Test 1 is a blank showing the degree of corrosion of the system in the absence of added inhibitor. Tests 2 through 6 show the effect on the degree of corrosion of the presence of certain substances representing the compounds of groups A, B and C previously described when those classes of compounds are used separately. Tests 7 through 12 show the synergistic effect of combining substances representing the same classes of compounds. It will be noted that the total amount of test substance in each test was the same, i. e. 100 parts of test substance per million parts by weight of total corrodant fluid in the test. From the table it can be seen that all of the synergistic combinations 7 through 12 were more effective in combating corrosion than the best of the same substances 2 through 6 used individually.

We claim:

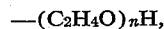
1. A composition effective in combating corrosion of ferruginous materials consisting essentially of a mixture of (A) from 25 to 65 per cent by weight of at least one quaternary ammonium halide wherein all of the organic substituents are hydrocarbon radicals containing up to 18 carbon atoms, at least one of such radicals being an aliphatic hydrocarbon radical containing from 8 to 18 carbon atoms and each of two of such radicals being lower alkyl radicals having from 1 to 3 carbon atoms; (B) from 2 to 30 per cent by weight of at least one amine having the general formula:



wherein R represents a member of the class consisting of tertiary alkyl radicals having 18 to 24 carbon atoms and the hydrocarbon radical of a rosin amine; and (C) from 20 to 60 per cent by weight of at least one compound having the general formula:

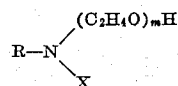


wherein R is as aforesaid, X represents a member of the group consisting of hydrogen and the radical



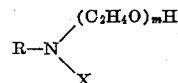
5 and m and n represent integers whose sum is 8 to 21.

2. A composition effective in combating corrosion of ferruginous materials consisting essentially of a mixture of (A) from 25 to 65 per cent by weight of at least one quaternary ammonium chloride wherein all of the organic substituents are hydrocarbon radicals containing up to 18 carbon atoms, at least one of such radicals being an aliphatic hydrocarbon radical containing from 8 to 18 carbon atoms and each of two of such radicals being lower alkyl radicals having from 1 to 3 carbon atoms; 15 (B) from 2 to 30 per cent by weight of a rosin amine; and (C) from 20 to 60 per cent by weight of at least one compound having the general formula:



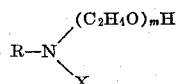
wherein R is the hydrocarbon radical of a rosin amine, X represents a member of the group consisting of hydrogen and the radical $-(C_2H_4O)_nH$, and m and n represent integers whose sum is 8 to 21.

3. A composition effective in combating corrosion of ferruginous materials consisting essentially of a mixture of (A) from 25 to 65 per cent by weight of a quaternary ammonium chloride wherein all of the organic substituents are hydrocarbon radicals, one of such radicals being an aliphatic hydrocarbon radical containing from 8 to 18 carbon atoms and three of such radicals being methyl radicals; (B) from 2 to 30 per cent by weight of a rosin amine; and (C) from 20 to 60 per cent by weight of at least one compound having the general formula:



wherein R is the hydrocarbon radical of a rosin amine, X represents a member of the group consisting of hydrogen and the radical $-(C_2H_4O)_nH$, and m and n represent integers whose sum is 8 to 21.

4. A composition effective in combating corrosion of ferruginous materials consisting essentially of a mixture of (A) from 25 to 65 per cent by weight of a quaternary ammonium chloride wherein all of the organic substituents are hydrocarbon radicals, one of such radicals being an aliphatic hydrocarbon radical containing from 8 to 18 carbon atoms, one of such radicals being the benzyl radical and two of such radicals being methyl radicals; (B) from 2 to 30 per cent by weight of a rosin amine; and (C) from 20 to 60 per cent by weight of at least one compound having the general formula:

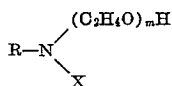


wherein R is the hydrocarbon radical of a rosin amine, X represents a member of the group consisting of hydrogen and the radical $-(C_2H_4O)_nH$, and m and n represent integers whose sum is 8 to 21.

