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CORROSION INHIBITION

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This invention relates to corrosion inhibiting compositions and more particularly to corrosion inhibiting compositions for use in aqueous solutions which normally corrode metals. The invention also relates to the resulting aqueous solutions containing the corrosion inhibitors of the invention, and to corrosion inhibiting processes employing such compositions.

Metal pickling involves treatment of a metal such as iron or steel with a strong acid bath to remove surface impurities such as oxide scale formed thereon in the course of manufacture. Since the strong acids employed are capable of attacking the metal itself, it is advantageous to add to the bath a corrosion inhibitor which enhances the selective action of the acid on the surface impurities, and substantially reduces or prevents attack of the metal by the acid.

Another field of metal treatment employing strong aqueous acids is in "acidizing" treatment of oil wells. A strong aqueous mineral acid is introduced into the oil well to increase the flow of oil by attacking the underground porous rock formations containing the oil. Since the acid solutions come in contact with metal equipment of the well, it is advantageous to incorporate a corrosion inhibitor in the acid solution to prevent excessive damage of the metal equipment.

It is an object of this invention to provide a composition, for use in aqueous solutions which come into contact with metals, which has improved corrosion inhibiting properties and improved solubility and stability in acids and the like. It is another object of this invention to provide improved aqueous solutions containing such compositions. A further object of this invention is to provide an improved process employing such compositions for inhibiting corrosion of metals. Other objects and advantages will appear as the description proceeds.

The attainment of the above objects is made possible by the instant invention which is based upon the discovery that a composition comprising (A) an aliphatic or alicyclic amine, (B) a condensation product of a primary or secondary aliphatic or alicyclic amine containing at least 10 carbon atoms with at least one mole of an alkylene oxide of 2 to 3 carbon atoms, and (C) a polyalkoxylated water soluble derivative of a compound containing at least 10 carbon atoms and an active hydrogen-containing group selected from the class consisting of hydroxy, carboxy, amido and mercapto groups is a highly effective corrosion inhibitor for metals, particularly iron and steel, unexpectedly exceeding the inhibiting effect weight for weight, of any of its respective components when used in strong acid solutions (e. g. solutions of a pH of less than 2). Stated otherwise, the compositions of this invention exhibit a synergistic effect with respect to inhibition of corrosion.

In addition to improved corrosion inhibiting efficiencies, the compositions of this invention have the added and desirable property of being soluble and stable in concentrated acids such as hydrochloric acid for long periods of time. This property is important since inhibitors are often sold as concentrates in strong acid such as muriatic acid.

The corrosion inhibiting compositions of this invention are highly effective in the acid baths employed for pickling which contain, for example, sulfuric, hydrochloric, nitric, hydrofluoric, phosphoric, formic or acetic acid in concentrations of about 5 to 25 percent by weight or in equivalent aqueous solutions of acid salts such as sodium bisulfate and the like. They are also effective and useful as corrosion inhibitors in the acidizing of oil wells with strong acids (e. g. hydrochloric or hydrofluoric acid) of 5 to 25 percent concentration by weight wherein the corrosion inhibiting compositions also act to prevent or inhibit formation of, and to resolve, water-in-oil emulsions.

The compositions of this invention are also effective in inhibiting the corrosive action on metals of aqueous solutions of many diverse types as for example distilled water, boiler water, automobile radiator cooling solutions, acids such as hydrochloric and the like used for boiler cleaning, oil well acidizing and descaling of metals, aqueous brine solutions containing sodium chloride, mixed calcium chloride-magnesium chloride and similar brines used for refrigeration purposes, and the like.

As indicated above, component A of the composition of this invention is an aliphatic or alicyclic amine. Such amine may be any primary, secondary or tertiary aliphatic or alicyclic amine whose properties are suitable for the particular use to be made of such a composition such as for corrosion inhibition. While more volatile amines may be employed such as butyl amine, dibutylamine, cyclohexylamine, and mono-, di- and triethanolamines, higher substantially water-insoluble aliphatic and alicyclic amines are preferred containing at least 10 and generally from 10 to 20 carbon atoms, particularly the primary amines derived from fatty acids and natural fats by replacement of the carboxyl group with an amino or an amino methyl group such as dodecylamine, didodecylamine, N-methyldodecylamine, N,N-dimethyldodecylamine, octadecylamine and the like, and the alicyclic primary amines derived from rosin or its hydrogenated or dehydrogenated derivatives, e. g. by replacing carboxyl groups with an amino methyl group in abietic, hydroabietic or dehydroabietic acid, or by introducing a primary amino group into the nucleus of abietyl compounds and their hydrogenated or dehydrogenated derivatives, e. g. by nitration and reduction as disclosed in U. S. P. 2,367,001 or by hydrogenation and amination as disclosed in U. S. P. 2,240,936. It will be understood that the substantially equivalent water insoluble salts of such amines with inorganic or organic acids may also be employed.

