United States Patent Office

3,003,955

Patented Oct. 10, 1961

3,003,955

METHOD OF INHIBITING CORROSION

Loyd W. Jones, Tulsa, Okla., assignor to Pan American Petroleum Corporation, a corporation of Delaware

No Drawing. Original application Oct. 30, 1953, Ser. No. 389,467. Divided and this application Aug. 2, 1956, Ser. No. 609,335

15 Claims. (Cl. 252—8.55)

This invention relates to inhibiting corrosion. More particularly it relates to amine salts of fatty acids as corrosion inhibitors.

The application is a division of U.S. patent application Serial Number 389,467, filed October 30, 1953, now abandoned, which is a continuation-in-part of my co-pending U.S. application 288,705, filed May 19, 1952, now U.S. Patent 2,756,211. In U.S. Patent 2,756,211 a combination of amines and carboxylic acids as corrosion inhibitors is disclosed. Such amines are aliphatic amines containing at least 10 carbon atoms per molecule. Examples are dodecyl and octadecyl amines. Straight chain primary amines are preferred. The acid portion is carboxylic in nature and contains at least 5 or 6 carbon atoms. Preferably this portion is obtained from the liquid phase partial oxidation of normally liquid petroleum fractions. Other acids such as lauric or oleic are also satisfactory.

These salts are unique in that they inhibit corrosion by hydrogen sulfide, carbon dioxide, light organic acids, oxygen or combinations of these materials. They are also unique in that at least certain of the salts avoid the usual emulsion and gel problems encountered when salts of fatty acids are added to oil. Some of the salts also prevent paraffin deposition on metallic surfaces. These salts may be employed in the form of oil solutions for systems in which the liquid is predominantly oil. For systems in which the liquid is predominantly water the inhibitor should be used in a water dispersible form. In the case of water having a low salt content, most of the non-ionic water-soluble emulsifiers of either the ester or ether type are suitable dispersing agents. If the water contains considerable salt, then a special class of non-ionic water-soluble dispersing agent should be employed. This class of dispersing agent is more particularly described and claimed in my co-pending application U.S. Serial Number 335,161, filed February 4, 1953, now U.S. Patent 2,839,465. In general, this class of dispersing agent has the formula RXW, wherein R is an aliphatic hydrocarbon radical containing at least 12 carbon atoms, X is an ether type linkage selected from the group consisting of oxygen and sulfur and W is a water-soluble portion selected from the group consisting of polyglycols and polyglycerols containing at least 4 ether linkages.

If it is desired to introduce inhibitors through the tubing in a well, or to provide a slowly dispersible form in any application, they may be produced in stick form by use of oil-soluble waxes such as paraffin or of water-soluble binders such as gelatin, as more fully described and claimed in the co-pending application U.S. Serial Number 288,345, filed on May 16, 1952, by Jack P. Barrett, now abandoned.

The salts are employed in concentrations of about 20 to 50 parts per million of corrosive liquids in mildly

corrosive systems consisting predominantly of oil. As much as 500 parts per million may be employed in highly corrosive liquids consisting predominantly of oil. If the corrosive liquid is predominantly water the concentration may vary from 10 to 20 parts per million in moderately corrosive systems up to about 200 parts per million in highly corrosive systems. As little as 10 parts per million gives appreciable protection in both oil and water systems. The inhibitor may be applied continuously or intermittently. If applied intermittently the concentration should be calculated on the basis of the entire volume of corrosive liquids to which the metal surface will be exposed before the next treatment.

The proposed amine-acid salts are, in general, highly effective corrosion inhibitors, but greater effectiveness in lower concentrations is, of course, desirable.

Many of the proposed salts have a tendency to cause emulsions of oil and water. In the petroleum industry corrosion normally requires the presence of water. Obviously, then, wherever the inhibitors are to be used, oil and water are normally both present so emulsion formation is often a problem.

Frequently, it is desirable to add the amine-acid salt inhibitors to liquids which are predominantly water. In such cases, for best effects, the inhibitor should be in the water phase. Most of the amine-salts are only slightly dispersible in water except by use of special agents such as those described in my co-pending U.S. application Ser. No. 335,161. An improved water dispersibility without the aid of special agents would be desirable. Improved stability of dispersions in the presence of dispersing agents would also be desirable.