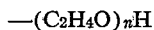
5. A method of rendering a ferruginous material resistant to corrosion when a surface thereof is exposed to fluids derived from a subterranean source, which includes the step of contacting such surface with a liquid comprising a mixture consisting essentially of (A) from 25 to 65 per cent by weight of at least one quaternary ammonium halide wherein all of the organic substituents are hydrocarbon radicals containing up to 18 carbon atoms, at least one of such radicals being an aliphatic hydrocarbon radical containing from 8 to 18 carbon atoms and each of two of such radicals being lower alkyl radicals having from 1 to 3 carbon atoms; (B) from 2 to 30 per cent by weight of at least one amine having the general for-

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mula: $R-NH_2$ wherein R represents a member of the class consisting of tertiary alkyl radicals having 18 to 24 carbon atoms and the hydrocarbon radical of a rosin amine; and (C) from 20 to 60 per cent by weight of at least one compound having the general formula:

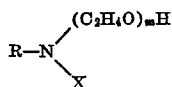


wherein R is as aforesaid, X represents a member of the group consisting of hydrogen and the radical



and m and n represent integers whose sum is 8 to 21.

6. A method of rendering a ferruginous material resistant to corrosion when a surface thereof is exposed to fluids derived from a subterranean source, which includes the step of contacting such surface with a liquid comprising a mixture consisting essentially of (A) from 25 to 65 per cent by weight of at least one quaternary ammonium chloride wherein all of the organic substituents are hydrocarbon radicals containing up to 18 carbon atoms, at least one of such radicals being an aliphatic hydrocarbon radical containing from 8 to 18 carbon atoms and each of two of such radicals being lower alkyl radicals having from 1 to 3 carbon atoms; (B) from 2 to 30 per cent by weight of a rosin amine; and (C) from 20 to 60 per cent by weight of at least one compound having the general formula:

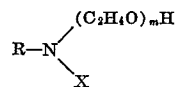


wherein R is the hydrocarbon radical of a rosin amine, X represents a member of the group consisting of hydrogen and the radical $-(C_2H_4O)_nH$, and m and n represent integers whose sum is 8 to 21.

7. A method of rendering a ferruginous material resistant to corrosion when a surface thereof is exposed to fluids derived from a subterranean source, which includes the step of contacting such surface with a liquid comprising a mixture consisting essentially of (A) from 25 to 65 per cent by weight of a quaternary ammonium chloride

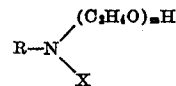
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wherein all of the organic substituents are hydrocarbon radicals, one of such radicals being an aliphatic hydrocarbon radical containing from 8 to 18 carbon atoms and three of such radicals being methyl radicals; (B) from 2 to 30 per cent by weight of a rosin amine; and (C) from 20 to 60 per cent by weight of at least one compound having the general formula:



wherein R is the hydrocarbon radical of a rosin amine, X represents a member of the group consisting of hydrogen and the radical $-(C_2H_4O)_nH$, and m and n represent integers whose sum is 8 to 21.

8. A method of rendering a ferruginous material resistant to corrosion when a surface thereof is exposed to fluids derived from a subterranean source, which includes the step of contacting such surface with a liquid comprising a mixture consisting essentially of (A) from 25 to 65 per cent by weight of a quaternary ammonium chloride wherein all of the organic substituents are hydrocarbon radicals, one of such radicals being an aliphatic hydrocarbon radical containing from 8 to 18 carbon atoms, one of such radicals being the benzyl radical and two of such radicals being methyl radicals; (B) from 2 to 30 per cent by weight of a rosin amine; and (C) from 20 to 60 per cent by weight of at least one compound having the general formula:



wherein R is the hydrocarbon radical of a rosin amine, X represents a member of the group consisting of hydrogen and the radical $-(C_2H_4O)_nH$, and m and n represent integers whose sum is 8 to 21.

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