Component B is the condensation product of at least one mole of ethylene oxide or propylene oxide with a primary or secondary aliphatic or alicyclic amine containing at least 10 and generally from about 10 to 20 carbon atoms. The amine which is subjected to condensation with the ethylene oxide or propylene oxide may be any of the higher aliphatic and alicyclic amines described above for use as component A and is preferably though not necessarily the same amine as that employed as component A. In general condensation products containing from about 1 to 40, and particularly from about 15 to 35 alkoxy groups may be employed. The condensation to produce the component B compounds may be carried out in a manner well known in the art, as disclosed for example in U. S. Patent Nos. 1,970,578 and 2,510,063.

Component C is a polyalkoxylated water soluble (easily water dispersible) derivative of a compound containing at least 10 and generally from about 10 to 20 carbon atoms and an active hydrogen-containing group selected from the class consisting of hydroxy, carboxy, amido and mercapto groups. As representative of such compounds may be mentioned alkyl phenols such as nonylphenol, 2,4,4 trimethylpentyl phenol and diamyl phenol and the like, aliphatic alcohols such as dodecyl alcohol and octadecyl alcohol, alicyclic alcohols such as abietyl, hydroabietyl, and dehydroabietyl alcohols, carboxylic acids such as abietic acid, stearic acid, palmitic acid, oleic acid, lauric acid, ricinoleic acid and the glycerides from which they are derived, the corresponding amides of the foregoing carboxylic acids, alkyl and alkyl aryl sulfonamides such as octadecyl sulfonamide and dodecylbenzene sulfonamide, mercaptans such as dodecyl mercaptan and octadecyl mercaptan, and the like. While these compounds are preferably condensed with ethylene oxide, propyleneoxide and polymers of propylene oxide and ethylene oxide may also be used. In general, component C should contain sufficient ethoxy or propoxy groups to render the product water soluble or easily water dispersible. From about 4 to 60 such groups are usually sufficient. The manner of producing the component C compounds is well known in the art as disclosed for example in U. S. Patent Nos. 1,970,578, 2,194,429, 2,213,477, 2,564,757 and 2,564,759.

In general, the components may be employed in relative proportions of about 3 to 35 parts of component A, 28 to 75 parts of component B, and 10 to 50 parts of component C, although proportions of about 8 to 18 parts of A, 50 to 70 parts of B and 15 to 35 parts of C are preferred as ordinarily yielding optimum results.

The following compositions prepared in each case by thoroughly mixing the mentioned ingredients at a suitable temperature until a homogeneous mixture was obtained, illustrate a number of representative corrosion inhibiting compositions in accordance with this invention. Parts are by weight.

EXAMPLE 1

	Parts
Rosin amine D (a primary amine made from a modified rosin—Hercules Powder Co.)	10
Rosin amine D condensed with 32 moles of ethylene oxide	65
Nonylphenol condensed with 9.5 moles of ethylene oxide	25

EXAMPLE 2

Rosin amine D	10
Rosin amine D condensed with 32 moles of ethylene oxide	65
Oleic acid amide condensed with 10 moles of ethylene oxide	25

EXAMPLE 3

Rosin amine D	10
Rosin amine D condensed with 32 moles of ethylene oxide	65
Dodecyl benzene sulfonamide condensed with 14.75 moles of ethylene oxide	25

EXAMPLE 4

Rosin amine D	15
Rosin amine D condensed with 18 moles of ethylene oxide	60
Nonyl phenol condensed with 9.5 moles of ethylene oxide	25

The rosin amine D employed in the above examples is a mixture of rosin derivative hydrocarbon primary monoamines containing as its principal ingredient dehydroabietyl amine with smaller amounts of abietyl amine, di- and tetrahydroabietyl amine and dextro-primaryl amine.