An object of this invention is to provide an amine-acid salt having improved corrosion-inhibiting properties. A further object is to provide an amine-acid salt corrosion inhibitor having decreased tendency to form emulsions between oil and water. An additional object is to provide an amine-acid salt corrosion inhibitor of improved water dispersibility. A still further object is to provide an amine salt which will remove water blocks from oil-producing formations by reducing the interfacial tension between oil and water to nearly zero dyne per centimeter.

I have found that if amine salts are formed of certain carboxylic acid residues from the treatment of vegetable oils, animal oils or acids derived from such oils, these salts have the desired decreased emulsion-forming tendency and increased water dispersibility. They are also unusually effective as corrosion inhibitors and in removing water blocks. Certain classes of amines are preferred in combination with these acids.

The preferred acid residue is that produced by distilling, at about 270° C. under about 4 mm. of mercury pressure, the by-product acids obtained in the preparation of sebacic acid by fusing castor oil with alkali. Production of this residue is described in more detail in U.S. Patent 2,267,-269, Cheetham et al.

In the manufacture of sebacic acid from castor oil, the oil is heated with a caustic alkali. This splits the oil, forming octanol-2, methyl hexyl ketone, the alkali salt of sebacic acid, and the alkali salts of various other long-chained acids. The alcohol and ketone are readily removed from the reaction mixture by distillation. The alkali salts which remain may then be dissolved in water

and, upon slight acidification of the resulting solution, an oily layer separates. At a pH of about 6, the aqueous phase contains the alkali salt of sebacic acid, while the oily layer contains various other acids from the reaction. The term "by-product acids" is generally applied to the mixture of acids forming the oily layer.

These by-product acids may then be separated into two parts. After these acids have been washed with a dilute mineral acid, such as sulfuric or hydrochloric, they may be washed with water and dried. They may then be distilled under reduced pressure. Fatty acids which are primarily monobasic carboxylic acids may be taken off at 100° C. to 270° C. at pressures as low as 4 mm. This treatment leaves a residue which is a mixture of fatty acids, apparently primarily polybasic in character. It is this residue which I prefer to employ in forming corrosion inhibitors with amine salts. The residue is commercially available from Rohm & Haas Company under the trademark VR–1.

The decreased emulsion-forming tendency of amine salts of this acid residue is thought to be due, at least in part, to the presence of carboxylic acids which contain, in the molecule, oxygen in addition to that present in the acid radical. These acids are usually hydroxy acids. That is, they contain a hydroxyl group in the molecule. Such acids are highly polar, which apparently imparts some demulsifying properties to the salts. In addition, the residue contains esters, higher alcohols, and probably other oxygen-containing hydrocarbon derivatives. These materials affect the interfacial tension between oil and water, and the mutual solubilities of the oil and water. The decreased emulsion-forming tendency of amine salts of this acid residue is undoubtedly due in part to this decreased interfactial tension and increased mutual solubility. The other characteristic of the acid residue which affects the emulsion-forming tendency is the presence of a mixture of acids. It has been found that in general amine salts of mixtures of acids have less tendency to form gels in oil or emulsions between oil and water than the amine salt of a single acid, or small group of acids. The reason for this observed tendency is not well understood.

Increased water dispersibility is due in part, at least, to the increased water solubility caused by the presence of alcohols, esters and the like. It is probably also due to the highly oxidized acids present which are more polar and, hence, more hydrophilic.

Improved corrosion inhibition can be accounted for in part by decreased emulsion-forming tendency. If less emulsion exists, there is less oil-water interface. Therefore, less of the salt can be concentrated at the interface and more is available for adsorption on the metal surface to be protected. The reduced interfacial tension between oil and water, caused by the more polar highly oxidized acids, and the alcohols, esters and the like, also probably facilitate displacement of water from the metal surface by a protective oil film. The principal reason for the improved corrosion inhibition is probably the presence of polybasic acids in the acid residue. The effectiveness of the amine salts of carboxylic acids is thought to be due in large part to the formation on the metal surface of closely packed molecules of acids and amines, the hydrocarbon portions being bound tightly together by lateral cohesive forces. The polybasic acids in the acid residue are thought to have been formed from unsaturated acids such as oleic by polymerization at a double bond. These acid molecules are held together not only by the usual lateral bonds between aligned similar molecules, but are actually held by chemical bonds, thus forming a much stronger film. This film is much more impenetrable by corrosive agents than those formed by unpolymerized monobasic acids, thus accounting for the improved corrosion inhibition. The polymerized acids are attached to the metallic surface at several points and are higher in molecular weight and hence form more permanent films not easily removed by mechanical action or the solvent action of oil.

