

1

3,063,790

PREVENTING CORROSION

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No Drawing. Filed July 13, 1960, Ser. No. 42,506
6 Claims. (Cl. 21—2.7)

This is a continuation-in-part of my copending application Serial No. 658,778, filed March 27, 1957, now abandoned, and relates to the use of novel water soluble inhibitors in preventing corrosion of metallic surfaces upon contact with water.

Corrosion of metallic surfaces, particularly iron and steel, in contact with fresh or salt water or various aqueous solutions, results in a serious economical loss. There is an urgent need for, and the present invention provides, improved water soluble corrosion inhibitors which will retard and/or prevent such corrosion.

While the novel inhibitors of the present invention may be used in any system wherein water or aqueous solutions contact metallic surfaces, the following specific examples are set forth as illustrative, but not limiting, instances in which the inhibitors of the present invention are useful. Storage tanks, pipe lines and the like containing petroleum oils or other organic compounds generally contain water which causes corrosion of the metallic surfaces. For example, in storage tanks the water settles to the bottom and causes corrosion of the internal surfaces of the storage tank. The water soluble corrosion inhibitor of the present invention will dissolve in the water phase and will serve to retard and/or prevent such corrosion. Another example is in the stamping, rolling or other working of metal in which a water stream is sprayed or otherwise used as a coolant. Because these operations are effected at high temperature, the water fuses into or otherwise is intimately attached to the metal, and this in turn results in subsequent corrosion. Such corrosion is avoided by incorporating the corrosion inhibitor of the present invention in the water spray. Still another application is in the salt-ice water solutions used as refrigerants, for example, in railroad cars, trucks, etc. When used in railroad cars, the salt solution not only effects corrosion of the railroad cars but also drips onto the rails and causes corrosion thereof. It is readily seen that such corrosion is a serious economical problem because it requires frequent replacement of rails, which is expensive both in manpower and in material cost. Still other applications include boiler water, acid solutions such as pickling solutions, etc.

The novel corrosion inhibitor of the present invention is prepared by the reaction of an epihalohydrin compound with both an oleophilic amine and with a lyophilic amino compound. The term lyophilic is used in the present specifications as being synonymous with hydrophilic and these terms are used interchangeably herein. The relatively polar amine groups serve to attract the inhibitor to the metal surface where the hydrocarbon substituent of the oleophilic amine covers the surface and exerts a protective action by keeping water soluble corrodents away from the metal. The lyophilic amino group renders the inhibitor compound water soluble so that it will penetrate the water layer or film covering the metallic surfaces and thereby will cover and protect the metallic surfaces in the manner hereinbefore set forth.

Any suitable epihalohydrin compound may be utilized in preparing the inhibitor compound. Epichlorohydrin is preferred. Other epichlorohydrin compounds include 1,2-epoxy-4-chlorobutane, 2,3-epoxy-4-chlorobutane, 1,2-epoxy-5-chloropentane, 2,3-epoxy-5-chloropentane, etc. In general, the chloro derivatives are preferred, although

2

it is understood that the corresponding bromo and iodo compounds may be employed. In some cases, epidi-halohydrin compounds may be utilized. It is understood that the different epihalohydrin compounds are not necessarily equivalent in the same or different applications and that, as hereinbefore set forth, epichlorohydrin is preferred. In some cases, mixtures of epihalohydrin compounds and particularly of those set forth above may be employed.

