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POLYALKYLENE POLYAMINE DERIVATIVES OF HYDROXYBENZOIC ACID

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4 Claims. (Cl. 260—559)

This application is a continuation-in-part of my copending application Serial No. 144,321, filed October 11, 1961, now abandoned.

This invention relates to an improved corrosion inhibiting composition and its method of preparation and use. More particularly, it relates to the dehydration reaction product of hydroxy benzoic acid and a polyalkylene polyamine, possessing superior effectiveness in retarding corrosive attack upon ferrous metals.

Oxygen corrosion is a well-known type of corrosion, and discussion of the problems presented thereby is considered unnecessary. It might be well, however, to discuss filiform corrosion, which is a particularly troublesome and insidious type of corrosive attack.

Filiform corrosion was observed and reported as early as 1944 by C. F. Sharman, "Filiform Underfilm Corrosion of Lacquered Steel Surfaces," Nature 153, 621 (1944); also Chem. and Ind. (London) 46, 1162. Sharman observed this phenomenon on steel surfaces coated with transparent oil-modified synthetic lacquers in atmospheres containing acetic acid and water vapor, and appreciated the probable importance of the problem in connection with all painted steel surfaces.

Another report on this usual type of corrosion was published by M. Van Loo, D. D. Laiderman, and R. R. Bruhn, in "Filiform Corrosion," Corrosion 9, 277 (1953). They report the existence of filiform corrosion on ferrous metals, magnesium and aluminum and under tinplate, silverplate, goldplate, and certain phosphate coatings. It was suggested that the type of vehicle or binder represented in the coatings under which filiform had been detected was not critical, and that several vehicles had been examined, such as drying oils and oleoresinous binders, pure and modified phenolic varnishes, alkyds including amine modifications, lacquers, vinyl copolymer coatings and amine modified ether resin and ether ester coatings, in both clear and pigmented films. Van Loo et al. also discuss the fact that a relatively high humidity is an important factor in the growth of filiform corrosion on steel. Following a rather comprehensive theoretical discussion, the authors concluded by indicating that much work yet remained to be done in connection with filiform corrosion and that the known preventative techniques were limited in applicability and effectiveness.

In an article entitled, "Mechanism of Filiform Corrosion," Ind. Eng. Chem., 46 (5), 1014–16, May 1954, W. H. Slabaugh and M. Grotheer present a brief summary of the findings of Van Loo et al., state the problem, and proceed with a theoretical discussion of the mechanism of filiform.

The above-mentioned prior art thus defines filiform corrosion as a unique type of corrosion characterized by the formation of a maze or network of thread-like corrosion products, each thread usually represented (structurally) by a V-shaped active head and a long inactive body, and further characterized in that its growth is directional (linear and regular rather than radial and haphazard).

It is further recognized: that filiform corrosion occurs on steel at room temperature in the relative humidity range of 65 to 95%; that it occurs under organic films which are not impermeable to moisture; and that there is no adequate solution to the problem presented by such corrosion.

We have discovered that filiform corrosion also occurs in an environment containing certain alkanolamines such as diethanolamine. 1020 mild steel strips were immersed in an unstirred, aerated, 1% diethanolamine, 5% sodium chloride brine. A highly directional type of corrosion began at the sharp edges, grew rapidly (up to ½ in. per hour) in the form of thin, threadlike filaments. After 3 days the metal surface beneath the filament was severely corroded. This discovery was significant because there are a number of commonly-occurring situations in which ferrous metals are exposed to alkanolamine systems, for example: soldering and welding fluxes often contain alkanolamines; lacquers used to coat ferrous metals sometimes contain such compounds; and aqueous alkanolamine (monoethanolamine or diethanolamine) solutions are frequently used for removing acid gases (such as H_2S—CO_2 mixtures) from gas streams in oil refineries. Filiform corrosion has been a serious problem in the canning industries, where alkanolamines are frequently used in the fluxes employed in the soldering of the seams of the cans. In the diethanolamine refinery gas sweetening systems corrosion is a serious problem, and we have observed, in the lining of the reactivator reboiler shell of such a system, the threadlike corrosion tracks being characteristics of the phenomenon known as filiform corrosion. Previously-known corrosion inhibitors have not been successful in preventing this serious corrosion in refinery gas sweetening units, and the use of alloys has been only moderately successful. The use of stainless steel and certain alloys has reduced corrosion rates somewhat; but these materials are expensive.