Other carboxylic acid residues are known which contain highly oxidized fatty acids at least some of which are polybasic in nature. Most of these residues also contain alcohols, esters, and other oxygenated hydrocarbon materials. They also generally contain a mixture of acids having a range of molecular weights. So far as is known these other acid residues also produce amine salts having at least some decreased emulsion-forming tendencies, improved water dispersibility and increased corrosion inhibiting ability. Examples of such acid residues are those produced by the propane extraction of animal and vegetable fats, oils and fatty acids. The process is well described and illustrated in Industrial and Engineering Chemistry, February 1949, page 280. One such acid residue can be obtained from Swift and Company under the trademark Ebony Fat. This is the residue remaining from propane extraction of animal fats. Another specific acid residue is obtainable from West Virginia Pulp and Paper Co. under the trademark Tallene. This is a residue from propane extraction of tall oil. Others are mentioned in the Industrial and Engineering Chemistry article and still others will occur to those skilled in the art.

The term "carboxylic acid residue" is intended herein to include all residue from the treatment of animal or vegetable fats, oils or fatty acids derived from them, in which the residues contain highly oxidized polybasic acids containing at least about 12 carbon atoms per acid radical. The term "highly oxidized" is intended to indicate that the acid molecule contains more oxygen than that present in the acid radical.

The amine portion of the salt may be aliphatic, alicyclic or aromatic, saturated or unsaturated, primary, secondary or tertiary and the hydrocarbon portion may be straight or branched. It is preferred, however, to use straight-chain primary aliphatic amines such as lauryl aminer or octadecyl amine to obtain closer spacing of the molecules in the protective corrosion-inhibiting film which the amine and acid form on metal surfaces. As indicated in U.S. Patent 2,756,211 the amine must contain about 10 carbon atoms per molecule if it is to be effective in inhibiting corrosion by combinations of corrosive materials such as hydrogen sulfide and oxygen.

While many monoamines are very satisfactory, polyamines are, in general, greatly preferred because of their more highly polar character. The increased degree of polarity aids in decreasing emulsion-forming tendencies of the salts with carboxylic acids in much the same way as explained in connection with the highly polar hydroxy acids in the acid residues. That is, the multiplicity of amine groups near the end of a long hydrocarbon chain imparts improved surface activity to the molecule, apparently lending increased demulsifying properties to the amine and its salt with carboxylic acids.

The preferred polyamine is obtainable from Armour and Company under the trademark Duomeen-T. Other satisfactory polyamines from Armour and Company are Duomeen-S and Duomeen-C. In Duomeen-T the long hydrocarbon chain is derived from tallow acids, and, hence, most of these chains are saturated. In Duomeen-S, on the other hand, most of the hydrocarbon chains are unsaturated since they are derived from soy bean oil acids. With Duomeen-C, the acids are derived from coconut oil and constitute a mixture of saturated and unsaturated acids. Most of the hydrocarbon chains in Duomeen-T and Duomeen-S contain from 16 to 18 carbon atoms. Since coconut oil is made up of acids having a wide range of molecular weights, the resulting amines have a correspondingly varied range of chain lengths, for example from about 8 to 18 carbon atoms. As indicated in U.S. Patent 2,756,211, a hydrocarbon radical of at least about 10 carbon atoms should be present. Such radicals insure the formation of a film of sufficient thickness on the metal to resist penetration even by combina-

tions of corrosive materials such as oxygen and hydrogen sulfide. The straight chain aliphatic hydrocarbon radicals are very much preferred to insure closer packing of the molecules forming the film. However, other hydrocarbon radicals having at least about 10 carbon atoms are also effective to a smaller degree.

The polar portion of the amine should contain at least two amino groups separated by from 2 to 4 carbon atoms. This portion may be heterocyclic in nature but preferably should be aliphatic since the salts of the non-cyclic aliphatic polyamines have surprisingly superior corrosion inhibiting abilities compared to salts of the cyclic polyamines.