Preferably the epihalohydrin compound first is reacted with an oleophilic amine. Any suitable oleophilic amine may be employed and preferably comprises an aromatic or alkyl amine containing at least six and still more particularly at least twelve carbon atoms and generally will range up to about 40 carbon atoms per molecule. A preferred aromatic amine comprises dodecylaniline. Other aromatic amines include aniline, methyl aniline, ethyl aniline, propyl aniline, butyl aniline, amyl aniline, hexyl aniline, heptyl aniline, octyl aniline, nonyl aniline, decyl aniline, undecyl aniline, dodecyl aniline, tridecyl aniline, tetradecyl aniline, pentadecyl aniline, hexadecyl aniline, heptadecyl aniline, octadecyl aniline, nonadecyl aniline, eicosyl aniline, heneicosyl aniline, docosyl aniline, tricosyl aniline, tetracosyl aniline, pentacosyl aniline, hexacosyl aniline, heptacosyl aniline, octacosyl aniline, nonacosyl aniline, triacontyl aniline, hentriacontyl aniline, dotriacontyl aniline, tritriacontyl aniline, tetratriacontyl aniline, pentatriacontyl aniline, hexatriacontyl aniline, heptatriacontyl aniline, octatriacontyl aniline, nonatriacontyl aniline, tetracontyl aniline, etc. or mixtures thereof. In general, a long chain alkyl substituent on the aromatic nucleus is preferred, the long chain alkyl substituent containing at least six carbon atoms. However, in another embodiment, two or more alkyl substituents may be attached to the aromatic nucleus of the aniline molecule. Illustrative preferred compounds in this class include dihexyl aniline, diheptyl aniline, dioctyl aniline, dinonyl aniline, didodecyl aniline, diundecyl aniline, didodecyl aniline, ditridecyl aniline, ditetradecyl aniline, dipentadecyl aniline, dihexadecyl aniline, diheptadecyl aniline, dioctadecyl aniline, etc., or mixtures thereof.

Illustrative examples of alkyl amines include hexyl amine, heptyl amine, octyl amine, nonyl amine, decyl amine, undecyl amine, dodecyl amine, tridecyl amine, tetradecyl amine, pentadecyl amine, hexadecyl amine, heptadecyl amine, octadecyl amine, nonadecyl amine, eicosyl amine, heneicosyl amine, docosyl amine, tricosyl amine, tetracosyl amine, pentacosyl amine, hexacosyl amine, heptacosyl amine, octacosyl amine, nonacosyl amine, triacontyl amine, hentriacontyl amine, dotriacontyl amine, tritriacontyl amine, tetratriacontyl amine, pentatriacontyl amine, hexatriacontyl amine, heptatriacontyl amine, octatriacontyl amine, nonatriacontyl amine, tetracontyl amine, etc., dihexyl amine, diheptyl amine, dioctyl amine, dinonyl amine, didodecyl amine, diundecyl amine, didodecyl amine, ditridecyl amine, ditetradecyl amine, dipentadecyl amine, dihexadecyl amine, diheptadecyl amine, dioctadecyl amine, dinonadecyl amine, dieicosyl amine, etc., or mixtures thereof. Conveniently the long chain amines are prepared from fatty acids or more particularly from mixtures of fatty acids formed as products or by-products. Such mixtures of amines are available commercially, generally at lower prices and, as another advantage of the present invention, the mixtures may be used without the necessity of separating individual amines in pure state. An example of such a mixture is hydrogenated tallow amine which is available under various trade names including "Alamine H26D" and "Armeen HTD." These products comprise mixtures predominating in alkyl amines containing 16 to 18 carbon atoms per molecule, although they contain a small amount of octadecenyl amine. Another example of such a

mixture available commercially is "Armeen 2HT" which consists primarily of dioctadecyl amine and dihexadecyl amine.

A preferred class of alkyl amines for use in the present invention is N-alkyl polyamines. Preferred compounds comprise N-alkyl-1,3-diaminopropanes in which the alkyl group contains at least six and still more particularly at least twelve carbon atoms. Illustrative examples include N-hexyl-1,3-diaminopropane, N-heptyl 1,3-diaminopropane, N-octyl-1,3-diaminopropane, N-nonyl-1,3-diaminopropane, N-decyl-1,3-diaminopropane, N-undecyl-1,3-diaminopropane, N-dodecyl-1,3-diaminopropane, N-tridecyl-1,3-diaminopropane, N-tetradecyl-1,3-diaminopropane, N-pentadecyl-1,3-diaminopropane, N-hexadecyl-1,3-diaminopropane, N-heptadecyl-1,3-diaminopropane, N-octadecyl-1,3-diaminopropane, N-nonadecyl-1,3-diaminopropane, N-eicosyl-1,3-diaminopropane, N-heneicosyl-1,3-diaminopropane, N-docosyl-1,3-diaminopropane, N-tricosyl-1,3-diaminopropane, N-tetracosyl-1,3-diaminopropane, etc., or mixtures thereof. As before, mixtures are available commercially and advantageously are used for the process of the present invention. Such mixtures include "Duomeen T" and "Diam" which comprise N-tallow-1,3-diaminopropane and predominate in alkyl groups containing from 16 to 18 carbon atoms each, although the mixtures contain a small amount of alkyl groups containing 14 carbon atoms each. Another mixture available commercially is N-coco-1,3-diaminopropane which contains alkyl groups predominating in 12 to 14 carbon atoms each. Still another example is N-soya-1,3-diaminopropane which predominates in alkyl groups containing 18 carbon atoms per group, although it contains a small amount of alkyl groups having 16 carbon atoms.