In my copending application Serial No. 747,097 (Patent No. 3,061,553), I disclose the reaction products of alkyl polyalkylene polyamines with hydroxybenzoic acid as oil well inhibitors; however, the inhibitors of Serial No. 747,097 are not suitable for filiform corrosion, and the inhibitors of this invention are not suitable as oil well inhibitors.

The principal object of this invention is therefore to provide a new composition of matter effective to prevent the corrosion of ferrous metals. Another object is to provide a method for preventing the oxygen corrosion of ferrous metals, involving the addition of a new corrosion inhibiting composition to the corrosive medium surrounding the metal to be protected. Another object is to provide an inhibitor and method of use therefor to prevent the filiform corrosion of ferrous metals.

THE POLYALKYLENE POLYAMINE

The suitable polyalkylene polyamines may be structurally represented by the formula

$$H_2N(\text{-alkylene-NH})_x\text{-alkylene-}NH_2$$

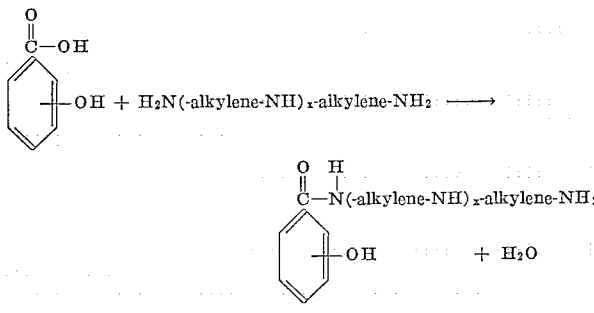
wherein the alkylene radical is selected from the group consisting of ethylene and propylene groups and x is an integer varying from 0 to 4; for example, suitable polyamines are ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexylamine, trimethylene diamine, bistrimethylene triamine, tristrimethylene tetramine, tetratrimethylene pentamine, and pentatrimethylene hexylamine.

PREPARATION OF THE REACTION PRODUCT

The hydroxy benzoic acid (preferably ortho hydroxy benzoic acid, but the para and meta forms are also appropriate) and the polyalkylene polyamine may simply be mixed (preferably in equimolar quantities, but possibly from about ½–2 mole equivalents of amine per mole equivalent of the diol). The mixture of acid and amine is then heated slightly to initiate the reaction, in a reaction vessel equipped for the azeotropic removal of water. When the reaction commences, the temperature begins to

rise at an accelerated rate, due to the exothermic nature of the reaction, and heating should be discontinued and the mixture allowed to cool. An azeotropic solvent such as benzene or toluene is then added, and azeotropic distillation conducted to trap out the water of reaction. The solvent is then stripped from the mixture by raising the temperature. A total of about one mole of water per pole of reactants should be obtained.

The reaction mechanism is as follows:



to yield a salicylamide and water.

The resulting composition is effective to prevent filiform as well as oxygen corrosion.

Examples of applications for the reaction products of this invention include inhibition of corrosion in cooling towers and other cooling systems, diethanolamine systems such as refinery gas sweetening units, air drilling and aerated mud systems, brine injection for flooding and/or disposal purposes, ballast systems on sea-going vessels, pipeline cleaning and weighting, incorporation in paint, coating and lacquer formulations where filiform corrosion is a problem, and incorporation into diethanol amine-based solder fluxes.

The following examples illustrate the best mode of preparation of the corrosion inhibitors of this invention.

Example 1

One gram mole each of hydroxy benzoic acid and tetraethylene pentamine are placed into a standard 3-necked round-bottom flask equipped for refluxing and for the removal of water by azeotropic distillation. The mixture is heated slightly to initiate the reaction. The temperature rises rapidly as a result of the exothermic nature of the reaction, so the source of heat is removed. Moderate stirring is carried on throughout the reaction. The mixture is then allowed to cool to 70° C., and then 50 ml. of toluene is added. The temperature is raised to about 145° C. to initiate reflux of azeotrope. Azeotropic distillation is continued until about one gram mole of water has been recovered, which is normally completed at about 180° C. The toluene is then stripped by continuing the distillation to a temperature of about 200° C.

Examples 2–5

Similar products are prepared from amines other than tetraethylene pentamine, using the same method as that of Example 1. The preferable temperatures are modified slightly depending upon the weight of the amine selected. For example, in using the lighter amines such as ethylene diamine, and propylene diamine, the temperatures for initiation of azeotropic reflux, completion of azeotropic distillation, and toluene stripping are preferably about 135° C., 170° C., and 190° C. instead of 145° C., 180° C., and 200° C., respectively. For the heavier amines such as pentaethylene hexylamine and pentapropylene hexylamine, no adjustment in procedure is needed.