So far as I have been able to determine, the aliphatic polyamines preferred in my invention may best be represented by the formula:

$$RNXR'NHY$$

In this formula R is a hydrocarbon radical, preferably aliphatic, containing from about 10 to 20 carbon atoms, N is a nitrogen atom, X is a radical selected from the group consisting of R, H and R'NHY, R' is a hydrocarbon radical containing from 2 to 4 carbon atoms, H is a hydrogen atom and Y is a radical selected from the group consisting of H and R. The Duomeens are members of this class, having the simplified formula:

$$RNHR'NH_2$$

The preferred amine is Duomeen-T having the formula:

$$R''NH(CH_2)_3NH_2$$

As previously noted, R'' in this formula is an aliphatic hydrocarbon radical containing from about 16 to 18 carbon atoms.

The principal application of the disclosed salts is as inhibitors for corrosion by oxygen, hydrogen sulfide, carbon dioxide, carboxylic acids containing from 2 to 4 carbon atoms per molecule, or combinations of these individual corrosive materials. One or more of these materials, or combinations thereof, occur in various types of oil wells. In treating such wells it is recommended that at least about 5 parts of the corrosion inhibitor be added per million parts of well liquids, including both water and oil. This concentration should be used whether the inhibitor is added in slugs, for example once a day or so, or is added continuously. Preferably, a preliminary period of treatment at higher concentrations up to 50 times the suggested steady rate should be employed for a week or so at the beginning of the treatment. If the oil well produces predominantly oil, an oil solution of the inhibitor should be added. If the well produces more than about 50 percent water, then a water-dispersible form of the inhibitor may be added. Such a form is described more fully and claimed in my co-pending application U.S. Serial Number 335,161, previously noted. Although a treatment of 5 parts per million produces appreciable protection which is, in many cases, quite adequate, for more severe corrosive conditions higher concentrations in the range of 10 to 50 or more parts per million may be used. In general, higher concentrations are required for systems consisting predominantly of oil than for systems which are substantially oil-free.

If wells have been treated, auxiliary field equipment such as flow lines, separators and the liquid space of tanks will also be protected by the inhibitor in the oil from the wells. If at least some wells have not been treated, then introduction of inhibitor into the auxiliary equipment in the previously-suggested concentrations and forms may be advisable.

An important application of my invention is in preventing corrosion of metal parts in water-flooding or water-disposal systems. In such systems the inhibitor should be maintained in all parts of the system intermittently or continuously, preferably in a water-dispersible form.

For protecting metal surfaces exposed to corrosive vapors such as the inside of casing and outside of tubing near the tops of wells, the vapor space of tanks or gas pipe lines, the inhibitor may be applied by brush or spray, preferably as an oil solution. The inhibitor may be applied more effectively, as well as more simply, by introducing it into the vapors in the form of a fog. For such applications it is suggested that the inhibitor, in a solution containing about 50 percent by weight each of the inhibitor and an oil such as kerosene, be sprayed into the vapor space in an amount equal to about 1 gallon of solution per thousand square feet of metal surface to be protected. The film which is formed in this manner can then be maintained by injecting smaller amounts of from ½ to 1/10 the volume of the original treatment at intervals of from about one week to one month, depending upon the severity of corrosion and erosion by flowing gases.

Another field application of the inhibitor is in drilling fluids to inhibit oxygen corrosion of drilling equipment, particularly the drill pipe. Concentrations of inhibitors should be approximately the same as for well treatments. Since the drilling fluid is recycled continuously, addition of inhibitor is necessary only to make up for the amount lost into the formations or on bit cuttings separated from the drilling fluid. A similar application is in prevention of corrosion of the ballast tanks on submersible drilling barges. This also suggests the application to any marine vessel into which air-containing water is occasionally introduced.

Excellent slushing compounds can be prepared by adding the inhibitor to the greases or gels normally employed for this purpose.