While the N-alkyl-1,3-diaminopropanes are preferred compounds of this class, it is understood that suitable N-alkyl ethylene diamines, N-alkyl-1,3-diaminobutanes, N-alkyl-1,4-diaminobutanes, N-alkyl-1,3-diaminopentanes, N-alkyl-1,4-diaminopentanes, N-alkyl-1,5-diaminopentanes, N-alkyl-1,3-diaminohexanes, N-alkyl-1,4-diaminohexanes, N-alkyl-1,5-diaminohexanes, N-alkyl-1,6-diaminohexanes, etc., or mixtures thereof may be employed, but not necessarily with equivalent results.

In general, it is preferred that the aliphatic amine is an alkyl amine and thus is a saturated compound which does not contain a double bond in the chain. However, in some cases, unsaturated compounds may be employed, provided they meet the other requirements hereinbefore set forth, although not necessarily with equivalent results. Such amine compounds conveniently are prepared from unsaturated fatty acids and, therefore, may be available commercially at lower cost. Illustrative examples of such amine compounds include dodecylenic amine, didodecylenic amine, N-dodecylenic ethylene diamine, N-dodecylenic-1,3-diaminopropane, oleic amine, dioleic amine, N-oleic ethylene diamine, N-oleic-1,3-diaminopropane, linoleic amine, dilinoleic amine, N-linoleic ethylene diamine, N-linoleic-1,3-diaminopropane, etc., or mixtures thereof.

As hereinbefore set forth, the epihalohydrin compound preferably is reacted first with the oleophilic amine and then the reaction product is further reacted with a lyophilic amino compound, the latter also being named as hydrophilic amino compound. In one embodiment, the lyophilic amine comprises an alkylene polyamine, a particularly preferred alkylene polyamine being tetraethylene pentamine. Other alkylene polyamines include triethylene tetramine, pentaethylene hexamine, etc., tetrapropylene pentamine, pentapropylene hexamine, etc., or mixtures thereof. As hereinbefore set forth, the corrosion inhibitor of the present invention is water soluble, this property being achieved, in this embodiment of the invention, through the use of an alkylene polyamine or polyaminoalkane which is sufficiently water soluble to impart water solubility to the complete inhibitor molecule. Therefore, the particular lyophilic amine used

must be selected with regard to the other constituents of the inhibitor so that the final inhibitor compound is water soluble. For example, when the oleophilic amine comprises a long chain amine, the lyophilic amine selected must impart sufficient water solubility to counter the contrary effect of the oleophilic amine. Thus, as an example, when the oleophilic amine comprises dodecyl aniline or N-tallow-1,3-diaminopropane, the lyophilic amine preferably comprises tetraethylene pentamine or the like.

In another embodiment of the invention, the lyophilic amino compound is an alkanolamine and preferably a dialkanolamine. Illustrative amino compounds include monoethanolamine, diethanolamine, monopropanolamine, dipropanolamine, trishydroxymethylaminomethane, etc., or mixtures thereof. In still another embodiment, lyophilic amino compounds may be prepared by reacting an alkylene polyamine with a suitable hydroxy compound as, for example, by reacting one mol of tetraethylene pentamine with one mol of polyethylene glycol chloride. In still another embodiment, other suitable compounds containing amino and hydroxyl groups may be employed including, for example, N-methyl-glucamine, which is an amino derivative of glucose. As hereinbefore set forth, it is essential that the lyophilic group be sufficiently water soluble to impart water solubility to the final inhibitor compound. Thus, when the oleophilic amine comprises dodecyl aniline or N-tallow-1,3-diaminopropane, diethanolamine or similar lyophilic amino compound is employed. On the other hand, when the oleophilic amine comprises a shorter chain amine, the use of monoethanolamine as the lyophilic amino compound will be satisfactory to impart water solubility to the complete molecule.

The reaction of epihalohydrin compound with the oleophilic amine and with the lyophilic amino compound may be effected in any suitable manner. As hereinbefore set forth, generally it is preferred to react the epihalohydrin compound first with the oleophilic amine. In general, one mol of the oleophilic amine is reacted with one or two mols of the epihalohydrin compound. It is understood that, in some cases, an excess of amine or epihalohydrin may be supplied to the reaction zone in order to insure complete reaction, the excess being removed subsequently in any suitable manner. While the desired quantity of amine and epihalohydrin may be supplied to the reaction zone and therein reacted, it generally is preferred to supply one reactant to the reaction zone and then introduce the other reactant step-wise. Thus, when reacting equal mols of amine and epichlorohydrin, it is preferred to supply the oleophilic amine to the reaction zone and to add the epihalohydrin compound step-wise, with stirring. However, when reacting one mol of amine with two mols of epichlorohydrin, it is preferred to add the amine step-wise to the epichlorohydrin. The temperature at this stage is kept below about 70° C. and preferably is at 60-65° C. in order to avoid inter-reaction of the intermediate product. In one embodiment, the reaction product may be withdrawn from the reaction zone and purified as desired before reaction with the lyophilic amine. In another embodiment, following the reaction of the oleophilic amine with the epihalohydrin compound, the lyophilic amino compound is passed into the reaction zone and reacted therein with the first reaction product. Generally, it is preferred to utilize a solvent and, in a preferred embodiment, solutions of each amine and of the epihalohydrin compounds are each separately prepared, and these solutions then are commingled in the manner hereinbefore set forth. Any suitable solvent may be employed, a particularly suitable solvent comprising an alcohol including ethanol, propanol, butanol, etc., 2-propanol being particularly desirable.

The reaction is effected at any suitable temperature, which generally will be within the range of from about 20° to about 100° C. and preferably is within the range of from about 50° to about 75° C., the first stage reaction

generally being at the same or preferably lower temperature than the second stage reaction. A higher temperature range of from about 30° to about 150° C. or more, and preferably of from about 50° to about 100° C. is specified when the reaction is effected at superatmospheric pressure to increase the reaction velocity. Conveniently, this reaction is effected by heating an amine or amino compound solution in dilute alcohol at refluxing conditions, with stirring, gradually adding the epihalohydrin compound thereto, and continuing the heating until the reaction is completed. The other amine or amino compound solution then is added to the reaction product and the heating continued until the second reaction is completed.

Either before or after removal of the reaction product from the reaction zone, the product is treated to remove halogen, generally in the form of an inorganic halide salt as, for example, the hydrogen halide salt. This may be effected in any suitable manner and generally is accomplished by reacting the product with a strong inorganic base such as sodium hydroxide, potassium hydroxide, etc., to form the corresponding metal halide. The reaction to form the metal halide generally is effected under the same conditions as hereinbefore set forth. After this reaction is completed, the metal halide is removed in any suitable manner, including filtering, centrifugal separation, etc. It is understood that the reaction product also is heated sufficiently to remove alcohol and water and this may be effected either before or after the treatment to remove the inorganic halide.

While it generally is preferred to react the epihalohydrin compound with the oleophilic amine first and then react the product with the lyophilic amine, the reverse procedure may be employed. In the latter embodiment, the lyophilic amine is reacted with the epichlorohydrin and then one or two mols of the reaction product are reacted further with the oleophilic amine. These reactions are effected in substantially the same manner as described hereinbefore. It is understood that the temperature in the first stage will be controlled to prevent inter-action of the intermediate product.

The reaction products prepared in the above manner are new compositions of matter. Depending upon the reactants and conditions employed, the reaction product generally will comprise a mixture of different compounds, which mixture may include polymeric compounds. Another advantage to the present invention is that the mixture of compounds prepared in the above manner may be utilized without the added expense and time of separating a specific compound from the mixture. The reaction products will range from liquids to solids and, when desired, may be prepared as a solution in a suitable solvent for ease of handling and using.