Example 6

The composition prepared in accordance with Example 1 was tested and found to be effective in preventing filiform corrosion. Mild steel coupons were immersed for seven days in an unstirred, aerated 5% sodium chloride solution containing 1% diethanolamine. The corrosion inhibitor was employed in the concentrations of from 200–1000 parts per million, by weight, and prevented filiform corrosion in all cases. (Without the use of the inhibitor, a highly directional type of corrosion began at the edges of the coupons, and grew rapidly (up to ½ in. per hour) in the form of thin, threadlike filaments.)

Products formed in accordance with Examples 2–5 are also effective in preventing filiform corrosion.

As indicated above, one of the commonly-used methods of removing H_2S and CO_2 from refinery gases involves the treatment of such gases with an alkanolamine. U.S. Patent Re. 18,958 (original U.S. Patent 1,783,901, issued December 2, 1930, to Bottoms) described such a process, and is hereby made a part of this specification. Other U.S. patents relating to the alkanolamine removal of H_2S from hydrocarbon fluids are: 2,157,879; 2,164,194; 2,238,201; 2,220,138; 2,281,356; 2,311,342; and 2,383,416. Refinery sweetening units usually employ diethanolamine solutions, but monoethanolamine is sometimes used. Solutions of monoethanolamine and glycol are employed in the units of many gasoline plants where, in addition to H_2S and CO_2, water is to be removed.

Referring to the drawing of Re. 18,958, the gas sweetening process described therein is as follows. The gases to be purified are introduced to the bottom of the absorber 10, in which they are contacted with the aqueous alkanolamine solution introduced through line 11, and pass from the absorber through line 13. The spent amine solution, after being heated in exchanger 22, is delivered to the top of regenerator 15, in which acid gases are stripped from the amine. The gases from the top of the regenerator are passed to a condenser 24. The cooled acidic gases may then be removed by means of line 27, and the condensate trapped and refluxed to the regenerator through line 28. The regenerated amine is taken from the bottom of the regenerator, cooled, and returned to the absorber tower. The regenerator is usually equipped with heating means located near the bottom of the tower. This heating means is shown as a steam coil 18 in Re. 18,958, but is more conveniently a reboiler, separate from the regenerator, but located near the bottom of the tower.

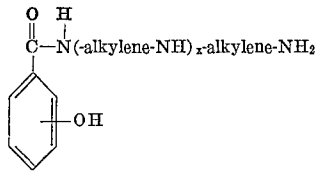
In alkanolamine systems, corrosion is usually found to affect that equipment handling a saturated solution of acid gas as this solution is being vaporized or condensed. In general, the corrosion is most severe in regions where the metal-skin temperature is highest and the acid-gas concentration the greatest. The equipment usually suffering the most severe corrosion includes the reactivator reboiler, the reactivator tower, rich- to lean-solution heat exchangers, and the acid-gas cooler. In addition to the alkanolamine, H_2S and CO_2, these systems contain small amounts of oxygen having an additional effect in causing corrosion.

The rate of corrosion taking place in the gas sweetening equipment may be reduced by the addition of a small amount of the above-described reaction product to maintain a concentration of at least 50 parts per million, and preferably about 100–200 parts per million, based on the liquid phase. The inhibitor may be added at any convenient point; for example, it may be added to the regenerator overhead line, to the regenerator reflux line, to the reboiler, or at any other convenient point or combination of points. The preferred inhibitor is the reaction product of hydroxy benzoic acid and tetraethylene pentamine, although other products formed in accordance with Examples 2–5, above, are also suitable.

While specific details of the method of preparation and use of the inhibitors of this invention have been given for purposes of illustration, it is to be understood that the invention is not limited thereby, but is to be taken as limited solely by the language of the appended claims.

I claim:

1. A hydroxybenzamide of the formula



wherein the alkylene radical is selected from the group consisting of ethylene and trimethylene groups and x is an integer varying from 2 to 4.

2. The amide of claim 1 wherein the alkylene group is an ethylene group and x is 2.

3. The amide of claim 1 wherein the alkylene group is an ethylene group and x is 3.

4. The amide of claim 1 wherein the alkylene group is an ethylene group and x is 4.

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