The inhibitor may also be employed in refinery operations, particularly those which handle sour oils. Refinery corrosion generally occurs in equipment such as fractionating columns, strippers, heat exchangers, and condensers where liquid water is present together with corrosive agents such as oxygen, hydrogen sulfide, carbon dioxide or the like. If the inhibitor is to be introduced into columns such as fractionators or strippers, it should be injected above the highest point at which liquid water occurs. The inhibitor, being non-volatile, will then run down the column, protecting the portions exposed to the corrosive agents in the presence of water.

If the inhibitor is to be employed to prevent corrosion of exchangers, condensers or the like, it is simply injected into the inlet to the equipment—preferably in oil solution if the system is predominantly oil, and in a water-dispersible form if the system is predominantly aqueous. If the inlet material is a vapor, spraying of the inhibitor into the stream as a fog is the preferred method of injection. As in other applications, introduction of the inhibitor may be either continuous or intermittent.

The concentration of inhibitor employed at the beginning of treatment of refinery equipment should be from about 50 to 200 parts per million by weight of liquid and vapors treated. After preliminary treatment at these concentrations, to establish inhibiting films, the concentration can usually be reduced over a period of time to a value as low as about 5 parts per million, or even lower in exceptional cases. It will be understood that when reference is made to refineries, the term is employed broadly to include all petroleum processing equipment such as natural gasoline plants, sulfur removing installations, or dehydrating apparatus.

The principal use of the described amine salts of acid residues is as corrosion inhibitors for the various types of corrosion previously discussed. The salts have other applications, however, particularly in wells such as those producing oil or water. For example, the salts may be introduced to decrease wear of sucker rods against the tubing, or to prevent paraffin deposition inside the tubing. They may also be employed to clear the water from water-blocked formations. Other applications will

occur to those skilled in the art. When the term "treating a well" is used, the term is intended to include treatment for any of these purposes.

If the purpose is to prevent wear the means of application and concentrations employed should be about the same as those suggested for inhibiting corrosion since the purpose in both cases is to establish a protective film.

The concentrations suggested for inhibiting corrosion will generally prevent paraffin deposition in the tubing. There is some indication that paraffin deposition is related to emulsion formation. If so, more effective prevention of paraffin deposition might be obtained by use of concentrations of the amine-acid salt 3 or 4 times those suggested for inhibiting corrosion.

When a water block is to be removed from a formation, a solution, preferably in a petroleum fraction such as kerosene, containing from about 0.01 to about 1.0 percent or more of the salt should be pumped into the formation and then be allowed to flow back out. A volume of solution sufficient to fill the pore volume out to a distance of at least about 4 or 5 feet should be injected. The solvent for the salt may be a water solvent such as ethanol, acetone or the like. In general, however, I prefer to employ a petroleum fraction such as kerosene or the crude petroleum itself since the cost is much less, and the effectiveness is substantially the same.

When the term "salt" is employed with reference to a process, the term means either preformed reaction product or the product formed in situ by use of the amine and acid separately. While the neutral salt is generally preferred, as much as twice the stoichiometric amount of either the amine or acid may be present and most of the advantages will still be retained. The salt is usually prepared by mixing the amine and acid at a temperature above their melting points, but below about 200° F. to avoid dehydration with consequent amide formation.

My invention will be better understood from consideration of the following examples.

EXAMPLE I

A corrosive gas stream was bubbled at a rate of ½ cubic foot per minute through glass bottles connected in series and containing 800 milliliters of 5 percent sodium chloride brine, and 16 milliliters of kerosene, in which the inhibitors were dissolved. Tared polished mild steel test panels, 1 inch by 1 inch by 1/16 inch, were suspended in the brine by metal rods from which the panels were insulated by plastic washers. The metal rods were held in the rubber stoppers used to close the bottles. The bottles were vigorously shaken 16 consecutive minutes every two hours. The gas stream was composed of 2 percent hydrogen sulfide and 98 percent air. The tests were run for 7 days at 100° F. At the end of that time the panels were dipped in dilute inhibited hydrochloric acid solution, rubbed lightly to remove adhering scale, rinsed in distilled water, dried and weighed. The results are presented in Table I:

Table I

Amine	Acid	Conc., p.p.m. by weight	Weight loss, grams		Avg. percent inhibition	Remarks
			Control	Test		
Armeen-RT	VR-1	100	0.7109 0.6607	0.0324 0.0333	95.1	Slight emulsion and slight scattered attack.
Duomeen-T	VR-1	300	1.4867 1.3496	0.0121 0.0156	99.0	Slight emulsion, uniform protection.
Do	VR-1	150	1.4867 1.3496	0.0059 0.0049	99.6	Do.
Do	VR-1	100	0.8181 0.7550	0.0127 0.0086	98.7	Slight emulsion and pitting.
Do	Oleic	100	0.7109 0.6607	0.0201 0.0877	92.1	Extreme, thick emulsions, local etching.
Do [1]	VR-1	100	0.7109 0.6607	0.0058 0.0045	99.2	No emulsion. No visible local attack.