To illustrate the improved corrosion inhibition produced by the compositions of this invention, the following tests were carried out. Solutions containing 0.01 percent and 0.2 percent by weight of the various inhibitors in 10 percent aqueous hydrochloric acid were prepared. One 2" x 2" 0.036" freshly cleaned cold rolled steel panel (SAE 1008) was immersed into each solution and maintained therein for two hours at 155° F. Each panel was weighed before and after this period of immersion to determine the weight losses in the various solutions. The results are given in Table 1.

Table 1

CORROSION TESTS IN HYDROCHLORIC ACID

Inhibitor	Weight Loss (lbs./sq. ft./24 hrs.)	
	0.01%	0.2%
None added	1.91	1.91
Rosin Amine D	1.37	0.80
Rosin Amine D condensed with 32 moles of ethylene oxide.	0.36	0.030
Nonylphenol condensed with 9.5 moles of ethylene oxide.	0.42	0.45
Red oil amide condensed with 10 moles of ethylene oxide.	0.21	0.22
Dodecyl benzene sulfonamide condensed with 14.75 moles of ethylene oxide.	0.42	0.41
Composition given as Example 1 above	0.29	0.026
Composition given as Example 2 above	0.14	0.029
Composition given as Example 3 above	0.23	0.014

The above data indicate that the ternary compositions of this invention are more effective than any of their individual components when used alone in similar concentrations as corrosion inhibitors in acid.

A similar test was conducted to compare the corrosion inhibiting properties of a binary mixture of rosin amine D (10%) and rosin amine D condensed with 32 moles of ethylene oxide (90%) with the compositions of this invention when employed in 0.01% concentration in 10% hydrochloric acid. The steel panel immersed in the aforementioned binary mixture showed a weight loss of 0.31 as compared with 0.29 for the composition of Example 1 above, 0.14 for the composition of Example 2 above and 0.23 for the composition of Example 3 above. This indicates the importance of component C in contributing to the improved corrosion inhibiting properties of the compositions of this invention.

Tests were also conducted to compare the solubility and stability of the compositions of this invention in 30% hydrochloric acid with similar compositions omitting component C. The results are shown in Table 2.

Table 2

SOLUBILITIES IN 30% HCl

Component C[1]		Formulation A[2]			Formulation B[3]		
Base	Moles of Ethylene Oxide	As Is	0.3% Solution in 30% HCl		As Is	0.3% Solution in 30% HCl	
			Original Appearance	Appearance After 3 Weeks		Original Appearance	Appearance After 3 Weeks
None		C	H	S	C	H	S
Nonylphenol	4	C	C	S	C	Sl. H	D
Do	6	C	C	C	C	C	C
Do	9.5	C	C	C	C	C	C
Do	15	C	C	C	C	C	C
Do	20	Sl. H	C	C	C	C	C
Do	30	Sl. H	C	S	C	C	C
Do	50	Sl. H	C	S	C	C	C
Oleic Acid amide	5	C	C	C	C	C	C
Do	10	C	C	C	C	C	C
Do	15	Sl. H	C	S	C	C	S
Do	50	Sl. H	C	S	C	C	S
Dodecyl benzene Sulfonamide.	10	C	C	C	C	C	S
Agent X[4]		C	C	C	C	C	C
Agent Y[5]		C	C	S	C	C	S

The condensation product of the listed bases with the indicated moles of ethylene oxide.

	Percent
[2] The condensation product of rosin amine with 32 moles of ethylene oxide	65
Rosin Amine	10
Component C	25
[3] The condensation product of rosin amine with 18 moles of ethylene oxide	69
Rosin Amine	6
Component C	25
[4] The condensation product of nonylphenol with 4 moles of ethylene oxide	33⅓
The condensation product of nonylphenol with 6 moles of ethylene oxide	33⅓
The condensation product of nonylphenol with 9.5 moles of ethylene oxide	33⅓
[5] The condensation product of nonylphenol with 4 moles of ethylene oxide	30
The condensation product of castor oil with 30 moles of ethylene oxide	70

Legend:
C—Clear.
Sl. H—Slightly hazy.
H—Hazy.
D—Cloudy dispersion.
S—Separation.

The results shown in Table 2 indicate the improved stability and solubility of the compositions of this invention in concentrated acid as compared with compositions omitting component C. In fact the two acid solutions containing condensation product of nonylphenol with 9.5 moles of ethylene oxide were still clear after 14 months' storage at room temperature.