As hereinbefore set forth, the reaction product prepared in the above manner is utilized as a water soluble corrosion inhibitor. It is incorporated in water, aqueous solutions or substrates containing water in a sufficient concentration to effectively retard corrosion of metallic surfaces. Generally, it will be utilized in a concentration of below about 1% by weight of the water, aqueous solution, or substrate containing water, and usually in concentration within the range of from about 0.0001% to about 1% and particularly from about 0.01% to about 0.5% by weight thereof, although higher concentrations may be employed when excessive corrosion is encountered. It is understood that the corrosion inhibitor may be used in conjunction with other additives which are incorporated in the substrate for various reasons.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

Example I

The corrosion inhibitor of this example was prepared by the reaction of dodecyl aniline with epichlorohydrin,

followed by reaction with diethanolamine. Specifically, a dilute solution of dodecyl aniline in 2-propanol was prepared and was supplied to an autoclave and heated to 80°–90° C., with stirring. The dodecyl aniline was utilized in an amount of 0.5 mol. One mol of epichlorohydrin, separately prepared as a solution of 2-propanol, was added gradually to the autoclave, and the heating and mixing continued for 5 hours. 0.1 mol of the resultant product then was refluxed with 0.22 mol of diethanolamine, separately prepared as a solution in 2-propanol, for 4 hours. Following completion of the reaction, sodium methoxide was added, and the resultant sodium chloride was removed by filtration, following which the solvent was removed by distillation. The remaining product was a reddish brown semi-solid, which turns to a dark yellow viscous, but free flowing, liquid at about 85° C., and is water soluble.

The product prepared in the above manner was evaluated as a corrosion inhibitor by the following method. A 600 cc. beaker was used as the reaction vessel and 300 cc. of a 5% sodium chloride solution containing the inhibitor was introduced into the beaker. A 0.5" x 3" x 1/8" mild steel strip was inserted in the beaker and held in a horizontal position with one end resting on a glass rod. The sodium chloride solution was stirred by a single blade stirrer revolving at 250 r.p.m. Air was continuously bubbled in at the rate of 5.6 liters per hour.

When evaluated in the above manner, a steel strip, after six hours' exposure in a brine not containing inhibitor, showed a weight loss of 22–24 mg.

0.1% by weight of the corrosion inhibitor prepared in the above manner was incorporated in another sample of the brine and, when evaluated in the manner described above, the loss in weight was 10.6 mg. It will be noted that the loss in weight was reduced to substantially one-half of that occurring in the absence of this inhibitor.

Example II

The corrosion inhibitor of this example was prepared by the reaction of one mol of dodecyl aniline with one mol of epichlorohydrin, followed by the reaction of the product with one mol of tetraethylene pentamine. These reactions were effected in substantially the same manner as hereinbefore set forth; namely, dodecyl aniline dissolved in 2-propanol was heated with stirring to refluxing conditions and one mol of epichlorohydrin gradually added thereto. After the reaction was completed, one mol of tetraethylene pentamine was added gradually to the reaction zone while the heating and mixing were continued. Thereafter, sodium hydroxide was added to the mixture, with the heating and stirring being continued, followed by filtering to remove sodium chloride and distillation to remove the solvent. The remaining product was a light yellow viscous liquid, having an index of refraction n_D^{20} of 1.521, and is water soluble.

0.01% by weight of the inhibitor prepared in the above manner was incorporated in the brine solution and evaluated in the manner described in Example I. After six hours' exposure, the steel strip lost 8.6 mg. heating. The visual appearance of the strip was good. On the other hand, the visual appearance of the strip exposed to the brine in the absence of inhibitor was poor, i.e., the strip was essentially completely covered with rust. It will be noted that 0.01% of the corrosion inhibitor served to reduce corrosion loss from 22–24 mg. to 8.6 mg.

Example III

Another corrosion inhibitor was prepared in substantially the same manner as described in Example II, except that one mol of dodecyl aniline was added dropwise to and reacted with two mols of epihalohydrin, and then reacted with two mols of tetraethylene pentamine. This reaction product was a yellowish orange viscous liquid, having an index of refraction n_D^{20} of 1.523, and is water soluble.

