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CORROSION INHIBITOR

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This invention relates to inhibiting corrosion. More particularly it relates to inhibitors for most types of corrosion occurring in oil wells and associated equipment or combination of the various types of corrosion discussed herein. The corrosion inhibitors also act as demulsifiers and paraffin removing agents. They may also be employed to clear water-blocked formations.

This application is a continuation-in-part of my copending application U. S. Serial Number 288,705 filed May 19, 1952, now U. S. Patent 2,756,211. In the parent application 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 other 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 copending application U. S. Serial Number 335,161 filed February 4, 1953. 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 copending 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

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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.

While the salts disclosed in the parent application constitute a considerable improvement over prior art inhibitors, they are still susceptible to improvement in certain respects. For example, while the use of oxidized petroleum acids to form the salt gives a product which usually avoids emulsion formation between water and oil, in many areas positive demulsifying action is also desired. While prevention of paraffin deposition has been noted, a more positive paraffin-removing action would be desirable in many locations. Also, while amine salts of the oxidized petroleum acids taught in the parent application have been found to possess only limited gel forming ability in oil, the concentration of the inhibitor which can be added to oil for purposes of storage in a convenient liquid form is limited by the high pour point of the oil solutions. Some pour points are as high as around 40° F., making their use in colder areas difficult. A salt with a decreased gel forming tendency and, consequently, reduced pour point would therefore be desirable. An improved corrosion inhibiting ability would also obviously be desirable even though the disclosed amine salts are highly superior compared to inhibitors previously taught in the prior art.

With the above problems in mind, an object of the present invention is to provide an improved corrosion inhibitor for the types of corrosion encountered in oil wells, and combinations of the various types. A more particular object is to provide a corrosion inhibitor which does not cause emulsions between oil and water. A still more particular object is to provide a corrosion inhibitor which also possesses positive demulsifying ability. An additional object is to provide a corrosion inhibitor which also acts not only to prevent paraffin deposition but removes paraffin which has already been deposited on metal surfaces. A further object of the invention is to provide a corrosion inhibitor with decreased tendency to gel hydrocarbons so that high concentrations of inhibitors in oil can be handled without encountering excessively high pour points. A still further object is to provide a corrosion inhibitor which may also be used to remove water blocks from formations.

In general, I accomplish the objects of my invention by using a salt of carboxylic acids produced by the liquid phase partial oxidation of normally liquid petroleum fractions and certain highly polar aliphatic polyamines having two or more amino groups located at one end of at least one long hydrocarbon chain. A preferred example of such a compound is the salt of Duomeen-T and Alox 425. Duomeen-T is a trademark of Armour and Company for the highly polar polyamines having the formula



In the formula R'' is an aliphatic hydrocarbon radical containing from about 16 to 18 carbon atoms. Alox 425 is a trademark of the Alox Corporation for a mixture of acids derived from normally liquid hydrocarbons by liquid phase partial oxidation. This salt has several unique properties such as, for example:

- (1) It is highly soluble in oil.
- (2) Oil solutions of the salt have low pour points.

(3) It reduces the interfacial tension between oil and water to nearly zero dynes per centimeter.

(4) It tends to remove water from many water-blocked formations.

(5) It does not act as an emulsifier of oil and water.

(6) It has a positive demulsifying action on emulsions of water and oil.

(7) It is a highly effective corrosion inhibitor even compared to other amine salts.

(8) It prevents deposition of paraffin from oil onto metallic surfaces, and there is evidence indicating that it exerts a positive paraffin-removing action on paraffin already deposited.

All these properties are attributable to the strongly polar nature of portions of both the amine and the acid. Since both the amine and the acid have strongly polar portions, the salt also is highly polar. Being highly polar, the salt is not readily solvated by oil. Therefore, it has less tendency to form gels in oils than less polar materials which are more highly solvated by the oils. This decreased gel-forming tendency in turn presumably accounts for the increased oil solubility. It also apparently accounts for the lower pour point of oil solutions. That is, it is necessary to cool oil solutions of the salt to lower temperatures before gellation of the solution becomes sufficient to prevent pouring.