[1] Water dispersible form.

Armeen-HT is a trademark of Armour and Company for a mixture of amines containing about 70 percent octadecyl amine with most of the remainder being hexadecyl amine. All other trademark materials have been previously defined chemically.

The water dispersible form noted in Table I was prepared by mixing the constituent in the proportion indicated in Table II.

Table II

Material:	Amount, Percent by volume
Corrosion inhibiting salt	50
Kerosene	38
Brij 35	5
Methanol	2
Water	2
	100

Since this material was water dispersible it was not introduced as an oil solution as in the case of the other salts, but was diluted with 10 volumes of water and introduced in this form. Brij 35 is a trademark of the Atlas Powder Company for a polyoxyethylene ether of lauryl alcohol containing about 23 moles of ethylene oxide per molecule.

Three points will be noted in this table:

(1) The VR–1 acid salt of Duomeen-T is superior to the oleic acid salt of the same amine both as to corrosion inhibition and emulsion formation.

(2) The VR–1 acid salt of the polyamine Duomeen-T is superior in corrosion inhibiting ability to the VR–1 acid salt of the monoamines present in Armeen-HT.

(3) The water-dispersible form of the VR–1 acid salt of Duomeen-T is superior to the oil-soluble form in that the water-dispersible form does not cause emulsion formation and is slightly superior in corrosion inhibiting ability.

EXAMPLE II

The ability of the amine salts of acid residues to reduce the interfacial tension between aqueous brines and hydrocarbon liquids was measured to determine the possible applicability of such salts to removing water blocks from oil-producing formations penetrated by wells. The salt was prepared by melting and mixing approximately equal weights of Duomeen-T and VR–1 acids. The brine was prepared synthetically and contained 96,000 p.p.m. by weight of sodium chloride, 9,000 p.p.m. calcium chloride and 3,000 p.p.m. magnesium chloride. The hydrocarbon phase was a narrow-boiling petroleum fraction containing hydrocarbons predominantly in the range having from 10 to 12 carbon atoms per molecule. Interfacial tension measurements were made by use of a DuNouy torsion wire instrument. The results are presented in Table III.

Table III

Salt concentration, percent by weight	Interfacial tension, dynes per centimeter
1.0	0.0
0.1	0.0
0.01	0.0
0.001	32

It will be apparent that in those cases in which a water block can be removed by reducing the interfacial tension between oil and water to zero, the amine salts of VR–1 acid residue, when forced back into the formation, will effectively remove the water block.

From consideration of the foregoing description and examples it will be seen that I have accomplished the objects of my invention. An amine-acid salt has been provided with increased corrosion inhibiting ability compared even to other amine-acid salts. The salt has greatly decreased tendency to cause emulsions between oil and water compared to most other amine-acid salts. In spite of the decreased emulsion-forming tendency the salt is highly susceptible to use in a water-dispersible form since in this form it does not tend to form emulsions between oil and water, forms an extremely stable dispersion, and affords excellent corrosion inhibition. Due to the unusual potency of the salt in decreasing the interfacial tension between oil and water, the material is also highly useful in removing water blocks from oil-producing formations penetrated by wells.

I claim:

1. A method of inhibiting corrosion by fluids containing water and a member of the group of corrosive materials consisting of oxygen, hydrogen sulfide, carbon dioxide, carboxylic acids containing from 2 to 4 carbon atoms per molecule, and combinations of the individual corrosive materials, comprising adding to said fluids at least about 5 parts per million (by weight) of a polyamine salt of a carboxylic acid residue, said polyamine having the formula $RNHR'NH_2$, wherein R is a hydrocarbon radical containing at least about 10 carbon atoms, N is a nitrogen atom, H is a hydrocarbon atom, and R' is a hydrocarbon radical containing from 2 to 4 carbon atoms, and said carboxylic acid residue containing highly oxidized polybasic acids having at least about 12 carbon atoms per acid radical.