The compositions of this invention are employed in aqueous solutions in small amounts (readily determined in any particular instance by routine experimentation) only sufficient to inhibit corrosion of metal surfaces by such solutions. Generally, concentrations of about 0.01 to 0.3% by weight are sufficient although concentrations of from about 0.001 to 2 or 3% may be used if desired. The pickling baths may contain about 5 to 25 percent of mineral acid such as hydrochloric, sulfuric, hydrofluoric, phosphoric, nitric or in some cases, organic acids such as formic or acetic acids. Such baths have a pH of less than 2 and generally less than 1. In pickling operations, elevated temperatures of the order of 80° C., e. g. 50 to 100° C. are employed and the bath is preferably maintained in motion relative to the metal to be treated. In the acidizing of oil wells, mineral acids, especially hydrochloric or hydrofluoric acids are used in concentrations of about 5 to 25% and the solution is not heated but is introduced at ambient temperature into the oil well. When employed in oil well treating solutions, the corrosion inhibiting compositions of this invention not only inhibit corrosion of the metal equipment, but also inhibit formation of water in oil emulsions.

While the compositions of this invention are especially advantageous for preventing corrosion of iron and steel, they are also effective for inhibiting corrosion of other metals such as stainless steel, Monel metal, lead, copper, brass and bronze when contacted with aqueous solutions which would normally cause corrosion.

Various modifications and variations of this invention will be obvious to a person skilled in the art and it is to be understood that such modifications and variations are included within the purview of this application and the spirit and scope of the appended claims.

We claim:

1. A corrosion inhibiting composition for addition to aqueous solutions normally corrosive to metal surfaces comprising (A) from about 3 to 35 parts by weight of a primary rosin amine, (B) from about 28 to 75 parts by weight of a condensation product of at least one mole of an alkylene oxide of 2 to 3 carbon atoms for each mole of a compound selected from the group consisting of primary and secondary rosin amines and (C) from about 10 to 50 parts by weight of a polyalkoxylated water-soluble derivative of a compound containing at least ten carbon atoms and an active hydrogen-containing group selected from the class consisting of hydroxy, carboxy, amido and mercapto groups.

2. A composition as defined in claim 1 wherein component A is a rosin amine.

3. A corrosion inhibited aqueous composition comprising an aqueous solution, normally corrosive toward metal surfaces, containing dispersed therein a small amount sufficient to inhibit such corrosion of a composition as defined in claim 1.

4. A method of inhibiting the corrosion of metal surfaces in contact with an aqueous solution normally corrosive thereto which comprises dispersing in said solution a small amount sufficient to inhibit such corrosion of a composition as defined in claim 1.

5. A process for pickling iron and steel which comprises immersing the metal in an acid bath having a pH of less than 2 and containing dispersed therein a small amount of a corrosion inhibiting composition as defined in claim 1.

6. A process for the treatment of oil wells which comprises introducing into the well an acid bath having a pH of less than 2 and containing dispersed therein a small amount of a corrosion inhibiting composition as defined in claim 1.

7. A composition as defined in claim 2 wherein com-

ponent B is the condensation product of a rosin amine with a plurality of moles of ethylene oxide.

8. A corrosion inhibited aqueous composition comprising an aqueous solution, normally corrosive toward metal surfaces, containing dispersed therein a small amount sufficient to inhibit such corrosion of a composition as defined in claim 2.

9. A composition as defined in claim 7 wherein component C is the condensation product of nonylphenol with a plurality of moles of ethylene oxide.

10. The composition of claim 7 wherein component C is the condensation product of red oil amide with a plurality of moles of ethylene oxide.

11. The composition of claim 7 wherein component C is the condensation product of dodecylbenzene sulfonamide with a plurality of moles of ethylene oxide.

12. A corrosion inhibited aqueous composition comprising an aqueous solution, normally corrosive toward metal surfaces, containing dispersed therein a small amount sufficient to inhibit such corrosion of a composition as defined in claim 7.

13. A corrosion inhibited aqueous composition comprising an aqueous solution, normally corrosive toward

metal surfaces, containing dispersed therein a small amount sufficient to inhibit such corrosion of a composition as defined in claim 9.

14. A corrosion inhibited aqueous composition comprising an aqueous solution, normally corrosive toward metal surfaces, containing dispersed therein a small amount sufficient to inhibit such corrosion of a composition as defined in claim 10.

15. A corrosion inhibited aqueous composition comprising an aqueous solution, normally corrosive toward metal surfaces, containing dispersed therein a small amount sufficient to inhibit such corrosion of a composition as defined in claim 11.

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