0.05% by weight of the inhibitor prepared in the above manner was evaluated in the same manner as described in the previous examples. After six hours' exposure, the steel strip appeared only lightly rusted and lost only 7.6 mg. In this case, it will be noted that the corrosion was reduced to substantially one-third of that occurring in the absence of the inhibitor.

Example IV

The oleophilic amine used in this example is 2-ethylhexylamine. It was reacted with two mols of epichlorohydrin and the product then was reacted with two mols of diethanolamine. The final product was a bright yellow, slightly viscous liquid, having an index of refraction n_D^{20} of 1.4796 and is fluid at 45° C. and water soluble.

When incorporated in a concentration of 0.05% by weight in the brine and evaluated in the manner hereinbefore described, the steel strip after six hours' exposure lost 8.5 mg. Here again, it will be noted that the inhibitor served to considerably reduce corrosion, in this case reducing the loss from 22-24 mg. to 8.5 mg.

Example V

The corrosion inhibitor of this example was prepared by the reaction of one mol of 2-ethylhexylamine with two mols of epichlorohydrin and the product then was reacted with two mols of trishydroxymethylaminomethane. The reaction was effected in substantially the same manner as hereinbefore set forth. The final product was a light yellow semi-solid which became fluid at 40°-45° C. and is water soluble.

When incorporated in a concentration of 0.05% by weight in the brine and evaluated in the manner hereinbefore described, the steel strip after six hours' exposure lost only 2.5 mg. It will be noted that this inhibitor was extremely effective in reducing the corrosion.

Example VI

The lyophilic amino compound used in this example was prepared by the reaction of one mol of tetraethylene pentamine with one mol of polyethylene glycol chloride 410, i.e., of average mol weight 410 or containing 9-10 oxyethylene units. This reaction was effected by refluxing the reactants at 78° C. in ethanol solution, followed by filtering to remove sodium chloride. The resultant tetraethylene pentamine-glycol was reacted with the reaction product of one mol of N-tallow-1,3-diaminopropane (Duomeen T) with epichlorohydrin. The final reaction product was a light brown viscous liquid, having an index of refraction n_D^{20} of 1.4828 and is water soluble.

0.01% by weight of the inhibitor prepared in the above

manner was incorporated in another sample of the brine and evaluated in the manner hereinbefore described. After six hours' exposure, the steel strip lost about 11 n.g. In contrast, a control sample, exposed to the brine not containing this inhibitor, lost about 24 mg. Here again, it will be noted that the inhibitor served to considerably reduce corrosion.

I claim as my invention:

1. The method of retarding corrosion of metal upon contact with water which comprises effecting said contact in the presence of a water soluble corrosion inhibitor comprising the reaction product of an epichlorohydrin with an oleophilic amine and with a hydrophilic amino compound.

2. The method of retarding corrosion of metal upon contact with water which comprises effecting said contact in the presence of a water soluble corrosion inhibitor comprising the reaction product of an epichlorohydrin with an oleophilic amine selected from the group consisting of aromatic amines and alkyl amines and with a hydrophilic amino compound.

3. The method of retarding corrosion of metal upon contact with water which comprises effecting said contact in the presence of a water soluble corrosion inhibitor comprising the reaction product of epichlorohydrin with dodecyl aniline and with tetraethylene pentamine.

4. The method of retarding corrosion of metal upon contact with water which comprises effecting said contact in the presence of a water soluble corrosion inhibitor comprising the reaction product of epichlorohydrin with dodecyl aniline and with diethanolamine.

5. The method of retarding corrosion of metal upon contact with water which comprises effecting said contact in the presence of a water soluble corrosion inhibitor comprising the reaction product of epichlorohydrin with 2-ethylhexyl amine and with trishydroxymethylaminomethane.

6. The method of retarding corrosion of metal upon contact with water which comprises effecting said contact in the presence of a water soluble corrosion inhibitor comprising the reaction product of epichlorohydrin with N-tallow-1,3-diaminopropane and then reacting the resultant product with the reaction product of tetraethylene pentamine and polyethylene glycol chloride.

References Cited in the file of this patent

UNITED STATES PATENTS

1,845,403	Eisleb	Feb. 16, 1932
2,598,213	Blair	May 27, 1952
2,864,775	Newey	Dec. 16, 1958