2. The method of claim 1 in which R is an aliphatic hydrocarbon radical containing at least about 10 carbon atoms.

3. The method of claim 1 in which said amine is a polyamine having the formula $R''NH(CH_2)_3NH_2$ wherein R'' is a hydrocarbon radical containing from 16 to 18 carbon atoms.

4. The method of claim 1 in which said carboxylic acid residue is produced by distilling at about 270° C. under about 4 millimeters of mercury pressure, the by-product acids obtained in the preparation of sebacic acids by fusing castor oil with alkali.

5. The method of claim 3 in which R'' is an aliphatic hydrocarbon radical containing from 16 to 18 carbon atoms.

6. The method of claim 4 in which said amine is a polyamine having the formula $R''NH(CH_2)_3NH_2$ wherein R'' is a hydrocarbon radical containing from 16 to 18 carbon atoms.

7. The method of claim 6 in which R'' is an aliphatic hydrocarbon radical containing from 16 to 18 carbon atoms.

8. A method for inhibiting corrosion of ferrous metals by fluids containing water and hydrogen sulfide comprising adding to said fluids a polyamine salt of a carboxylic acid residue, said polyamine having the formula $RNHR'NH_2$, wherein R is a hydrocarbon radical containing at least about 10 carbon atoms, N is a nitrogen atom, H is a hydrogen atom, and R' is a hydrocarbon radical containing from 2 to 4 carbon atoms, and said carboxylic acid residue containing highly oxidized polybasic acids having at least about 12 carbon atoms per acid radical.

9. The method of claim 8 in which said amine is a polyamine having the formula $R''NH(CH_2)_3NH_2$ wherein R'' is a hydrocarbon radical containing from 16 to 18 carbon atoms.

10. The method of claim 8 in which said carboxylic acid residue is produced by distilling at about 270° C. under about 4 millimeters of mercury pressure, the by-product acids obtained in the preparation of sebacic acids by fusing castor oil with alkali.

11. The method of claim 8 in which R is an aliphatic hydrocarbon radical containing at least about 10 carbon atoms.

12. The method of claim 9 in which R'' is an aliphatic hydrocarbon radical containing from 16 to 18 carbon atoms.

13. The method of claim 10 in which said amine is a polyamine having the formula $R''NH(CH_2)_3NH_2$ wherein R'' is a hydrocarbon radical containing from 16 to 18 carbon atoms.

14. The method of claim 13 in which R'' is an aliphatic hydrocarbon radical containing from 16 to 18 carbon atoms.

15. A method of inhibiting corrosion by corrosive fluids containing mixtures of water and oil comprising adding to the said fluids at least 5 to about 500 parts per million by weight of a polyamine salt of a carboxylic acid residue and a polyamine having the formula $R—NH—R'—NH_2$ wherein R is a hydrocarbon radical containing at least 10 carbon atoms and R' is an alkylene radical having 2 to 4 carbon atoms, said carboxylic acid residue containing a mixture of poly basic acids produced by distilling at about 270° C. under 4 millimeters of mercury pressure the by product acids obtained in the preparation of sebacic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,587,546	Matuszak	Feb. 26, 1952
2,675,355	Lytle	Apr. 13, 1954
2,723,233	Lytle	Nov. 8, 1955
2,736,658	Pfohl et al.	Feb. 28, 1956
2,750,339	Steinhauff	June 12, 1956
2,756,211	Jones	July 24, 1956

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,003,955 October 10, 1961

Loyd W. Jones

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Columns 7 and 8, Table I, column 1, line 1 thereof, for "Armeen-RT" read -- Armeen-HT --; column 9, line 44, for "hydrocarbon" read -- hydrogen --.

Signed and sealed this 3rd day of April 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,003,955 October 10, 1961

Loyd W. Jones

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Columns 7 and 8, Table I, column 1, line 1 thereof, for "Armeen-RT" read -- Armeen-HT --; column 9, line 44, for "hydrocarbon" read -- hydrogen --.

Signed and sealed this 3rd day of April 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents