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METHOD OF PROTECTING METAL WITH AMINES AND COMPOSITION THEREFOR

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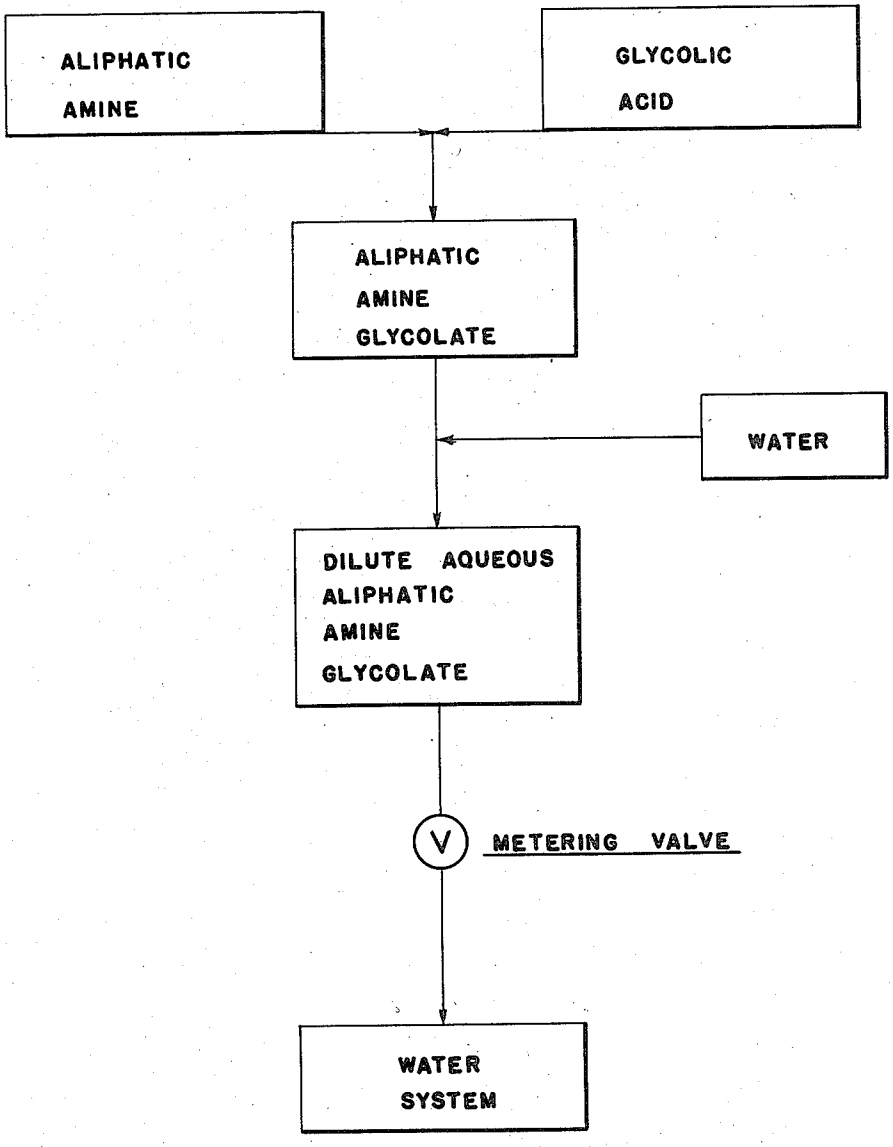

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METHOD OF PROTECTING METAL WITH AMINES AND COMPOSITION THEREFOR

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The instant invention relates to aliphatic amine materials for water treating and processes of feeding such materials to water and effecting corrosion inhibition by their use in water systems or aqueous media.

In particular, the invention relates to a method of protecting the surfaces of metal pipe lines and apparatus in contact with transported aqueous media having corrosive qualities with respect to the metal. The systems wherein such media are transported are generally known as water systems, which, as the term is used herein, are intended to include any of a wide variety of systems in which water is used commercially or industrially, including steam boiler systems, steam return condensate systems, steam distribution systems, heat transfer water systems, evaporator systems, processing water systems, wet pipe fire systems, cooling water systems, etc.

In U. S. Patent No. 2, 460,259, issued to Kahler, there is described a corrosion inhibiting method using high molecular weight amines, amine salts or amine oxides.

In U. S. Patent No. 2,712,531, issued to Maguire, there are described corrosion inhibiting compositions and methods involving the use of a blend of octadecyl amine and octadecyl amine acetate.

The instant invention is based upon the discovery that an aliphatic amine salt, not heretofore considered by or suggested by the workers in the art as useful in this field, has uniquely superior properties when used alone or in combination with an aliphatic amine for the purpose of inhibiting corrosion in aqueous media exposed to metal surfaces. The specific aliphatic amine salt employed in the practice of the instant invention is the glycolate and this salt is unique in its corrision inhibiting properties and also in its greater solubility or dispersibility in aqueous media.

It is, therefore, an important object of the instant invention to provide an improved method of effecting corrosion inhibition of metal surfaces exposed to aqueous media and an improved composition for such use.

It is a further object of the instant invention to provide an improved composition and method of feeding the same into a flowing aqueous media for effecting corrosion inhibition of metal surfaces exposed thereto.

Other and further objects, features and advantages of the present invention will become apparent to those skilled in the art from the following detailed disclosure thereof and the drawing attached hereto and made a part hereof.

The invention consists in a method of protecting metal contacting surfaces in a continuously flowing system for transporting aqueous media having corrosive qualities, which comprises the step of adding to the transporting media an aliphatic amine glycolate wherein each aliphatic radical is a C_{12}–C_{20} hydrocarbon radical, in concentrations of not more than 100 p. p. m. but sufficient for forming a protective film on the surfaces, and conveying the media sufficiently to allow the film to form.

As shown in the drawing, which is essentially diagrammatic, aliphatic amine and glycolic acid are first reacted to obtain aliphatic amine glycolate. Water is added to obtain about a 1% solution which is fed through a metering valve into an aqueous system where it performs its corrosion inhibiting function.

Another aspect of the instant invention comprises using the aliphatic amine glycolate in combination with an aliphatic amine; and still another aspect of the instant invention involves the use of an aliphatic amine in combination with an aliphatic amine glycolate and aliphatic amine acetate.

The aliphatic amine glycolate which may be used in the practice of the instant invention is preferably derived from a primary n-alkyl amine wherein the alkyl radical is C_{12}–C_{20} alkyl radical (or contains from 12 to 20 carbon atoms). Such aliphatic amine salts include lauryl (dodecyl), myristyl (tetradecyl), cetyl (hexadecyl), stearyl (octadecyl), oleyl, eicosyl (C_{20}) amine glycolates. The preferred amine salt is octadecyl amine glycolate; and the preferred amine for use in combination therewith is octadecyl amine, but it will be appreciated that any of the aforementioned amines may be employed in the practice of the instant invention.

Heretofore, considerable difficulties were encountered in using the known aliphatic amine materials for corrosion inhibition particularly because of the difficulty in handling these materials. First of all, only very minute amounts should be added to the aqueous medium involved or the use of the aliphatic amine materials would not be practical. Secondly, these materials were found to be substantially insoluble in water and very difficult to disperse therein. In the Maguire patent, it is pointed out that octadecyl amine is extremely difficult to disperse in water and thus very difficult to adequately feed into the system; whereas octadecyl amine acetate is more readily dispersed in water, but it is per se strongly acidic so that corrosion may be caused at the point of injection of octadecyl amine acetate into an aqueous system. As will be appreciated, the aliphatic amine material must be prepared in a dispersion or solution of something in the neighborhood of 1% concentration (perhaps within the range of 0.1 to 5% concentration) and this dispersion is then fed into the aqueous medium so as to maintain a concentration therein that is relatively minute, in the neighborhood of 1 or 2 p. p. m. (parts per million). It is important to maintain a reasonably great concentration of the aliphatic amine material in the dispersion feed tank and increased dispersibility or solubility is of particular importance for this reason, even though the instant materials will be ultimately employed in extremely dilute concentrations in the aqueous medium.

One aspect of the instant invention is based upon the discovery that octadecyl amine glycolate is more readily soluble or dispersible than octadecyl amine acetate. In addition, it exhibits better corrosion inhibiting properties when used in the practice of the instant invention. Further, octadecyl amine glycolate (with or without octadecyl amine) is capable of preparation into a dispersion adequate for feeding into an aqueous system which dispersion contains a greater amount of aliphatic amine material than can be put into a stable dispersion using octadecyl amine acetate. Corresponding results are obtained using corresponding aliphatic amine and aliphatic amine glycolates, as herein described.

As a demonstration in the instant invention, 1 mol of technical grade octadecyl amine was melted and heated to about 170° F. A charge of 0.5 mol of 70% aqueous glycolic acid was slowly added with agitation to the melted amine; and it was observed that a gelatinous prod-

uct, insoluble in the molten amine, was first formed (and this product appears to be a water dispersion of amine glycolate). By heating the mixture to about 250–260° F. the water was liberated and the mixture gradually became homogeneous. The homogeneous melt or blend so obtained was cooled with agitation until solidification occurred in order to obtain a homogeneous solid product. A 1% solution of the product in distilled water was prepared by adding 1 part by weight of the solid to 99 parts by weight of distilled water and heating the solution to near the boiling point of water. Complete dispersion takes place after moderate stirring and a stable product results showing no signs of separation. The pH of this 1% solution was found to be 6.3.

It was found that the instant dispersion is much more stable than a corresponding dispersion of 50% acetic acid neutralized octadecyl amine. Also, dispersions at concentrations which may be employed for actual corrosion inhibition, such as dispersions ranging from 1 p. p. m. to 100 or even 500 p. p. m. are extremely stable. In an actual corrosion inhibition test, a circulating water system with metallic parts therein adapted to indicate rapidly the extent of corrosion is provided and the 1% solution is metered slowly into the aqueous system so as to maintain a concentration therein of about 2 p. p. m. At first, of course, corrosion continues to take place because some time is required for the film to form. The rate of corrosion decreases, however, until substantially no corrosion is obtained after twelve days of operation. This is an indication of excellent corrosion inhibition properties. For example, a corresponding treatment of the water with 50% acetic acid neutralized octadecyl amine requires a substantially longer period of time before substantially 100% corrosion inhibition is effected. In addition to the superior dispersibility and/or solubility of the glycolate salt, and its superior function as a corrosion inhibitor in the dilute concentrations employed in commercial use (i. e. from mere trace amounts of 0.5 p. p. m. to appreciable amounts such as 100 p. p. m.), the instant glycolate salt combinations thereof with the amine show distinct reduction in corrosion at the point of injection into the water system. As previously mentioned, for commercial purposes the aliphatic amine material should not be used (as a practical matter) in concentrations of more than 100 p. p. m., although the concentration should be sufficient to form a protective film on the metal surfaces, and such concentration may easily be as low as trace amounts or small amounts such as 2 p. p. m.

If the foregoing procedure is employed except that 0.2 mol of glycolic acid is used instead of 0.5 mol, the resulting procedure gives substantially the same results, except that the pH of a 1% solution is 6.7. The superior corrosion inhibition properties exhibited in the previous demonstration are comparable and the 1% solution, having a pH closer to neutral, has even less corrosive properties per se.

If the procedure is again repeated, this time using 1 mol of glycolic acid, the resulting glycolate salt possesses superior corrosion inhibition properties when employed in the aqueous test system. The pH of a 1% solution is 4.7, but this solution does not exhibit the corrosive properties of a corresponding acetate salt solution, and it is noted that the completely neutralized glycolate solution is somewhat thicker than partially neutralized ones although it is extremely stable showing no signs of separation (indicating perhaps a gel-like behavior).

If the foregoing procedure is again repeated except that 0.9 mol of glycolic acid is used to react with the 1 mol of octadecyl amine, the superior stability of dispersions is again noticed and a 1% solution of the resulting blend has a pH of 5.2. Although this material exhibits the superior corrosion inhibition properties typical of the instant invention, it has been found that it is preferable to employ aliphatic amine materials whose 1% solutions have a pH of 6 or more, which is comparable to about a 60–70% glycolic acid neutralized aliphatic amine. Blends containing as little as 10 or 20% aliphatic amine and 80–90% aliphatic amine glycolate possess certain advantageous properties over the 100% neutralized glycolate salt; but the greatest advantages are obtained in the case of aliphatic amine materials whose 1% solution has a pH of 6 or more. In fact, the 100% neutralized aliphatic amine glycolate per se has superior corrosion inhibition properties in the dilute concentrations employed commercially (i. e. not more than 100 p. p. m.) and this material has much less of a tendency to cause corrosion at the point of injection into the system than does the corresponding acetate salt.

It has further been found that the glycolate may be used in combination with the acetate (as the salt component of an aliphatic amine material) to distinct advantage in the practice of the instant invention. Preferably the aliphatic amine salt is at least 50% glycolate, although as much as 75% acetate with the remainder glycolate may be used to advantage.

For example, repeating the procedure hereinbefore described using 0.1 mol of glycolic acid and 0.1 mol of acetic acid per mol of octadecyl amine, it will be found that a product having good corrosion inhibiting properties is obtained and this blend in a 1% solution has a pH of 6.8 and may be readily dispersed in aqueous media for purposes of metering into the water system. Using, instead, 0.25 mol of glycolic acid and 0.25 mol of acetic acid, one obtains a blend whose 1% aqueous solution has a pH of 6.4. This material has been found to be preferred for use in the invention if it is desired to incorporate an acetate component in the salt. Such a composition comprises 1 part (by weight) octadecyl amine glycolate, 1 part octadecyl amine acetate, and 2 parts octadecyl amine. In general, the salt component (employing both glycolate and acetate) should be used in the same proportions as those hereinbefore set forth for the use of the glycolate alone as the only salt component; and it is generally preferable to employ a salt component equal in weight to amine component. The amount of acetate may range from 0% to as much as 75% of the salt component, but if it is desired to employ the acetate salt for economic reasons or to obtain some special advantage therefrom, it should be employed in a minimum amount of about 10% of the salt component (the maximum being, of course, 75%).

Again repeating the procedure using 0.45 mol of glycolic acid and 0.45 mol of acetic acid (per mol of octadecyl amine) it will be found that a 1% aqueous solution of the resulting blend has a pH of 5.3 and this solution possesses the characteristic high stability and superior corrosion inhibition properties of the invention.

In general, it is understood that these aliphatic amine materials form a thin (mono-molecular) film on the metal surface. Any metal surface may be thus protected, but low carbon steel is preferred as the structural material for water systems which must be protected (and the test metal pieces in the foregoing demonstrations included such steel) and this metal is afforded excellent protection. The water used in the systems protected by the invention (and in the previous demonstrations) contains the usual amounts of dissolved oxygen and carbon dioxide, which are believed to be the main corrosion inducing factors in the aqueous media usually employed in water systems. Such water systems often contain water having acid characteristics (pH 5.5 to 6.5), but the pH may sometimes reach a value of 8 (but ordinarily no higher).

In addition, it should be noted that the instant glycolates improve dropwise condensation of steam and thereby increase the heat transfer coefficient in heat exchange equipment, etc.

It will be understood that modifications and variations may be effected without departing from the spirit and scope of the novel concepts of the present invention.

I claim as my invention:

1. A method of protecting metal contacting surfaces in

a continuously flowing system for transporting aqueous media having corrosive qualities, which comprises the step of adding to the transporting media an aliphatic amine glycolate wherein each aliphatic radical is a C_{12}–C_{20} hydrocarbon radical, in concentrations of not more than 100 p. p. m. but sufficient for forming a protective film on the surfaces, and conveying the media sufficiently to allow the film to form.

2. A method of protecting metal contacting surfaces in a continuously flowing system for transporting aqueous media having corrosive qualities, which comprises the step of adding to the transporting media octadecyl amine glycolate, in concentrations of not more than 100 p. p. m. but sufficient for forming a protective film on the surfaces, and conveying the media sufficiently to allow the film to form.

3. A method of protecting metal contacting surfaces in a continuously flowing system for transporting aqueous media having corrosive qualities, which comprises the step of adding to the transporting media a composition comprising 10–80% of an aliphatic amine and 90–20% of an aliphatic amine glycolate wherein each aliphatic radical is a C_{12}–C_{20} hydrocarbon radical, in concentrations of not more than 100 p. p. m. but sufficient for forming a protective film on the surfaces, and conveying the media sufficiently to allow the film to form.

4. A method of protecting metal contacting surfaces in a continuously flowing system for transporting aqueous media having corrosive qualities, which comprises the step of adding to the transporting media an aliphatic amine salt which is 10%–75% aliphatic amine acetate with the remainder aliphatic amine glycolate, wherein each of said aliphatic radicals is a C_{12}–C_{20} hydrocarbon radical, in concentrations of not more than 100 p. p. m. but sufficient for forming a protective film on the surfaces, and conveying the media sufficiently to allow the film to form.

5. A method of protecting metal contacting surfaces in a continuously flowing system for transporting aqueous media having corrosive qualities, which comprises the step of adding to the transporting media octadecyl amine and octadecyl amine glycolate, in substantially equal proportions, in concentrations of not more than 100 p. p. m. but sufficient for forming a protective film on the surfaces, and conveying the media sufficiently to allow the film to form.

6. A method of protecting metal contacting surfaces in a continuously flowing system for transporting aqueous media having corrosive qualities, which comprises the step of adding to the transporting media a composition

comprising 2 parts octadecyl amine, 1 part octadecyl amine glycolate and 1 part octadecyl amine acetate.

7. A method of feeding aliphatic amine material to water, which comprises first blending an aliphatic amine and an aliphatic amine glycolate wherein each aliphatic radical is a C_{10}–C_{20} hydrocarbon radical, in proportions of 10–80% of the amine to 90–20% of the glycolate, then dispersing the blend and feeding the blend into water.

8. A method of feeding aliphatic amine material to water, which comprises first blending an aliphatic amine and an aliphatic amine salt wherein each aliphatic radical is a C_{10}–C_{20} hydrocarbon radical, in proportions of 10–80% of the amine to 90–20% of the salt, said salt consisting of 10–75% acetate and the remainder glycolate, then dispersing the blend and feeding the blend into water.

9. A method of feeding aliphatic amine material to water, which comprises first blending octadecyl amine and octadecyl amine glycolate, in proportions of 10–80% of the amine to 90–20% of the glycolate, then dispersing the blend and feeding the blend into water.

10. A method of feeding aliphatic amine material to water, which comprises first blending octadecyl amine and octadecyl amine salt, in proportions of 10–80% of the amine to 90–20% of the salt, said salt consisting of 10–75% acetate and the remainder glycolate, then dispersing the blend and feeding the blend into water.

11. A water treating composition, comprising a blend of an aliphatic amine and an aliphatic amine glycolate wherein each aliphatic radical is a C_{10}–C_{20} hydrocarbon radical, in proportions of 10–80% of the amine to 20–90% of the glycolate.

12. A water treating composition, comprising a blend of an aliphatic amine and an aliphatic amine salt wherein each aliphatic radical is a C_{10}–C_{20} hydrocarbon radical, in proportions of 10–80% of the amine to 20–90% of the salt, said salt consisting of 10–75% acetate and the remainder glycolate.

13. A water treating composition, comprising a blend of octadecyl amine and octadecyl amine glycolate, in proportions of 10–80% of the amine to 20–90% of the glycolate.

14. A water treating composition, comprising a blend of octadecyl amine and octadecyl amine salt, in proportions of 10–80% of the amine to 20–90% of the salt, said salt consisting of 10–75% acetate and the remainder glycolate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,460,259	Kahler	Jan. 25, 1949
2,712,531	Maguire	July 5, 1955