Having a more polar portion than most salts, particularly those of the amines, the salt of Duomeen-T and Alox 425 is more surface active. This accounts for the ability to decrease the interfacial tension between oil and water. A direct application of this property is the removal of water from water-blocked formations of oil wells. When the salt, preferably in oil solution, is injected into such formations the interfacial forces between water and oil are reduced to such an extent that they are insufficient to hold the connate water against the force of the oil flowing through the formation to the well. Therefore, the water flows from the formation and the water block is removed. The demulsifying action is also undoubtedly related to the increased surface activity of the salt due to its highly polar portion.

A combination demulsifying action between standard demulsifiers, such as various organic sulfonates, and the amine-acid salts has been noted. This is probably due to the reduction of interfacial tension between the water and oil phases by the salt, combined with the action of the standard demulsifier to counteract the effects of emulsion stabilizers such as electric charges and the like.

The highly polar salt is probably adsorbed on metallic surfaces to some extent. It is much more likely, as pointed out in the parent application referred to above, that the amine and acid portions of the loosely-bound salt are separately adsorbed on different portions of the surface. The proposed amine and acid, being more highly polar, become more strongly attached to the metallic surfaces to be protected than the less polar materials. The increased corrosion-inhibiting ability is due partly to this fact and partly to the decreased emulsion-forming tendency. The probable reason why emulsions decrease the corrosion-inhibiting abilities of most amine salts is that these salts, being surface active, tend to become concentrated at the large interfacial surface between the liquids rather than on the metal surface. When emulsion formation is decreased, more of the inhibitor becomes available for deposition on the metal surfaces to be protected. The reduced interfacial tension between oil and water also probably facilitates displacement of water from the metal surface by a protective oil film.

The strongly-adsorbed highly-polar amine and acid have been found to produce an excellent lubricating film which greatly reduces wear. In one pumping well, use of the salt has already extended by a factor of 5 or 6 the average period between pumping rod-pulling jobs. In the well, the corrosion problems were minor, but perhaps just sufficient to roughen the rubbing surfaces slightly and

accelerate wear. The reduced wear might also be due to the simple lubricating actions of the strongly adsorbed films on both rubbing surfaces.

The paraffin-removing ability of the salt may be due to several factors. One of these is an increased paraffin-solubilizing power of the polyamine salt compared to salts of monoamines. The solubilizing power of the salts has been demonstrated in connection with the Alox 425 acids. These acids are not completely soluble in oil. The oil-insoluble materials are probably hydroxy acids. Whatever the nature of the materials, however, they are apparently drawn into oil solutions by a solubilizing action of the amine salt. It has been observed that the polyamines are more effective in solubilizing these oil-insoluble constituents of Alox 425 acids. Therefore, they are undoubtedly also more effective in solubilizing materials such as paraffin. Another factor which may account for increased paraffin-removing ability is the presence of alcohols, ketones, esters and the like in Alox 425 acids. These materials are fair paraffin solvents. Since twice as much acid is required to neutralize Duomeen-T as is required to neutralize octadecyl amine, for example, more of the alcohols, ketones and esters which accompany the Alox 425 acids are present when the polyamine salt is employed. These solvents probably contribute in some degree to the improved paraffin-removing ability of the polyamine salts of Alox 425 acids.

The principal explanation of the paraffin-removing ability probably lies in the reduced interfacial tension between oil and water, and the consequent demulsifying action. It has been noted many times that the paraffin deposited in a well is generally associated with considerable quantities of water. Where little water is present, paraffin deposition is rarely a problem. Apparently it is an emulsion of paraffin and water which deposits. The amine-acid salt, by breaking this emulsion, causes its removal from wells where it is deposited.

When the term "salt" is employed with reference to a process, the term means either the preferred 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 acids used in forming the salts of my invention are those produced by the process described in U. S. Patents 1,690,768 and 1,690,769 issued to Burwell. The hydrocarbon feed to the oxidation process for producing the acids should be a petroleum fraction which is normally liquid. Kerosene is the preferred raw material. This class of hydrocarbons is preferred since it produces acids in the desired molecular weight range containing from about 5 to about 20 carbon atoms per molecule. Hydrocarbons of a paraffinic nature are preferred as feed stock to the oxidation process since they produce aliphatic acids having straight chains which align themselves to give closely-packed protective films.

In general, it is preferred to oxidize the hydrocarbon to such an extent that two phases separate. The lower phase has a higher content of acids which are superior for purposes of my invention, probably because of the presence of hydroxyl groups which make these acids much more polar in nature. Due to their higher polarity they are less oil-soluble and less susceptible to removal by oil from surfaces on which they have been deposited. Furthermore, their salts with polyamines are more polar, and hence more surface active and less strongly solvated by oils. Although the highly oxidized acids are preferred, those produced by a light oxidation of a normally liquid petroleum fraction produce unique non-emulsifying salts with polyamines. Salts of these lightly-oxidized acids also possess some of the same powers of reducing interfacial tension and removing paraffin possessed by salts of the highly oxidized acids, but to a lesser degree.

The preferred polyamine is 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 the parent application previously referred to, a hydrocarbon radical of at least 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 combinations 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:



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'NH₂, 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:



The preferred amine is Duomeen-T having the formula:



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 copending 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. The concentrations for preventing wear should be the same as those for inhibiting corrosion since the problem in both cases is to establish a protective film.

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 1/2 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 oil 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 tested with considerable success was concerned with 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 a 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.

If the amine-acid salt is employed as a demulsifier, it should preferably be introduced into the well producing the emulsion. In this way it can act on the water and oil at the bottom of the well, thus preventing formation of the emulsion. At the same time, the amine-acid salt acts to prevent corrosion and paraffin deposition. It is possible, however, to add the salt to the emulsion after it is formed by injecting it into flow lines, separators, tanks or the like. The amount of salt used as a demulsifier depends on the severity of emulsion in each case. In general, however, it is suggested that concentrations in the range of 2 to 4 or 5 times those suggested for inhibiting corrosion should be employed.

The amine-acid salt may be used to remove paraffin from two locations in a well. One location is the inside

general, however, I prefer to employ a petroleum fraction such as kerosene since the cost is much less and the effectiveness is substantially the same.

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

EXAMPLE I.

To determine the effectiveness as a corrosion inhibitor of the proposed salt of Duomeen-T and Alox 425 acids, compared to salts of other amines and acids, the following tests were conducted. Into 1-liter glass bottles, 800 ml. of an aqueous 5 percent sodium chloride brine were introduced; together with about 16 ml. of kerosene containing various amounts of the individual salts indicated in Table I. Polished and tared mild steel test panels, 1 inch by 1 inch by $\frac{1}{16}$ inch, were suspended in the brine by metal rods from which the panels were insulated by plastic washers. The rods were supported, in turn, by insertion into the rubber stoppers employed to close the bottles. A stream of corrosive gases was bubbled continuously through the liquids in the bottles at a rate of about $\frac{1}{2}$ cubic foot per hour, while the temperature was maintained at 100° F. The corrosive gases consisted of 2 percent hydrogen sulfide and 98 percent air. The bottles were shaken vigorously for 15 consecutive minutes every two hours. At the end of 7 days, 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. of Salt, p. p. m.	Weight Loss, Grams		Percent Inhibition, Av.	Remarks
			Control	Inhibited		
Armeen-HT	Alox 425	300	1.4867	0.0302	98.0	Slight emulsion, uniform protection.
Do	do	100	1.3496	0.0264	94.8	Slight emulsion, pitting and etching.
Duomeen-T	do	300	0.8181	0.0380	99.5	No emulsion, uniform protection.
Do	do	100	0.7550	0.0431	99.0	Do.
Do	Oleic	100	1.4867	0.0667	92.1	Thick emulsion, panels etched.

wall of the tubing through which the oil flows to the surface. The other is the pore space of formations through which oil flows to the well. For removing paraffin from inside tubing, the salt may be added in the same ways as suggested for inhibiting corrosion. It has been found that the concentrations of salt suggested for inhibiting corrosion are suitable for removing paraffin where paraffin problems are not too serious. Higher concentrations, in the range of 2 to 4 or 5 times as great, are suggested for more serious cases of paraffin deposition in tubing.

For removing paraffin from pore spaces, a solution, preferably in a petroleum fraction such as kerosene, containing from about 0.001 to about 1.0 percent or more of the amine-acid 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 treating cycle may be repeated one or more times with either fresh or previously-used solution. Paraffin solvents such as carbon tetrachloride, carbon disulfide, benzene or the like may be employed as a solvent for the salt, but since petroleum fractions are so effective, use of the more expensive solvents is rarely justified.

When a water block is to be removed from a formation, the procedure, concentrations and volumes should be substantially the same as when paraffin is removed from the pore space. The solvent for the salt may be a water solvent such as ethanol, acetone or the like. In

Armeen-HT is a trademark of Armour and Company for a mixture of about 70 percent octadecyl amine and about 30 percent hexadecyl amine. Duomeen-T and Alox 425 have been previously identified chemically.

The greatly decreased emulsifying tendency of the Alox 425 acid salts is to be noted. The salt of Alox 425 acids with Duomeen-T is particularly outstanding in that it caused no emulsion at all, even at higher concentrations. This particular salt is also outstanding in that its inhibiting power at 100 p. p. m. is superior to 300 p. p. m. of the salt of monoamines such as Armeen-HT.

EXAMPLE II

To compare the effectiveness of Alox 425 salts of aliphatic polyamines to salts of cyclic polyamines, static bottle tests were conducted as follows:

One-liter Florence flasks were flushed free of air by streams of nitrogen. Into each flask approximately 1 liter of air-free 5 percent sodium chloride brine containing known amounts of hydrogen sulfide was introduced. The corrosion inhibitor to be tested was then introduced, dissolved in 50 ml. of kerosene. A tared polished mild steel test panel, 1 inch by 1 inch by $\frac{1}{16}$ inch, was then lowered into each flask, supported by a glass hook which was in turn held by the rubber stopper used to seal the flask. Each panel was held in the oil layer 5 seconds at the start of the test and then exposed to the brine phase for the remainder of the 7-day test. Results are reported in Table II.

Table II

Amine	Salt Conc., p. p. m.	H ₂ S Conc., p. p. m.	Weight Loss, Grams		Percent Inhibition, Av.	Remarks
			Control	Inhibited		
Duomeen-T-----	100	850	{ 0.0267 0.0343 0.0263	{ 0.0007 0.0007 0.0018	97.7	{ Uniform protection. No emulsion.
2-Heptadecyl Imidazoline-----	200	600	{ 0.0266 0.0280 0.0263	{ 0.0016 0.0016 0.0019	93.7	{ Slight local attack and pitting. Some emulsion.
2-Heptadecyl 1-Hydroxyethyl Imidazoline.	200	600	{ 0.0266 0.0280	{ 0.0012 0.0012	94.1	Do.

Although the concentration of the Duomeen-T salt of AloX 425 acids was only one-half those of the corresponding salts of the cyclic imidazoline derivatives, the degree of protection was superior. It will also be noted that the protection was uniform, whereas the salts of the cyclic amines permitted some local attack. The tendency of the cyclic amine salts to form slight emulsions at 200 p. p. m. concentration should be compared to the absence of emulsifying tendency of 300 p. p. m. of the Duomeen-T salt noted in Example I. It is apparent that while the cyclic polyamine salts of AloX 425 acids are very good inhibitors, the aliphatic polyamine salts of the same acids are even better in several respects.

EXAMPLE III

To determine the effectiveness of the Duomeen-T salt of AloX 425 acids as an inhibitor for corrosion due to low molecular weight carboxylic acids and carbon dioxide, the following test was made:

About 1100 ml. of an aqueous 5 percent sodium chloride brine solution was placed in each of several 2-liter round-bottomed flasks together with about 900 ml. of kerosene. A reflux condenser was placed over each flask and the systems were freed of air by boiling the water while bubbling a stream of oxygen-free carbon dioxide through the liquids for a period of 2 hours. The rate of carbon dioxide introduction was about 1 cubic foot per hour. To the air-free liquids, 500 milligrams of glacial acetic acid were added (about 500 p. p. m. by weight based on the water phase). Then 100 milligrams of the salt of Duomeen-T and AloX 425 acids were added to each of two of the flasks. None of the amine-acid salt was added to another flask used as a control. A polished, tared, mild steel panel was then suspended in the water phase in each flask on a glass rod passing through a seal in the flask. A reflux condenser was placed on the flask and the flask heater adjusted to hold the temperature just at the boiling point of water. For 15 consecutive seconds out of each minute the panel was raised into the oil phase. After 24 hours, the panels were cleaned, dried and weighed as described in Example I. The control panel lost 0.1500 grams. One of the panels in the flasks containing inhibitor lost 0.0082 grams; the other lost 0.0020 grams. Thus, the average inhibition was 96.6 percent complete.

EXAMPLE IV

The effectiveness of the Duomeen-T salt of AloX 425 acids was tested as an inhibitor of corrosion of surface equipment of a brine-disposal system in the East Texas field. Corrosion products indicated the corrosive agents to be hydrogen sulfide and air. The tests were conducted on a surface pipeline from a pump to a disposal well. One test nipple was inserted a few feet downstream from the pump. Another was inserted a few feet upstream from the injection well, situated about ½ mile away. After 31 days exposure to the brine, these nipples were removed, cleaned and weighed. A second set of test nipples was substituted for the first set and injection of

the amine-acid inhibitor was started. The inhibitor was added as a kerosene solution containing 4 pounds of salt per gallon of solution. It was injected continuously into the pump suction through a small control valve. Attempted rates of injection were as follows:

First 3 days—1 quart of solution per 120 barrels brine.
Next 2 weeks—1 quart of solution per 240 barrels brine.
Remainder of 32-day test—1 quart of solution per 300 barrels brine.

These concentrations should have varied from about 22 p. p. m. by weight down to about 9 p. p. m. However, to treat the 81,000 barrels of brine according to this schedule should have required about 85 gallons of the solution. Actually, only 68 gallons were injected because of difficulty in adjusting the control valve. Therefore, the concentrations were somewhat smaller than those suggested, the average being only about 8.5 p. p. m.

After 32 days, the second set of test nipples was removed, cleaned and weighed. The results are presented in Table III.

Table III

Nipple	Position in Line	Treated	Weight Loss		Percent Inhibition
			Grams	Percent Total	
1-----	Near Pump---	No-----	70.71	1.10	93.4
20-----	do-----	Yes-----	4.70	0.075	
2-----	Near Well----	No-----	92.93	1.42	38.1
10-----	do-----	Yes-----	57.50	0.89	

Nipples 1 and 2 contained sulfide scale and were pitted. Nipples 10 and 20 were clean of sulfide scale and were not pitted. It will be apparent that the air-sulfide corrosion, which cannot be prevented by most inhibitors now on the market, was effectively inhibited by the proposed amine-acid salt. Examination of the nipples indicated most of the inhibitor was deposited near the pump, only traces of the oily material being carried through the line to the nipple near the well. Much more effective inhibition near the well would undoubtedly have been obtained by use of the water-dispersible form described and claimed in my copending application U. S. Serial Number 335,161.

EXAMPLE V

Pour points of oil solutions of amine-acid salts were determined by ASTM test D-97. The oil solutions were prepared by simply dissolving the amine-acid salt in kerosene. The water-dispersible samples were prepared according to my copending application U. S. Serial Number 335,161. They contained, in addition to 4 pounds of salt per gallon of solution, about 0.4 pound of a polyoxyethylene ether of lauryl alcohol containing about 23 mols of ethylene oxide per molecule of lauryl alcohol, about 0.4 pound of methyl alcohol and about 0.15 pound of water. The pour points are indicated in Table IV.

Table IV

Form of Inhibitor	Salt Constituents	Concentration, lbs./gal. Solution	ASTM Pour Point, °F.
Oil Solution.....	Armeen HT and Alox 425.	4	45.
Do.....	Duomeen-T and Alox 425.	4	-15.
Do.....	do.....	3	Below -20.
Water Dispersible.....	Armeen HT and Alox 425.	4	40.
Do.....	Duomeen-T and Alox 425.	4	15.

The melting point of Armeen HT averages about 135° F. That of Duomeen-T is about 105° F. The lower melting point of the Duomeen-T undoubtedly accounts in part for some of the decrease in pour point of solutions of its salts. However, a decrease of about 30° F. in the melting point of one constituent of the salt in the solution could hardly be expected to produce a drop in pour point of 60° F. in straight oil solutions and 25° F. in the complex water-dispersible composition. The pour point reduction is particularly important in northern areas where the temperature frequently remains at or below about 0° F. for considerable lengths of time. In such areas more dilute solutions of the water-dispersible form should be employed. The pour point of this form can also be reduced further by increasing the alcohol content of the preparation.

EXAMPLE VI

The ability of the salt to break emulsions and prevent their formation was recently demonstrated in connection with a well in the Chocolate Bayou field of Texas. The operator was using the salt of Armeen HT and Alox 425 acids as an inhibitor. The salt was added as a kerosene solution containing about 4 pounds of salt per gallon of solution. This inhibitor solution was added at a rate of about 2 quarts per day. The well production averaged about 6 to 10 million cubic feet of gas per day, together with about 50 to 100 barrels of condensate and about 1 to 2 barrels of water. Corrosion control was good, as indicated by a low iron content of the water. However, the amount of inhibitor employed caused the formation of a slight emulsion. When this emulsion was treated in the laboratory with about 200 to 400 parts per million of the Duomeen-T salt of Alox 425 acids, the emulsion broke immediately, thus demonstrating the ability of this particular salt to break even those emulsions caused by other amine salts. On the basis of this observation, the Duomeen-T salt of Alox 425 was employed in subsequent treatment of the well. No further emulsion troubles have been noted, thus demonstrating the emulsion-preventing ability of this salt.

EXAMPLE VII

The water-block removing ability of an oil solution of the salt of Duomeen-T and Alox 425 acids was determined in the laboratory by use of a core of Springer sand obtained from a well in the Velma field of Oklahoma. The core was drilled with oil, shipped in oil and stored in oil until used in the test. The core tested was drilled from the large core received, using oil as a lubricant during the drilling. The resulting test core was a cylinder having a circular cross-section of 2.78 square centimeters and a length of 2.71 centimeters. This core was mounted in a rubber stopper through which a hole had been bored slightly smaller than the core. The stopper was, in turn, mounted in a tapered Lucite holder to which inlet and outlet connections were made. Various liquids were forced through the core under a differential pressure of approximately one atmosphere and at a room temperature of about 75° to 80° F. Permeability values were obtained by measuring the volume of liquid flowing out of the core over a short period of time, such as a minute or

two, and calculating the permeability which would account for this rate of flow. In every case where brine was forced through the core, the brine was one prepared by dissolving in fresh water 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 employed for flushing and as a solvent for interfacial-tension-reducing agents was a narrow-boiling petroleum fraction containing hydrocarbons predominantly in the range having from 10 to 12 carbon atoms per molecule. The procedure and results were as follows:

(1) The permeability of the core to flow of the petroleum fraction was first determined to be 185 millidarcies.

(2) One liter of the brine was forced through the core. The permeability of the core to the flow of brine at the end of this operation was 164 millidarcies.

(3) The petroleum fraction was again introduced and after 616 ml. had been forced through the core, the permeability to the flow of the hydrocarbon was only 52 millidarcies, showing the core to be water-blocked.

(4) A solution of a polyoxyethylene sorbitol tetroate obtained from the Atlas Powder Company under the trademark G-2854 was then forced through the core to remove the water block. This material is known to reduce the interfacial tension between water and oil. A solution of 0.05 percent by weight in the petroleum fraction was employed. After 173 ml. of the solution had been forced through the core, the permeability to flow of the solution was found to be 179 millidarcies.

(5) The pure petroleum fraction was next pumped through the core to determine if the improved permeability was permanent. This flushing operation was continued until the interfacial tension between water and the effluent hydrocarbon returned to its normal value. The permeability to flow of the petroleum fraction at this time was 153 millidarcies.

(6) The blocking and cleaning steps were repeated, using a second Atlas interfacial tension reducer with approximately the same results.

(7) The core was again water-blocked by introducing the brine. Permeability to the flow of the petroleum fraction after the blocking operation was 52.4 millidarcies.

(8) A solution containing 0.001 percent of the Duomeen-T salt of Alox 425 acids in the petroleum fraction was then forced through the core. After 96 ml. had been introduced, the permeability to flow of the solution was 53.7 millidarcies.

(9) The concentration of the salt was increased to 0.005 percent. Introduction of 194 ml. of this solution increased the permeability to only 67 millidarcies.

(10) The concentration was again increased to 0.01 percent. After introduction of 167 ml. of this solution, the permeability was 84 millidarcies.

(11) Finally, the concentration was increased to 0.05 percent and permeability increased as indicated in Table V.

Table V

Volume Through, ml.	Permeability, Millidarcies
6.6.....	95.5
31.6.....	132.0
57.8.....	162.0
90.2.....	179.5
124.0.....	186.5
174.2.....	187.5

(12) Upon flushing the core with the pure petroleum fraction, the permeability increased to 189.5 millidarcies instead of decreasing, as had been characteristic of flushing after treatment with the Atlas compounds.

(13) The interfacial tensions between the brine and the petroleum fraction containing various concentrations of the amine-acid salt were determined. The results are presented in Table V.

Table VI

Concentration of Salt		Interfacial Tension, dynes/cm.
p. p. m.	Percent	
10.....	0.001	29.25
50.....	0.005	20.00
100.....	0.01	13.77
500.....	0.05	6.65
1,000.....	0.1	3.91
10,000.....	1.0	0.043

It will be apparent that the amine-acid salt is somewhat more effective than the non-ionic material for removing water block from formations. The reason for the greater effect is probably a stronger tendency to be absorbed on the sand grains, resulting in a greater ability to displace the water. Obviously, the concentration of the amine-acid salt in oil used for removing water blocks should be about 0.05 percent or more since a sharp increase in permeability occurred when the concentration was increased to this value from the 0.01 percent previously used.

From consideration of the above description and examples, it will be apparent that I have accomplished the objects of my invention. A considerably superior corrosion inhibitor has been provided in that lower concentrations produce the same or greater uniformity and degree of inhibition produced by higher concentrations of other inhibitors. In addition, the inhibitor exerts a positive demulsifying action, as well as avoiding the emulsion problems often caused by other inhibitors. The gel-forming tendency of the inhibitor is so low that high concentrations in oil can be handled without danger of

solidifying in cold weather. The material also acts to prevent paraffin deposition and to remove paraffin which has already been deposited. The ability of the salt to remove water blocks has also been demonstrated.

5 I claim:

1. The salt of a polyamine and a carboxylic acid, said acid being derived by liquid phase partial oxidation of a normally liquid petroleum fraction and said polyamine having the formula $\text{RNH}(\text{CH}_2)_x\text{NH}_2$ wherein R is a hydrocarbon radical containing at least about 10 carbon atoms, and x is an integer from 2 to 4 inclusive.

10 2. The salt of claim 1 in which said polyamine has the formula $\text{R}'\text{NH}(\text{CH}_2)_3\text{NH}_2$, wherein R' is an aliphatic hydrocarbon radical containing from 16 to 18 carbon atoms.

15 3. The salt of claim 2 in which said acid is derived by liquid phase partial oxidation of kerosene.

20 4. The salt of a polyamine and a carboxylic acid, said acid being derived by liquid phase partial oxidation of a normally liquid petroleum fraction and said polyamine having the formula $\text{RNH}(\text{CH}_2)_x\text{NH}_2$ wherein R is an aliphatic hydrocarbon radical containing at least about 10 carbon atoms and x is an integer from 2 to 4 inclusive.

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